

Study of Iron-based Cathode Materials for Lithium-ion Batteries

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Study of Iron-based Cathode Materials for Lithium-ion Batteries

The work described in this thesis focuses on the exploration of a series of metastable iron-based oxide materials as potential cathodes for lithium-ion batteries.

$\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Al}, \text{Ga}$) phases were synthesized by a low-temperature topochemical cation exchange reaction from the corresponding $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$ phases. Structures of $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ are described in space group $Pna2_1$ with the tetrahedral site containing a mixing of iron and aluminium. Structures of $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ are described in space group Pn exhibiting iron and gallium atomic ordering. $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ phases, with $x \geq 0.25$ are structurally stable and allow reversible extraction of 0.5 Li^+ /f.u. on oxidative delithiation reactions. $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ phases, with $x \geq 0.3$ are found structurally stable and allow reversible lithium intercalation of 0.5 Li^+ /f.u. under reductive conditions. Under oxidative conditions, $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ phases, with $x \geq 0.5$ are found to be structurally stable and allow reversible extraction of 0.5 Li^+ /f.u. In the electrochemical cycling of $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ samples, $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox is found to be reversibly operational but “anion-redox” is found to be operating irreversibly.

To achieve aliovalent substitution in the $A\text{Fe}_{1-x}\text{M}_x\text{O}_2$ phase ($A = \text{Na}, \text{Li}$), Si, and Ge were incorporated in place of iron which resulted in the compositions: $A_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $A_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $A_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. The structures of the Na-phases are considered as ordered variants of $\gamma\text{-NaFeO}_2$, which contains four distinct tetrahedral sites for Fe-M-N cations to occupy. The distribution of cations in these tetrahedral sites is determined carefully and detailed in Chapter 6. Lithium exchange was performed on these phases to synthesize the corresponding Li- phases. A relaxation of the Na-structure (described in the $Pca2_1$ space group) to either a structure described in the Pc or Pn space group is observed for the Li-phases. This relaxation of the structure is accompanied by a migration of Fe/Al/Si/Ge/Ga atoms from one tetrahedral site to another adjacent tetrahedral site during the lithium exchange. The electrochemical performance of the aliovalent substituted samples reveals better retention of the initial capacities in comparison to the isovalent substituted LiFeO_2 materials. For instance, $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ exhibits a stable capacity of 100 mAh/g up to 20 cycles (equivalent to the cycling of 0.75 Li^+ /f.u. in each cycle), which is an improvement compared to $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$.

$\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases were synthesized by ceramic synthesis method, which were subjected to lithium exchange to prepare the corresponding $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases. Gallium in $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases was found to be preferentially occupying the tetrahedral sites in the structure for phases with $x \geq 4$. A complete ordering of Fe and Ga is demonstrated in the case of $A_3\text{FeGa}_4\text{O}_9$, where Ga cations occupy the tetrahedral sites and Fe cations occupy the octahedral sites in the structure. Based on the analysis of NPD, EXAFS and Mössbauer data, it is found that during lithiation, Fe^{3+} in tetrahedral sites (FeO_4) exhibited a higher preference for reduction to Fe^{2+} than Fe^{3+} in octahedral sites (FeO_6). During delithiation, Fe^{3+} in octahedral sites (FeO_6) showed a higher preference for oxidation to Fe^{4+} than Fe^{3+} in tetrahedral sites (FeO_4). During the electrochemical cycling, $\text{Li}_3\text{Fe}_5\text{O}_9$ exhibited rapid capacity fading (from 420 to 19 mAh/g in 20 cycles), while $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ retained a stable capacity (60mAh/g up to 20 cycles) with cycling of 1 Li^+ /f.u., indicating gallium substitution stabilized the structure allowing reversible electrochemical cycling.

Declaration

The work described in this thesis was carried out at the Inorganic Chemistry Laboratory at the University of Oxford between October 2019 and January 2024 under the supervision of Professor Michael A. Hayward. All the work presented in this document is my own except where I have either given reference to a published source or acknowledged help from a named person. None of this work has been submitted by the author for any other degree at any other university.

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To the MAHATOS

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Chapter 1 – Introduction

1.1 Origin of lithium-ion batteries

The intercalation of alkali metals into layered host materials, as observed in graphite¹ (1926) and dichalcogenides^{2–4} (1959), dates back nearly six decades, but it was not until 1976, that the concept of employing reversible intercalation in rechargeable batteries was initially proposed. M.S. Whittingham, a researcher at Exxon Research and Engineering Company in Liden, introduced the idea of a battery configuration with titanium sulfide (TiS_2) as the positive electrode and lithium metal as the negative electrode⁵. Although the TiS_2 battery exhibited promising rate capabilities, it soon encountered challenges stemming from the instability of metallic lithium and its limited energy density, prompting a re-evaluation of battery materials^{3,6–8}.

In 1981, a pivotal discovery by John B. Goodenough revealed LiCoO_2 ⁹ as a novel cathode material, opening the door to further advancements in battery technology. By 1983, Rachid Yazami of CNRS and Akira Yoshino of Kyoto demonstrated the reversible intercalation of lithium ions into carbonaceous materials, a development that greatly enhanced battery stability. Subsequent breakthroughs, including cathode materials like spinel LiMn_2O_4 ¹⁰ and olivine LiFePO_4 ¹¹, expanded the range of cathodes. After years of refining the requisite technologies for commercialization, the first lithium-ion batteries made their debut in the early 1990s, marking a transformative leap forward in the realm of energy storage^{12–14}.

1.2. Concept of a lithium-ion battery

Batteries serve as devices designed to transform the chemical energy stored inherently within their constituent electrode materials into a usable form of electrical energy through electrochemical redox reactions. In lithium-ion batteries, this conversion process primarily involves the movement of monovalent lithium ions across the internal electrochemical cell, driven by the difference between the electrochemical potential of the electrodes. This movement of lithium ions leads to a flow of electrons through an external circuit, thereby resulting in electrical power for practical applications.

As shown in Figure 1.1, Lithium-ion batteries contain one positive and one negative electrode (cathode and anode respectively) with an electrolyte which is electronically insulating but ionically conducting.

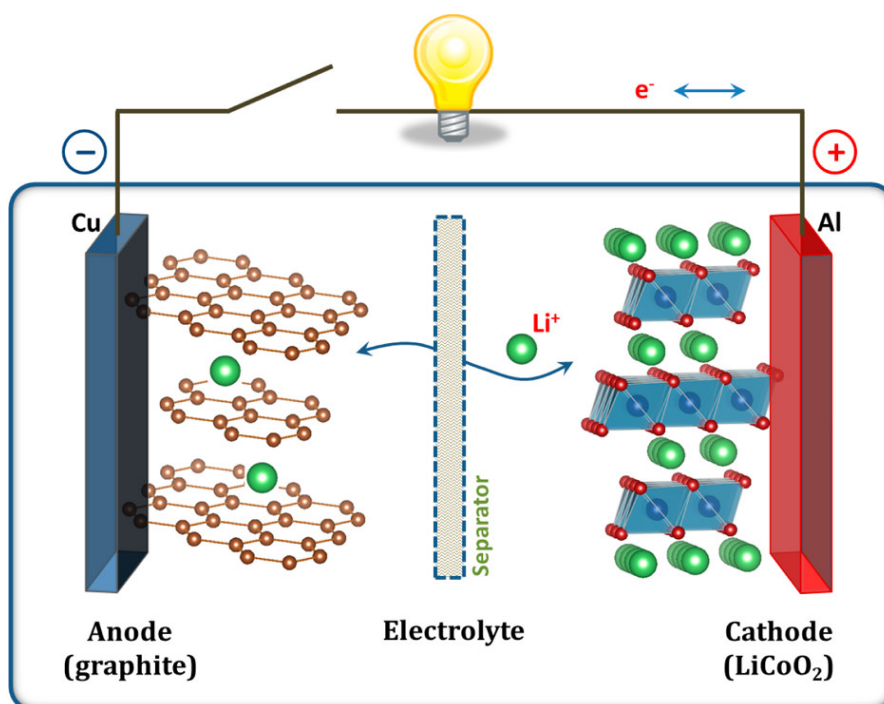


Figure 1. 1 Schematic illustration a lithium-ion battery. Reprinted with permission from Ref¹⁵. Copyright 2018 American Chemical Society.

In the discharge process of a battery, lithium ions are transported from the anode to the cathode through the electrolyte and electrons pass through the circuit. Consequently, an oxidation of the anode is followed by a reduction of the cathode. The reactions occurring at the cathodes and anodes due to the discharge process are illustrated below.

At the anode: $\text{Li}_x\text{C} \rightarrow \text{C} + x\text{Li}^+ + xe^-$

At the cathode: $\text{LiM}^{(n+x)+}\text{O}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_{1+x}\text{M}^{n+}\text{O}_2$

During the charging process, reverse events occur, involving the migration of lithium ions from the cathode to the anode through the electrolyte. This leads to the oxidation of the positive electrode (cathode) and the reduction of the negative electrode (anode). The associated reactions are described below.

At the anode: $\text{C} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}$

At the cathode: $\text{Li}_{1+x}\text{M}^{n+}\text{O}_2 \rightarrow \text{LiM}^{(n+x)+}\text{O}_2 + x\text{Li}^+ + xe^-$

1.3. Battery terminologies

The work presented in this thesis (Chapters 3 to 11) contain a set of frequently employed terms that hold significant relevance within the domains of energy storage systems. A selection of these terms is presented below.

Theoretical Capacity (C_{th}): The quantity of moles of electrons (denoted as 'n') generated in the electrochemical reaction for each unit mass of the material is referred to as the material's capacity. The theoretical capacity in milliampere-hours per gram (mAh/g) is mathematically expressed as follows:

$$C_{th} = \frac{1000 \times F \times n}{M \times 3600}$$

Where F is the Faraday constant (96485 C/mol) and M is the molecular weight of the material.

Current rate (C-rate): It refers to the speed at which the lithium ions are inserted or extracted during the charging or discharging process. A rate of C/T signifies that it takes T hours to charge or discharge the equivalent of the theoretical capacity. The rate is expressed as follows:

$$\text{Rate} = \frac{C_{th} \times m}{T}$$

where m represents the mass of the active material in grams, C_{th} is the theoretical capacity, and T stands for time.

Energy density: The energy stored per unit mass or volume of the active material is known as the energy density. It is defined as follows:

Gravimetric energy density (Wh/kg) = Specific capacity (Ah/kg) $\times$ cell voltage (V)

Volumetric energy density = Specific capacity (Ah/dm³) $\times$ cell voltage (V)

Coulombic efficiency (%): The ratio of discharge capacity to charge capacity is referred to as the Coulombic efficiency.

$$\text{Coulombic efficiency (\%)} = \frac{C_{discharge}}{C_{charge}}$$

1.4. Working principles for lithium-ion batteries

The electrochemical equilibrium potential (E) of an electrode is mathematically expressed using the Nernst equation:

$$E = E^\circ - \frac{RT}{zF} \ln \left(\frac{a_{red}}{a_{ox}} \right)$$

where, E° represents the standard potential, R is the universal gas constant (8.3145 J/K/mol), T signifies the absolute temperature, z corresponds to the number of moles of electrons participating in the reaction, F denotes the Faraday constant and a_{ox} , a_{red} stands for the concentration of oxidized and reduced species respectively.

The electrochemical behaviour of a battery is closely tied to the potentials of both the cathode and anode. In Figure 1.2, an open circuit energy diagram of a thermodynamically stable battery is presented, where the cathode functions as an oxidant, and the anode serves as a reductant. The energy E_g , which acts as the separator between the Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) of the electrolyte, defines the stability window of the electrolyte.

μ_C and μ_A are referred to as the electrochemical potentials of the cathode and anode, respectively. If the electrochemical potential of the cathode, falls below the HOMO, it will lead to the oxidation of the electrolyte unless a Solid Electrolyte Interphase (SEI) layer blocks this reaction. Similarly, an anode with an electrochemical potential exceeding the LUMO may result in the reduction of the electrolyte, unless a passivation layer prevents electron transfer from the anode to the LUMO of the electrolyte.

Battery stability relies on whether the electrochemical potentials μ_C and μ_A fall within the electrochemical window. The open circuit voltage (V_{oc}) of a cell, representing the difference between the electrochemical potentials of the anode and the cathode, is limited as follows:

$$eV_{oc} = \mu_A - \mu_C$$

Here, e stands for the elementary charge. Hence, a battery exhibits stable behaviour when eV_{oc} is less than E_g , ensuring a secure electrolyte.

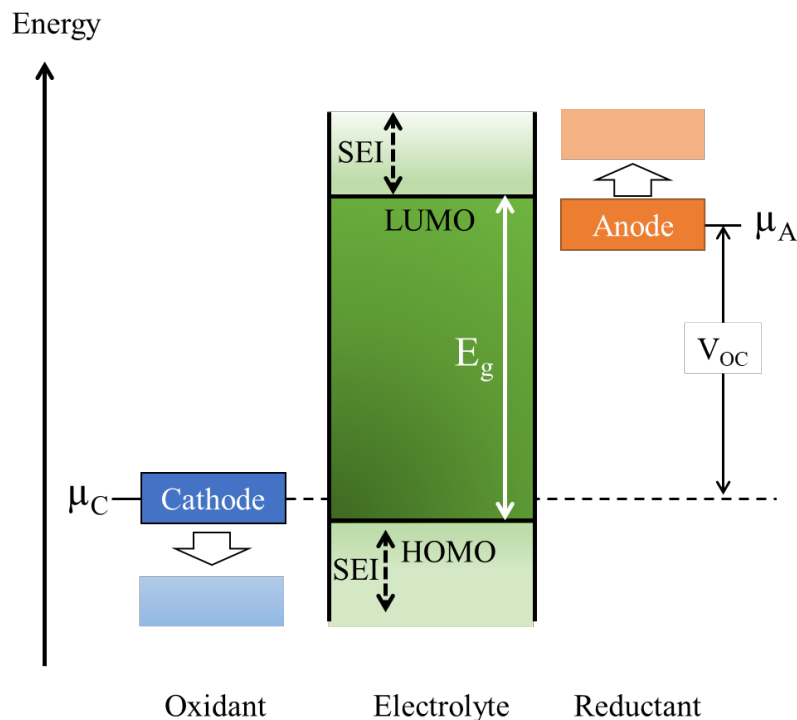


Figure 1. 2 Open circuit energy diagram of thermodynamic stable battery; Adapted with permission from Ref¹³ Copyright {2010} American Chemical Society.

1.5. Desired properties of a cathode

Based on previous reports^{14,16,17}, key requirements of a successful cathode in a rechargeable battery are as follows: Firstly, the material's electrochemical potential window must align with the voltage range permitted by the battery's electrolyte. Secondly, a cathode should possess a structure that includes pathways enabling the migration of lithium ions (high ionic conductivity). These pathways are crucial for the easy movement of ions within the material. Thirdly, the material should interact with lithium in a reversible manner, allowing for guest-host interactions without altering its structural integrity. Fourthly, the reactions between the electrode and lithium should preferably deliver a high free energy output. Ideally, these reactions should involve multiple lithium ions and operate at elevated voltages, resulting in superior energy density. Finally, the material must exhibit stability under ambient conditions. It should also be cost-effective and environmentally friendly, contributing to sustainable battery technologies.

1.6. Examples of commercialized cathode materials

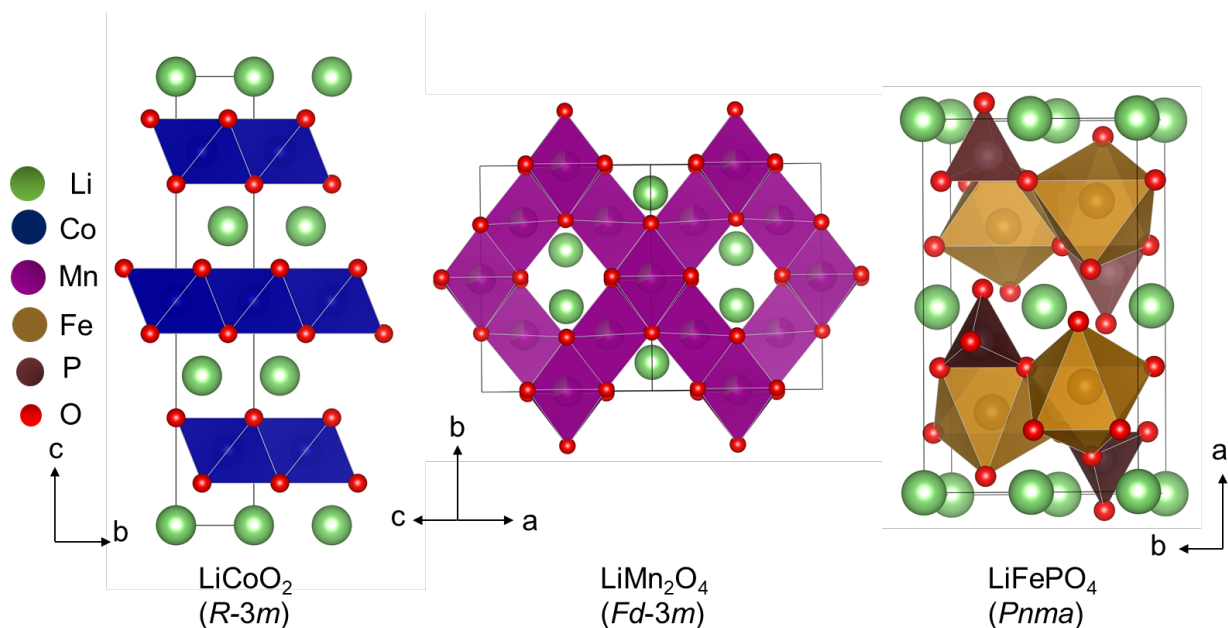


Figure 1. 3. Structures of LiCoO_2 (left), LiMn_2O_4 (right), LiFePO_4 (right)

1.6.1. LiCoO_2 and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) cathodes

In 1981, Mizushima, a member of Goodenough's research group, introduced LiCoO_2 as a cathode material for lithium-ion batteries⁹. Subsequently, in 1991, Sony commercialized lithium-ion batteries utilizing LiCoO_2 as the cathode material and a graphite anode. As illustrated in Figure 1.3, LiCoO_2 possesses a layered structure in which monovalent Li^+ and trivalent Co^{3+} ions are arranged on alternating (111) planes within the rock salt structure, inside a cubic close-packed array of oxide ions. This arrangement is also referred to as the O3 structure, as there are three parallel layers of edge-sharing octahedral CoO_6 sites oriented perpendicular to the c -axis of the unit cell (Figure 1.3)¹⁴. LiCoO_2 exhibits excellent electronic conductivity, and during cycling, $\text{Li}_{1-x}\text{CoO}_2$ transitions into a metal due to the introduction of holes in the $\text{Co}^{3+/4+}:t_{2g}^{6-x}$ band¹⁸. Its high electrical and lithium ionic conductivity along with its reasonable structural stability, positions LiCoO_2 as one of the best cathode materials to date, with an operating voltage of 4 V.

During lithium extraction in LiCoO_2 , initially, electrons are removed from Co-3d states. However, upon extracting more than 0.55 lithium ions, electrons are extracted from the O-2p band due to strong $\text{Co}^{3+/4+}$ mixing with O 2p. This process oxidizes oxide ions, releasing oxygen gas, which poses a combustion risk¹⁹. As a result, despite its theoretical capacity of 274 mAh/g, the practical capacity of LiCoO_2 is restricted to 140 mAh/g. Furthermore, the constrained availability and toxic nature of cobalt diminish the appeal of LiCoO_2 as a cathode material for lithium-ion batteries.

To address these limitations, researchers have substituted cobalt with nickel and manganese, giving rise to $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) cathodes with varied combinations of these metals^{20–23}. The absence of an overlap between the $\text{Mn}^{3+/4+}$ and O 2p band mitigates the promotion of oxygen oxidation²². Furthermore, the oxidation of manganese to Mn^{4+} leads to the reduction of Ni^{3+} to Ni^{2+} , which serves as a structural stabilizer during cycling²⁰. However, manganese faces certain challenges, due to the migration from the transition metal plane to the lithium-ion plane through a tetrahedral site, primarily due to its lower crystal field stabilization energy (CFSE), resulting in a transformation from the O3 layered structure to a spinel phase²³.

Nevertheless, NMC cathodes offer enhanced thermal stability and cost-effectiveness, providing a capacity of approximately 200 mAh/g at a C/20 rate with minimal capacity degradation after 100 cycles^{24,25}. Ongoing research continue to drive improvements and advancements in NMC cathodes, as a prominent subject of global research interest.

1.6.2. LiMn_2O_4 cathode

In 1983, M. Thackeray from Goodenough's group first introduced insertion of lithium into manganese spinels (Mn_3O_4 and LiMn_2O_4)²⁶. As shown in Figure 1.3, spinel LiMn_2O_4 consist of a cubic close-packed array of oxide ions with $\text{Mn}^{3+/4+}$ ions occupying the 16d octahedral sites, and Li^+ ions residing in the 8a tetrahedral sites. LiMn_2O_4 spinel offers three-

dimensional diffusion pathways that enable faster migration of lithium ions within its structure. LiMn_2O_4 ²⁷ operates at voltage higher than 4.1 V and provides a reversible capacity of 130 mAh/g²⁸. Additionally, manganese is more abundant and environmentally friendly compared to cobalt.

However, lithium insertion in LiMn_2O_4 results in reduction of $\text{Mn}^{3.5+}$ to Mn^{3+} which is associated with Jahn-Teller distortion, driven by the $t_{2g}^3 e_g^1$ configuration²⁹. This causes a transformation of the structure from a cubic to a tetragonal phase and promotes capacity fading. Furthermore, Mn^{3+} disproportionates into Mn^{4+} and Mn^{2+} , and Mn^{2+} tends to leach out from the cell and dissolve into the electrolyte^{30,31}.

To enhance the electrochemical performance of LiMn_2O_4 , various successful strategies are employed. Surface coating LiMn_2O_4 with 2 wt % $\text{TiO}_2\text{-B}$ (bronze) suppresses the Mn^{2+} dissolution and allows 93.7% capacity retentions up to 50 cycles³². Another strategy is partial substitution Mn^{3+} in LiMn_2O_4 with Ni^{2+} , Cr^{3+} , or Al^{3+} ^{33,34}. For instance, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ effectively suppresses Jahn-Teller distortions, offering a reversible capacity of 140 mAh/g with an operating voltage of 4.7 V²⁵.

1.6.3. LiFePO_4

A. Manthiram, G. Ahuja, and A. K. Padhi, researchers from Goodenough's group, conducted an extensive study involving polyanion cathodes^{35–37} like $\text{Li}_2\text{Fe}_2(\text{MoO}_4)_3$, $\text{Li}_2\text{Fe}_2(\text{WO}_4)_3$, $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$, $\text{LiTi}_2(\text{PO}_4)_3$, $\text{LiTiZr}(\text{PO}_4)_3$, $\text{SbTi}(\text{PO}_4)_3$, and $\text{NbTi}(\text{PO}_4)_3$, which ultimately resulted in the development of LiFePO_4 in 1997¹¹. Currently, LiFePO_4 stands as the most widely utilized iron-based cathode material in electric vehicles and electronic devices.

LiFePO_4 exhibits a capacity of 120-160 mAh/g and operates at 3.45 V vs Li^+/Li , displaying no signs of capacity loss even after 1000 cycles³⁸. It offers significant advantages,

including its low cost and remarkable thermal stability. Notably, it does not generate oxygen, even at elevated temperatures close to its decomposition point, thanks to the robust covalent P-O bonds within the PO_4 structure^{39,40}.

In contrast to layered or spinel cathodes, polyanion cathodes exhibit a notable drawback originating from their limited electronic conductivity^{38,40}. To mitigate this issue, it is imperative to synthesize LiFePO_4 either in small particles or coat it with conductive carbon materials. Moreover, the substantial size of the polyanion component results in a diminished volumetric energy density. Consequently, the quest for alternative cathode materials continues to be an ongoing pursuit in the field of energy storage research.

1.7. Fe-based cathodes

Iron-based materials hold particular appeal as cathodes for Li^+ ion batteries, primarily due to the abundant and cost-effective nature of iron. This characteristic makes them well-suited for extensive applications such as in electric grid storage and electric transportation devices. However, within the extensive array of Fe-based materials currently under global research, it becomes apparent that, apart from LiFePO_4 , all other candidates present substantial drawbacks^{41,42}. As detailed in Section 1.6.3, even though LiFePO_4 surpasses its Fe-based counterparts in various aspects, it suffers from low volumetric energy density and inherent poor electrical conductivity^{43,44}. These issues necessitate further modifications or alternative energy materials.

Prior investigations have indicated that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple operates seamlessly at low voltages in lithium-ion batteries, while achieving reversible $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox poses significant challenges. These challenges arise from the absence of crystal field stabilization energy (CFSE) in the Fe^{3+} (d^5) configuration, the inherent redox inactivity of Fe^{3+} , and the mixing of $\text{Fe}(3d)$ - $\text{O}(2p)$ electronic bands. In the Fe^{4+} state, the energy of the $3d$ orbitals is

further lowered due to reduced core electron screening, facilitating hybridization between Fe(3d) and O(2p) orbitals. In $\text{Li}_4\text{FeSbO}_6$, the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox process is associated with oxygen loss during cycling^{45,46}. In $\text{Li}_2\text{FeSbO}_5$, the delithiation results in its disproportionation of Fe^{4+} into Fe^{3+} and Fe^{5+} ($2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$)⁴⁷. Furthermore, manganese-doped layered iron oxide, $\text{Na}_x\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$, exclusively engages in $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox during cycling, effectively suppressing the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox^{48,49}. $\text{Li}_2\text{FeSiO}_4$ is susceptible to spontaneous reduction of Fe^{4+} once more than one lithium ion is extracted⁵⁰. In the case of Li_5FeO_4 , oxygen loss is observed when more than two lithium ions are removed^{51,52}. Regrettably, to date, there is no cathode material that exhibits pure $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox behaviour during cycling without facing challenges such as Fe atom migration or irreversible oxygen loss from the lattice^{53–58}.

For systems like $\text{Sr}_3\text{Fe}_2\text{O}_7$ ⁵⁹, CaFeO_3 ^{60,61}, $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$ ⁶², $\text{Ca}_2\text{FeMnO}_6$ ⁶³, etc, the concept of ligand hole is introduced to compensate for the oxidation of iron centre. The chemical instability of Fe^{4+} in these systems leads to charge disproportionation as $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$, which is represented as $2d^5\text{L} \rightarrow d^5 + d^5\text{L}^2$.

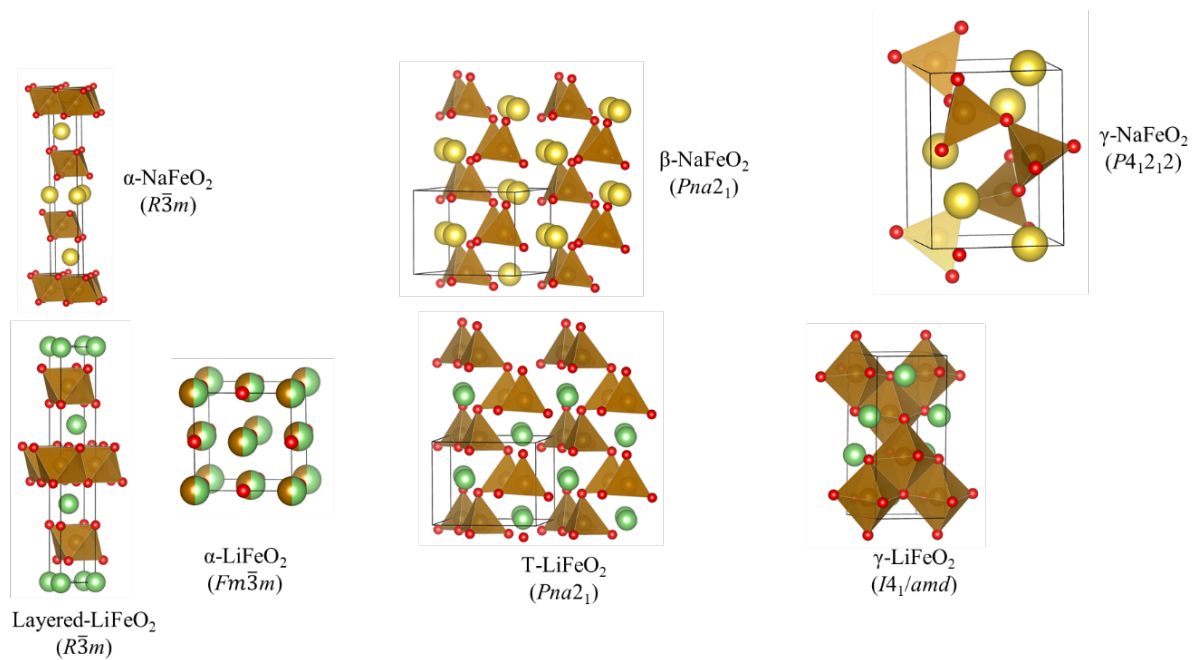


Figure 1. 4 Different polymorphs of NaFeO_2 and LiFeO_2

Depending on the synthesis conditions, different polymorphs of $A\text{FeO}_2$ phases (where A is Li or Na) could be obtained. A comparison of the different stable polymorphs is presented in Figure 1.4. The structural variation can be credited to the versatilities of iron sharing a site with lithium, occupying tetrahedral or octahedral sites. The layered $\alpha\text{-NaFeO}_2$ when oxidised shows the formation of Fe^{4+} , which is spontaneously reduced to Fe^{3+} followed by migration of the iron atoms to nearby octahedral sites blocking the sodium diffusion⁶⁴. $\alpha\text{-NaFeO}_2$ also takes part in anion redox when oxidised up to 4.5V⁶⁵. For $\beta\text{-NaFeO}_2$ during oxidation, a structural transformation is said to be the reason for the capacity fading but the nature of phase transformation is not specified yet⁵⁴. For $\gamma\text{-NaFeO}_2$ there is no previous study with electrochemical cycling at this point. It is worth mentioning that even though a stable Fe^{4+} is not obtained by electrochemical/chemical desodiation, thermodynamically Na_4FeO_4 could be synthesized, and the structure consists of isolated Fe-tetrahedra, which contains Fe^{4+} ion⁶⁶.

Although LiFeO_2 has a high theoretical capacity of 280 mAh/g owing to cycling of one Li per formula unit, so far there is no report achieving a capacity close to the theoretical capacity or either preserving the initial capacities to later cycles. The layered-O3-type LiFeO_2 could be prepared by topochemical exchange from $\alpha\text{-NaFeO}_2$, which converts to LiFe_5O_8 spinel phase when cycled^{67,68}. Unlike the Na-analogue, $\alpha\text{-LiFeO}_2$ has Li-Fe sites disordered in the octahedral site which leads to poor lithium conduction, and the conductivity is improved by tuning the particle size by producing nano particles of $\alpha\text{-LiFeO}_2$ ^{57,58}. The $\gamma\text{-LiFeO}_2$ is the high-temperature, thermodynamically favoured phase, which shows appreciable performance as an anode^{69,70}. A new type of orthorhombic LiFeO_2 polymorph shows a capacity of 150 mAh/g but undergoes structural transformation of LiFe_5O_8 during the cycling⁵³ (Figure 1.5). The orthorhombic LiFeO_2 also exhibits irreversible oxidation in high voltage as shown in Figure 1.5. The other polymorphs where iron is in an octahedral site namely corrugated layer LiFeO_2 ^{53,71}, Goethite-type LiFeO_2 ⁷², and hollandite-type LiFeO_2 ⁷³ which are prepared by low-

temperature solution-based techniques, show poor electrochemical behaviour mostly due to structural rearrangement followed by iron migration.

T-LiFeO₂ (another polymorph, T stands for Tetrahedral), was first synthesized via low-temperature cation exchange by Armstrong et al⁵⁵. The structure of T-LiFeO₂ could be interpreted as an ordered version of the wurzite (ZnS) structure where the anions are arranged in an array of hexagonal close packing and the cations (Li⁺ and Fe³⁺) are ordered in the tetrahedral sites. It was reported that the structure undergoes a transformation to LiFe₅O₈ spinel during the charge, releasing oxygen gas irreversibly from the lattice.

Based on all these reports, iron-based materials as a cathode for Li⁺ ion battery, when cycled, undergo a structural transformation owing to Fe-migration^{55,56,74,75}, and are often associated with irreversible loss of the lattice oxygen^{50,76,77}. To overcome such difficulties, engineering Fe-based materials is an active research topic globally at this point.

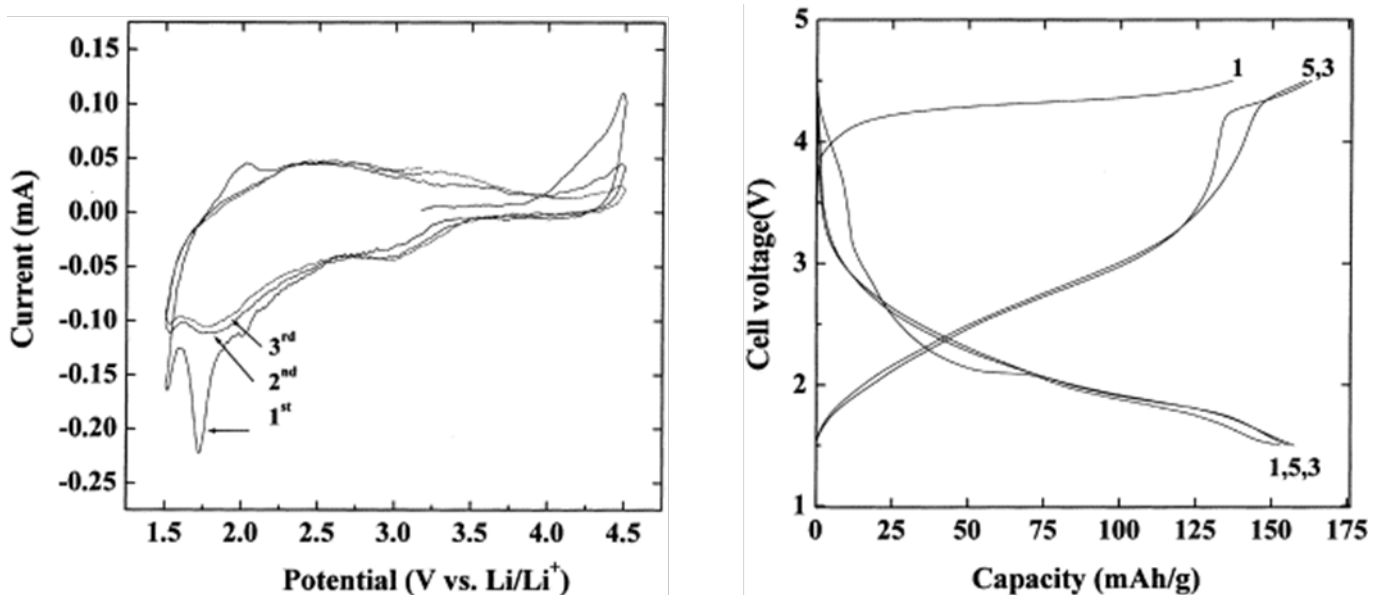


Figure 1. 5 Electrochemical performance of O-LiFeO₂, (orthorhombic LiFeO₂); CV (left), Charge/discharge profile (right), Reprinted from Journal of Power Sources, 119, Y.S. Lee, S. Sato, Y.K. Sun, K. Kobayakawa, Y. Sato, A new type of orthorhombic LiFeO₂ with advanced battery performance and its structural change during cycling, 285-289., Copyright (2003), with permission from Elsevier

1.8. Structural complexity of $A\text{FeO}_2$ phases ($A = \text{Na}, \text{Li}$)

The work in this thesis explores the structural evolution observed in $A\text{FeO}_2$ phases (where A stands for Na or Li) during cation exchange, reductive lithium insertion, and oxidative lithium extraction processes. The structural complexity is amplified by the ordered arrangement of cations and structural changes arising from translations of atomic planes within the system. The following description introduces the structures of β and γ polymorphs of NaFeO_2 , highlighting the impact of cation ordering and plane gliding within the structure. This foundational comprehension will assist in better understanding the subsequent discussions covered in Chapters 6-8.

Structures of $\beta\text{-NaFeO}_2$ and $\gamma\text{-NaFeO}_2$

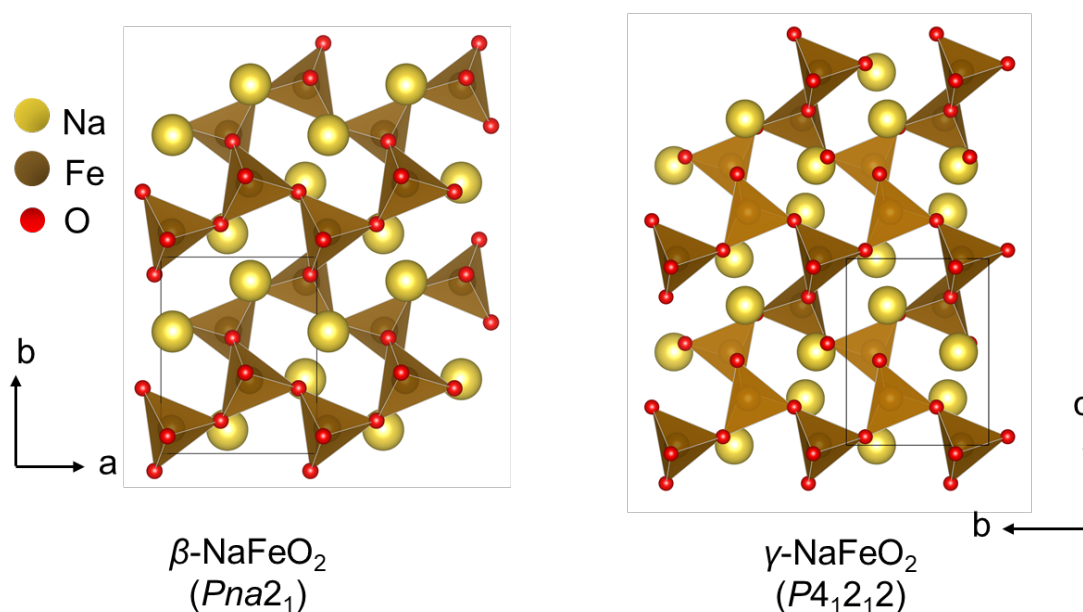


Figure 1. 6 Structure of $\beta\text{-NaFeO}_2$ (left), structure of $\gamma\text{-NaFeO}_2$ (right)

Figure 1.6 provides a comparative visualization of the structures of $\beta\text{-NaFeO}_2$ and $\gamma\text{-NaFeO}_2$. Both the polymorphs (β and γ NaFeO_2) exhibit a hexagonal close-packing arrays of oxygen atoms, where Na^+ and Fe^{3+} cations are located in the tetrahedral sites. This structure can be alternatively depicted as an ordered version of the wurtzite (ZnS) structure, where Na^+ and Fe^{3+} replace Zn^{2+} cations, while O^{2-} substitutes S^{2-} . In both the structures (β and γ NaFeO_2),

the iron tetrahedra are interconnected by sharing vertices within the structure. A significant dissimilarity between β -NaFeO₂ and γ -NaFeO₂ lies in the arrangement of the Fe-tetrahedra. In β -NaFeO₂, all Fe-tetrahedra point uniformly in one direction, whereas in γ -NaFeO₂, half of the Fe-tetrahedra point in one direction while the other half point in the opposite direction.

Within the structure of β -NaFeO₂, each Fe-tetrahedron possesses an opposing vacant tetrahedral site at its base. The migration of Fe atoms in β -NaFeO₂ from one tetrahedron to its oppositely facing counterpart results in the formation of the γ -NaFeO₂ phase. Thus, the transformation from β -NaFeO₂ to γ -NaFeO₂ can be elucidated as a consequence of the iron atoms migrating from one tetrahedron to another.

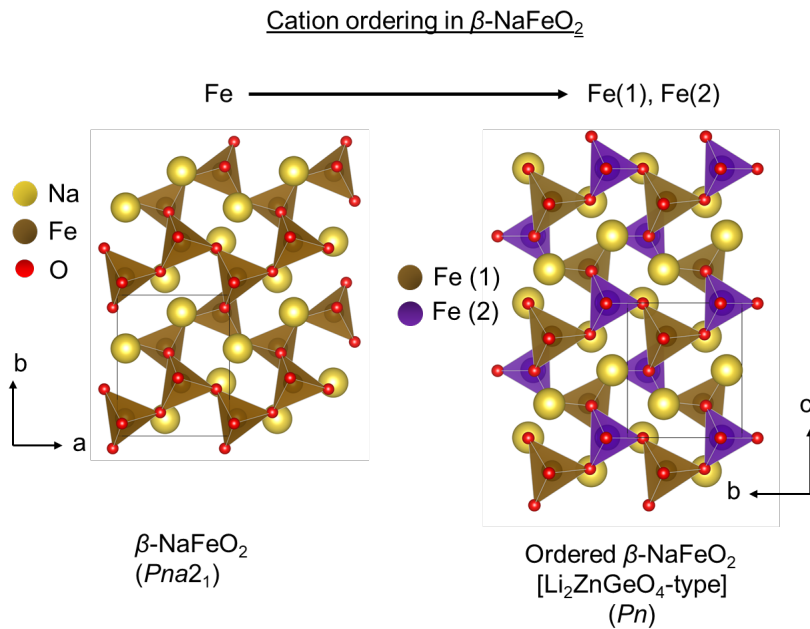


Figure 1. 7. Schematics of cation ordering in β -NaFeO₂

Figure 1.7 displays the cation ordering in β -NaFeO₂, depicting a transition from the space group *Pna2*₁ to *Pn*. This transition maintains the structural integrity, with the singular difference being the division of cation and anion sites into further distinct sites. As depicted in Figure 1.7, the Fe site in β -NaFeO₂ splits into Fe(1) and Fe(2) sites. This specific cation ordering in β -NaFeO₂ was observed in the gallium-substituted $A\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ samples (Chapters 3-5).

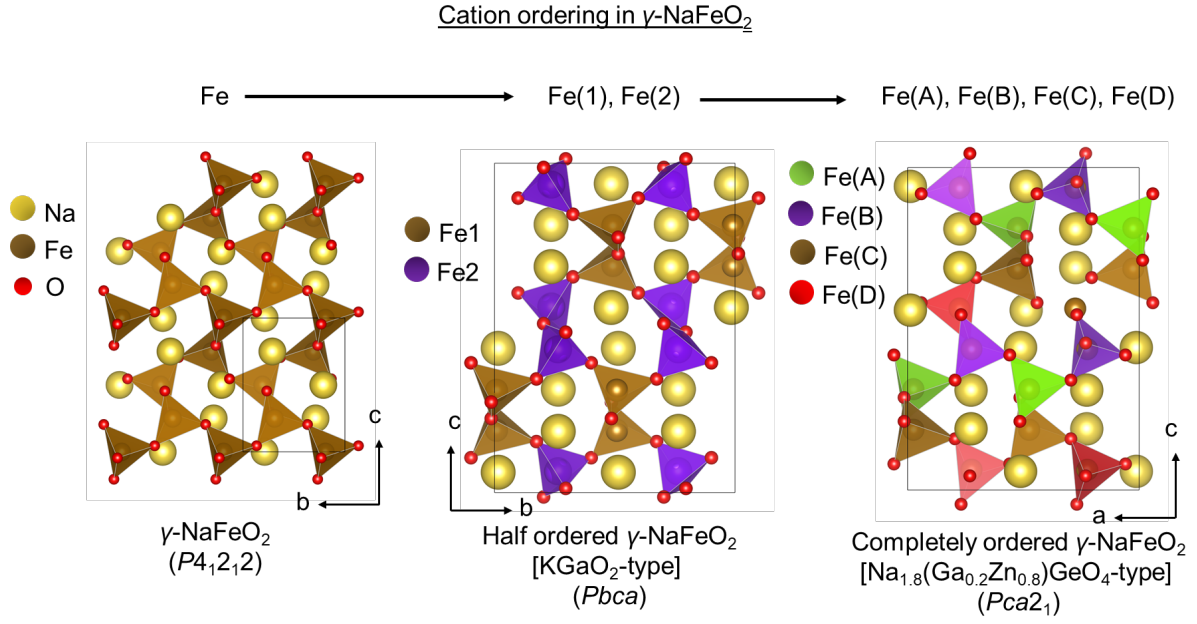


Figure 1. 8. Schematics of cation ordering in γ -NaFeO₂; γ -NaFeO₂ (left), half ordered γ -NaFeO₂ (middle), completely ordered γ -NaFeO₂ (right)

Figure 1.8 portrays the cationic ordering within γ -NaFeO₂ structure, exhibiting a shift in the space group from $P4_12_12$ to $Pbca$ or $Pca2_1$. This transition involves not only a change from a tetragonal to an orthorhombic structure but also an elongation of the γ -NaFeO₂ unit cell by a lattice vector of $1 \times 2 \times 2$. This expansion, along with the transition to a structure of lower symmetry, results in the division of four Fe sites in $P4_12_12$ into sixteen Fe sites.

For the structure described in the $Pbca$ space group, it features solely two distinct iron sites, Fe (1) and Fe (2), with the imposition of symmetry constraints generating an additional fourteen related sites. On the other hand, within the structure described in $Pca2_1$ space group, four independent sites—Fe (A), Fe (B), Fe (C), and Fe (D)—are present, with the remaining twelve sites symmetrically equivalent to the initially mentioned four.

The progression in structure from $P4_12_12$ to $Pbca$ and subsequently to $Pca2_1$, owing to cationic ordering, unfolds as follows: the Fe site in $P4_12_12$ splits into Fe (1) and Fe (2) in $Pbca$, following which Fe (1) further divides into Fe (A) and Fe (C), while Fe (2) splits into Fe (B) and Fe (D), resulting in the $Pca2_1$ structure (Figure 1.8).

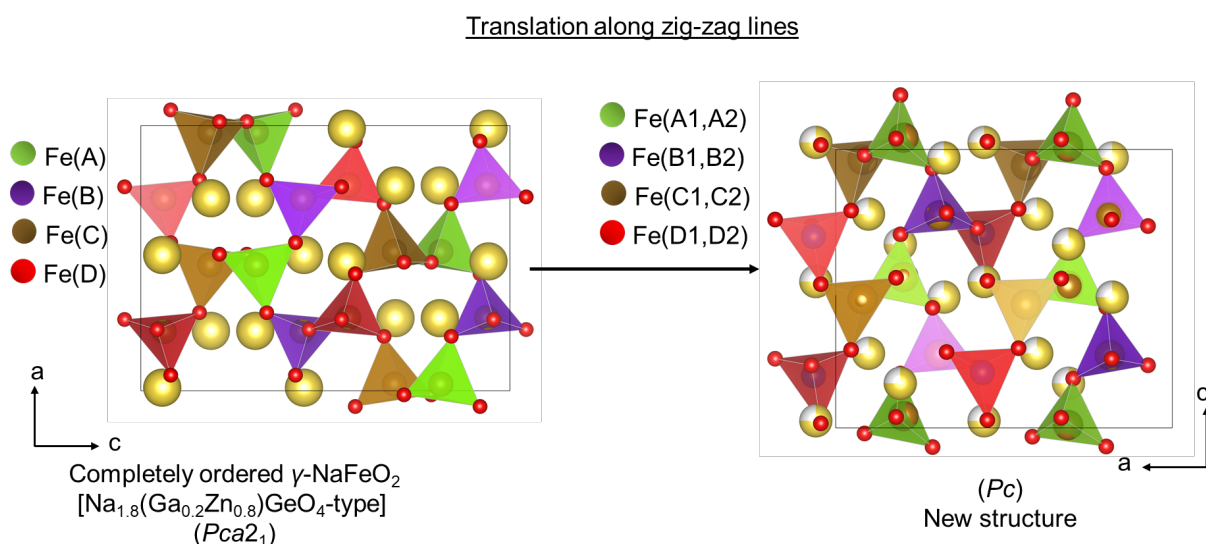


Figure 1. 9. Schematics of structural evolution in ordered γ -NaFeO₂ due to translation of zig-zag lines containing Fe-tetrahedra. Completely ordered γ -NaFeO₂ (left), translated-ordered γ -NaFeO₂ (right)

As mentioned earlier, in the γ -NaFeO₂ structure, half of the tetrahedra point in one direction, while the other half point in the opposite direction. Perpendicular to the orientation of the tetrahedra, a lattice plane can be constructed, accommodating the Fe-tetrahedra arranged in a zig-zag pattern. As shown in Figure 1.9, in the ordered γ -NaFeO₂ structure detailed within the *Pca*2₁ space group, the zig-zag lines containing Fe-tetrahedra are positioned within the *ac* plane. An irregular translation of the zig-zag line, which initially contained four independent Fe sites in *Pca*2₁, leads to a transition to the *Pc* structure (new structure type), thereby resulting in eight independent Fe sites. Figure 1.9 shows the division of the initial four independent iron sites, Fe (A), Fe (B), Fe (C), and Fe (D) in *Pca*2₁ into eight sites, Fe (A1, A2), Fe (B1, B2), Fe (C1, C2), and Fe (D1, D2) in *Pc* respectively.

The cation ordering in the γ -NaFeO₂ structure, was observed in the case of aliovalent-substituted NaFe_{1-x}M_xO₂ samples detailed within Chapters 6-8. Moreover, the movement of the zig-zag line within the *ac* plane was observed during the cation exchange from Na_{1.5}Fe_{0.5}Si_{0.5}AlO₄ to Li_{1.5}Fe_{0.5}Si_{0.5}AlO₄, as described in Chapter 6.

1.9. Oxygen redox

While cationic redox processes have conventionally dominated the landscape of battery technology, recent explorations of anion redox^{78–81} has attracted significant attention due to their potential to enhance the performance and capacity of electrochemical energy storage devices. This dual participation of both cations and anions in redox processes opens the door to higher energy density and increased capacity within electrochemical systems.

The thesis explores extensive oxygen redox engagement during the chemical oxidative delithiation process, characterized through the utilization of oxygen K-edge x-ray absorption spectroscopy (XAS) and energy maps acquired via resonant inelastic x-ray scattering (mRIXS) techniques. The subsequent sections offer a concise overview of the characterization techniques and fundamental concepts.

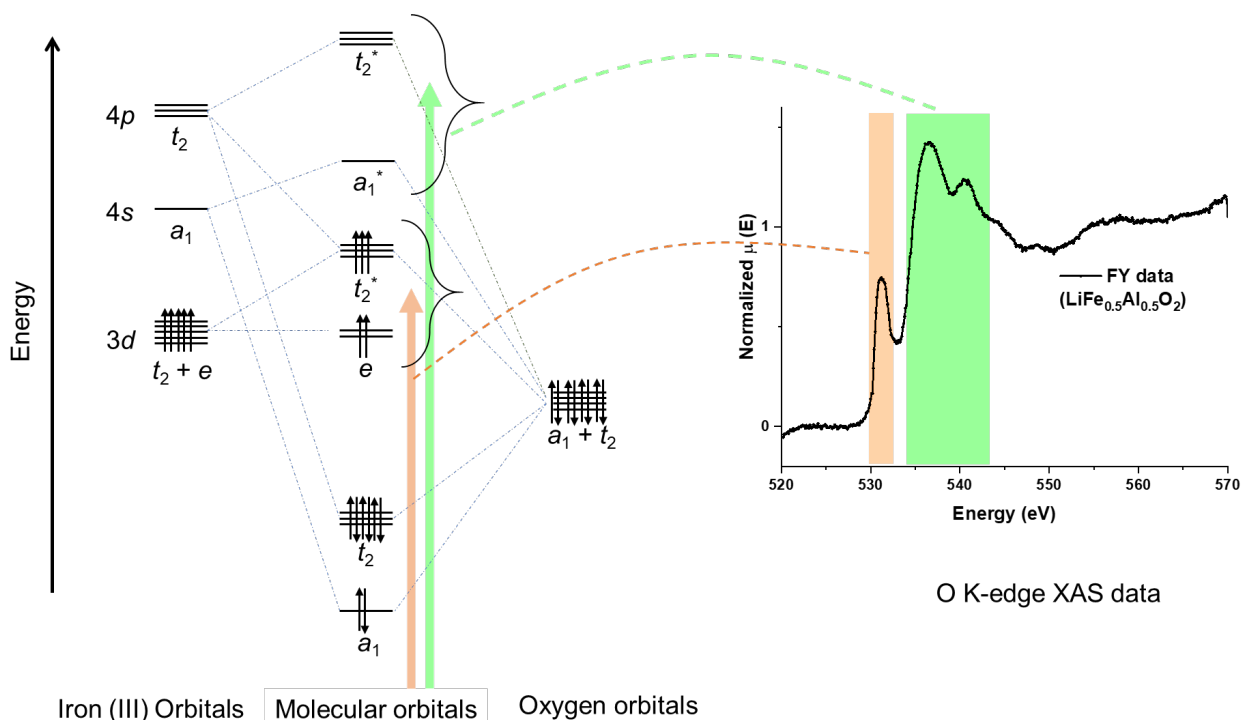


Figure 1. 10. Interpretation of the oxygen K-edge XAS spectrum of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$. Left: Molecular orbital diagram for FeO_4 tetrahedra determined from symmetry-adapted linear combinations (SALCs). Right: O K-edge XAS data. Orange arrow indicates the excitation of 1s oxygen electron to $\text{Fe}(3d)\text{-O}(2p)$ hybridisation, Green arrow indicates the excitation of 1s oxygen electron to $\text{Fe}(4s, 4p)\text{-O}(2p)$ hybridisation. Figure adapted from Ref⁸².

Figure 1.10 displays the molecular orbital diagram illustrating the iron (III) and oxygen orbitals within a tetrahedral environment, detailing the excitation of oxygen 1s to the available empty orbitals, which manifest as corresponding features in O K-edge XAS spectroscopy. Reports containing XAS data from transition metal oxides^{82,83}, as well as the data outlined in this thesis, reveal a sharp peak at approximately ~ 530 eV, attributed to the O (1s) $\rightarrow$ Fe (3d)-O (2p) excitation. Subsequently, a broader feature emerges at an excitation energy exceeding 536 eV, resulting from the O (1s) $\rightarrow$ Fe (4s, 4p)-O (2p) excitation.

The alterations in the XAS spectrum denote significant shifts in the material's electronic structure post-chemical oxidation. The observed changes in the XAS peak serve as robust evidence, successfully indicating the substantial involvement of oxygen in the oxidized materials.

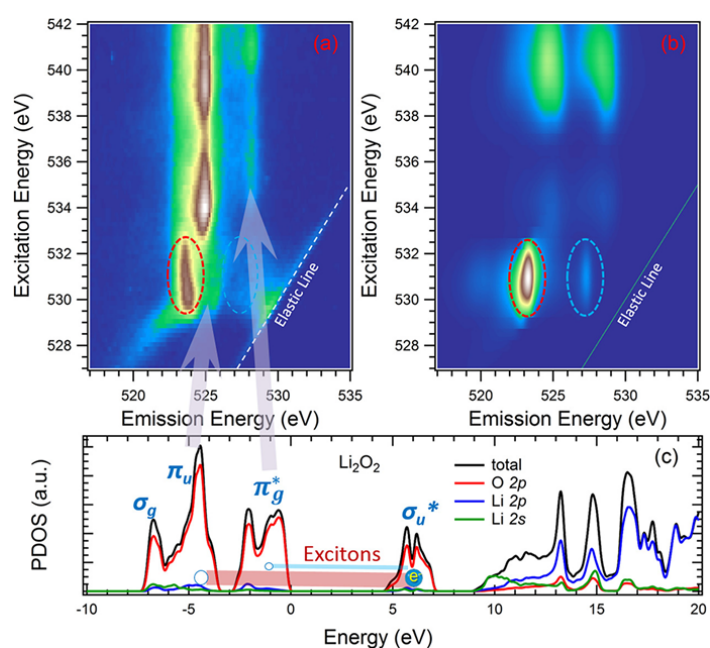


Figure 1. 11. (a) Experimental O K-edge mRIXS of Li_2O_2 . A specific feature centered at 523.7eV and two emission features at 525 and 528 eV emission energy are observed. (b) Calculated mRIXS of Li_2O_2 , which reproduces the experimental results with the striking feature at 523.7 eV emission energy (red circle). (c) Total and projected density of states of Li_2O_2 . Decay of the split valence band states lead to the two main emission features centered at 525 and 528 eV. However, the specific feature centered at 523.7 eV emission energy is from the excitations between the occupied and unoccupied O-2p states in the vicinity of the Fermi Level, due to the partially occupied O-2p states in peroxides. Reprinted with permission from Ref Copyright {2018} American Chemical Society.

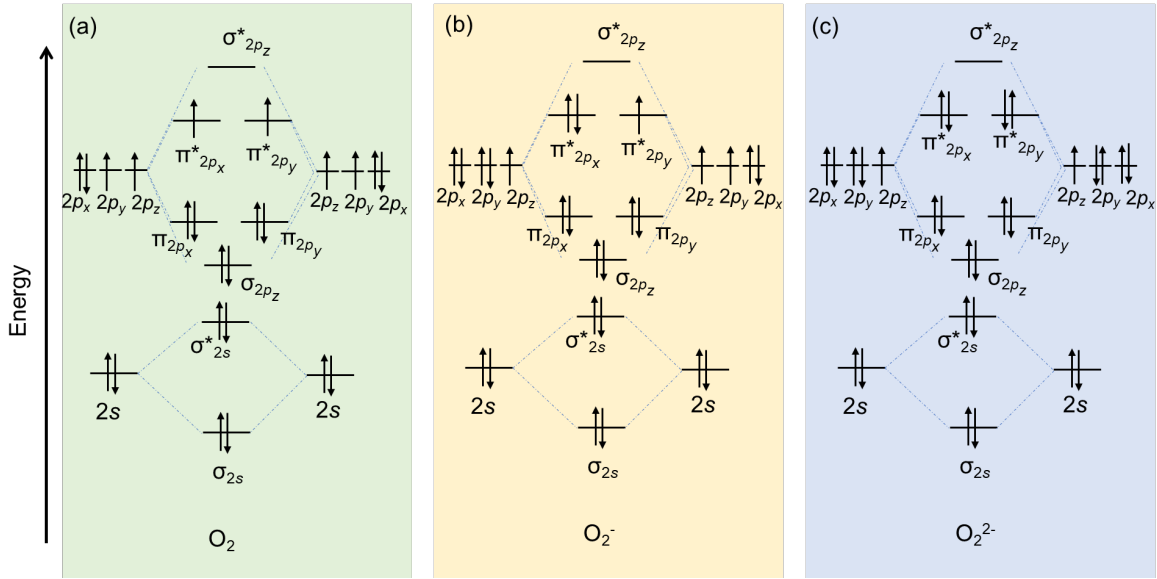


Figure 1.12. Molecular orbital diagram of (a) molecular oxygen, (b) superoxide and (c) peroxide species

To characterize oxidized oxygen species, RIXS line scans and RIXS energy maps (mRIXS) are extensively used for a charged cathode in a lithium ion battery^{84–92}. In the mRIXS plot, a periodic energy loss feature at low energy loss levels (<2 eV), provides a valuable clue. This is further complemented by conducting a Birge-Sponer plot, determining the fundamental vibrational frequency⁷⁸. Such findings serve to discern between various oxidised oxygen species—molecular oxygen, peroxide, and superoxide.

However, within the analysis of the RIXS data gathered from the samples featured in this thesis, challenges arose regarding the vibronic feature. At times, its presence seemed complicated as often it was found to appear in the unoxidized starting material as well.

Another distinctive characteristic, considered a hallmark of non-divalent oxygen species produced during oxidation, emerges in the mRIXS plot. It manifests as an excitation energy around ~531 eV and an emission energy of 523.7 eV⁹³. As detailed in Figure 1.11 by W. Yang et al, the energy loss feature at the emission energy of 523.7 eV is linked with an intraband excitons labelled as $\pi_u \rightarrow \sigma_u^*$, during the decaying of electron from filled oxygen bands^{94,95}. The molecular orbital diagram shown in Figure 1.12 for molecular oxygen,

superoxide, and peroxide species, revealing their potentials for such intraband transitions. This hallmark has been utilized in this thesis to successfully conclude the involvement of oxygen during the delithiation process. Additional research is necessary to precisely assign the origin of such fingerprint feature.

The integration of intensity within a selected emission energy range, derived from the mRIXS map, facilitates the generation of a partial fluorescence yield spectrum⁹³. This spectral information aids in untangling the participation of oxygen redox, often concealed in the O K-edge XAS data.

1.10. Low-temperature topochemical reactions

Low-temperature topochemical reactions involve a specific chemical species (e.g., alkali cation) within a complex oxide that exhibits greater mobility compared to the host lattice at a given temperature. This species can be exchanged, inserted or removed from the host structure, while the remainder of the structure remains virtually immobile under specific conditions. These chemical reactions are termed "topochemical" reactions^{96,97} since they preserve the fundamental structural framework both before and after the reaction. Low temperature reactions relevant to the thesis are presented below.

1.10.1. Topochemical cation exchange

The low-temperature solid-state exchange and the solution exchange method represent effective techniques for exchanging alkali or alkaline earth cations with protons or other alkali metal cations, and they have been extensively explored in solid-state synthesis to access new metastable phases. Several illustrative examples of these processes are provided below.

1. Treating Sr_2IrO_4 , LiMn_2O_4 , and KMnO_4 with perchloric acid (HClO_4) or hydrochloric acid (HCl) facilitates the exchange of alkali and alkaline earth metals with protons,

resulting in the formation of protonated phases: $\text{H}_{3.6}\text{IrO}_{4.3} \cdot 7\text{H}_2\text{O}$ ⁹⁸, $\text{H}_{1.17}\text{Li}_{0.02}\text{Mn}_2\text{O}_4$ ⁹⁹, and HMnO_4 ¹⁰⁰, respectively.

2. The scope of topochemical reactions extends beyond the replacement of alkali cations or protons. For instance, when $\text{Li}_2\text{SrTa}_2\text{O}_7$ is treated with five moles of MnCl_2 , it leads to the synthesis of $\text{MnSrTa}_2\text{O}_7$, which is a hybrid-improper magnetocaloric multiferroic material¹⁰¹.
3. The treatment of NaMO_2 (where M stands for Mn, Co, Cr, or Fe) with an excess of LiBr, LiCl, or LiNO_3 , either in the solid state or in solution, results in the formation of the corresponding LiMO_2 phases^{23,102–106}. This exchange method has been employed for the preparation of all the lithium samples discussed in this thesis.

1.10.2. Topochemical lithium intercalation

Reductive lithium insertion reaction can be considered as a chemical equivalent of the electrochemical discharge process of a cathode in a lithium ion battery¹⁰⁷. The outcome of such reaction produces either topochemical reduced phases³ or new conversion-type phases^{108,109}. Lithium insertion into spinel (Mn_3O_4 , Fe_3O_4 , LiFe_5O_8) leads to the formation of rock-salt type phases^{26,110,111}. Lithium intercalation in dichalcogenides and WO_3 materials leads to retention of the parent structure^{3,107,112}. As *n*-Butyl lithium solution in *n*-hexane has a redox potential of 1.04 V vs Li^+/Li which is capable of reductive lithium insertion into transition metal oxides, the iron-based cathode materials mentioned in this thesis were chemically reduced by treatment with *n*-BuLi in *n*-hexane solution.

1.10.3. Topochemical lithium deintercalation

Chemical oxidative delithiation reactions can be considered as the chemical equivalent of electrochemical charge process of a cathode in lithium-ion battery. Hydrogen peroxide¹¹³ (H_2O_2), peroxodisulfate¹¹⁴ ($\text{Na}_2\text{S}_2\text{O}_8$) in aqueous medium and nitronium tetrafluoroborate^{115,116}

(NO₂BF₄) in acetonitrile have been extensively used as a chemical delithiation agent for studying the delithiated/charged cathode materials. This method provides a cleaner way of obtaining the charged electrode without the contamination from the organic binder or the electrolyte which is utilized to produce large quantity of sample allowing bulk characterization.

NO₂⁺/NO₂ has a redox potential of 5.14 V against the Li⁺/Li redox couple and capable of oxidative delithiation from transition metal oxides. Thus, the iron-based samples mentioned in this thesis, were treated with NO₂BF₄ to achieve chemical oxidation/delithiation.

1.11. Aims and objectives

Recent studies discussing iron-based materials as cathodes for lithium and sodium ion batteries have shed light on the challenges associated with iron redox processes during electrochemical charge-discharge involving migration of iron and irreversibly oxygen loss from the structure^{55,56,117,58,63,64,69,72,74,75,116}. These challenges highlight the need for further research efforts to effectively address and resolve these issues. Consequently, there is a demand for the exploration of new phases and diverse structural types of iron, holding the potential for large-scale applications in battery technology.

In consideration of these imperatives, we have aimed to stabilize the tetrahedral framework of iron in NaFeO₂ through a series of strategic processes. Initially, we have substituted iron (III) by isovalent elements such as Al³⁺ and Ga³⁺, and then we have further incorporated aliovalent Si⁴⁺ and Ge⁴⁺ elements into the structure. The isovalent and aliovalent substituted NaFeO₂ samples, were subjected to cation exchange reactions to obtain the corresponding lithium exchanged phases. The impact of these substitutions on the LiFeO₂ structure, and then structural and electronic changes concerning chemical and electrochemical lithiation/delithiation has been thoroughly detailed in the chapters of this thesis.

Furthermore, we have performed the synthesis of $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ ($A = \text{Li}, \text{Na}$) phases, representing new potential cathode materials for lithium-ion batteries. This work not only presents the synthesis and structural characterization of these samples but also investigates the effects of gallium substitution in $\text{Li}_3\text{Fe}_5\text{O}_9$ during both chemical and electrochemical oxidation and reduction processes, providing a comprehensive understanding of metastable iron-based oxides as a cathode for lithium-ion batteries. The structure of $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases contains iron cations in both tetrahedral (FeO_4) and octahedral (FeO_6) environments, it further provides an opportunity to investigate the selective participation of iron cations undergoing reduction/oxidation as a function of coordination geometry.

Chapter 2 – Experimental methods and characterization techniques

To explore the structural, chemical and electrochemical properties of the material mentioned in this thesis, a series of synthetic and characterization methods were employed. These methods and techniques are described in this chapter.

2.1 Synthesis methods

2.1.1 Ceramic synthesis

Ceramic synthesis is a well-established method extensively used in academic and industrial laboratories to produce specific solid materials for various applications. This high-temperature synthesis process aims to obtain the most thermodynamically stable phase. The procedure commences with the precise weighing of reactants, which are then ground in a mortar and pestle to reduce particle size, thereby increasing the surface area. Using binary carbonates, nitrates, or similar materials as reactants necessitates a pre-heat treatment at a temperature above 600°C, but lower than the synthesis temperature, typically for a duration of 12 hours, to decompose these compounds into their respective oxides.

For enhancing inter-grain contact, the pre-heat-treated samples undergo regrinding and are compressed into pellets. Subsequently, they are reheated in a high-temperature furnace to facilitate the desired product formation, overcoming the high reaction potential. This process of grinding, pellet pressing, and re-heating is repeated until a pure phase is achieved. The presence of starting materials that are volatile at high temperatures, such as alkali and alkaline salts, requires an additional 10-15 mol % excess addition at the beginning or during subsequent heating cycles.

The synthesis process is adapted based on factors such as the stability of the reactants' oxidation state, the properties of product materials in air, and the hygroscopic nature of the

samples. Depending on these aspects, the synthesis is conducted inside a vacuum-sealed silica/Pyrex tube or in the presence of O₂ or Argon gas flow during the reaction's progression.

2.1.2 Cation exchange reactions

A typical mixed metal oxide is composed of different ions with different ionic diffusion rate. The higher ionic diffusion rate of the different cations can be utilized in a pathway involving an interchange of the cations. Since, the alkali cations (Na⁺) in a mixed metal oxide and exhibit higher ionic mobility in solids, treating them with another excess alkali metal (Li⁺) salt solution will result in the replacement of the original alkali cation (Na⁺) in the mixed metal oxide. As the exchange is performed at a lower temperature (< 350 °C) which does not provide sufficient energy to break any thermodynamic bonds, a metastable phase is produced after the exchange which could not be formed via the conventional high-temperature solid-state synthesis. If the parent structural topology is retained in the product material it is called a topochemical cation exchange reaction. However, the lattice planes could slightly slide/move and result in a rearrangement in the crystal structure and symmetry.

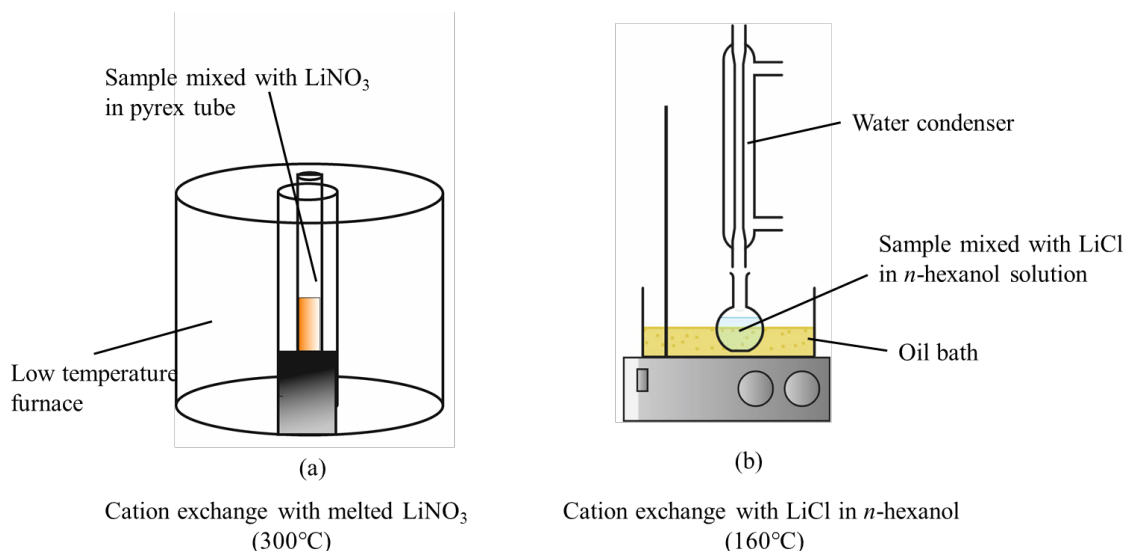


Figure 2.1 Different cation exchange schematics

For the synthesis of the lithium exchanged samples mentioned in this thesis, two types of cation exchange methods were used. Thermodynamically prepared pure Na-samples were

subjected to molten LiNO_3 at 300 °C or stirred with Li-salt (LiCl/LiBr) in *n*-hexanol in an oil bath at 160 °C. The second technique is comparatively milder and takes a longer period of time for completion (usually up to 2 weeks). The reaction with LiNO_3 is faster and takes only 2-3 days. However, this process being more aggressive, sometime leading to the rearrangement of the atomic constituents and the formation of some decomposed, impurity phases. The final exchanged product is obtained after washing with methanol and drying at 70 °C. Both these exchange techniques often lead to an asymmetric growth of the unit cell along a certain direction or plane in the production phase which leads to an anisotropic broadening of some peaks when the X-ray diffraction pattern is collected.

2.1.3 Ball-milling

Ball-milling is an effective method of reducing the particle size which plays an important role in the rate of the undergoing chemical or electrochemical reactions. It is a mechanical process where the powdered (~1g) sample is placed in a standard stainless-steel jar with steel balls and the closed jar is shaken mechanically by the machine for a set period of time with a set frequency. After the program finishes, the milled sample is taken out and treated for further reactions. In lithium-ion batteries, a longer migration path is attributed to Li^+ ions diffusing in the electrodes if the particle size is bigger. Thus, having a smaller particle size improves the rate performance of the battery making it more conductive. For instance, in LiFePO_4 material, the electrochemical rate is much improved after ball-milling and carbon coating^{118,119}.

To increase the electrochemical conductivity, the metastable lithium exchanged samples were ball milled but sadly, the SXRD analysis of the milled sample shows smaller particle size along with some decomposed phase formation. To avoid the decomposition the Na-samples were ball milled and then the Li-exchange was carried out. The value of particle

size before and after the ball-milled sample was calculated via the Rietveld refinement against the collected synchrotron X-ray diffraction pattern from the before and after ball-milled sample. To obtain the particle size value the Rietveld refinement method was carried out in TOPAS7 with the equation described below.

$$fwhm_{1/d}^{hkl} = \frac{\lambda}{D_{hkl} \cos \theta}$$

Where D_{hkl} is the average of the crystallite-size perpendicular to the hkl lattice plane. For an example, the particle size extracted using this method for a few samples is presented in the table below.

Table 2.1: Table of extracted particle size from the Rietveld refinement

Sample	Particle size estimated from synchrotron X-ray diffraction data (nm)		Ball-milling parameters
	Before ball-milling	After ball-milling	
LiFe _{0.5} Al _{0.5} O ₂	95 (7)	36 (2)	20Hz, 30min
LiFe _{0.5} Ga _{0.5} O ₂	75 (8)	16 (3)	20Hz, 30min
NaFe _{0.5} Al _{0.5} O ₂	90 (1)	26 (1)	30Hz, 30min
NaFe _{0.5} Ga _{0.5} O ₂	283 (4)	100 (7)	30Hz, 30min

2.1.4 Chemical lithiation and de-lithiation reaction

Chemical reagents with different redox potentials in the standard electrode potential table¹²⁰, display the stronger oxidizing or reducing power during an electrochemical reaction. To perform reductive insertion and oxidative extraction of lithium cations, a series of chemical agents could be selected based on their redox potential. A list of the redox potentials of the reagents relevant (or used) in this thesis is presented below in Figure 2.2. Chemical lithium extraction and insertion allow the oxidized and reduced samples to be characterized accurately without the contamination from the binder and electrolyte, unlike the electrochemical cell

assembly characterization. It gives more control over the extent of the oxidized or reduced material and further allows bulk characterization due to the ability to produce large (>3g) quantities of oxidised or reduced products. However, the chemical extraction and insertion method is found to be more aggressive in nature than the electrochemical counterpart, and often the final outcomes from these two methods differ significantly.

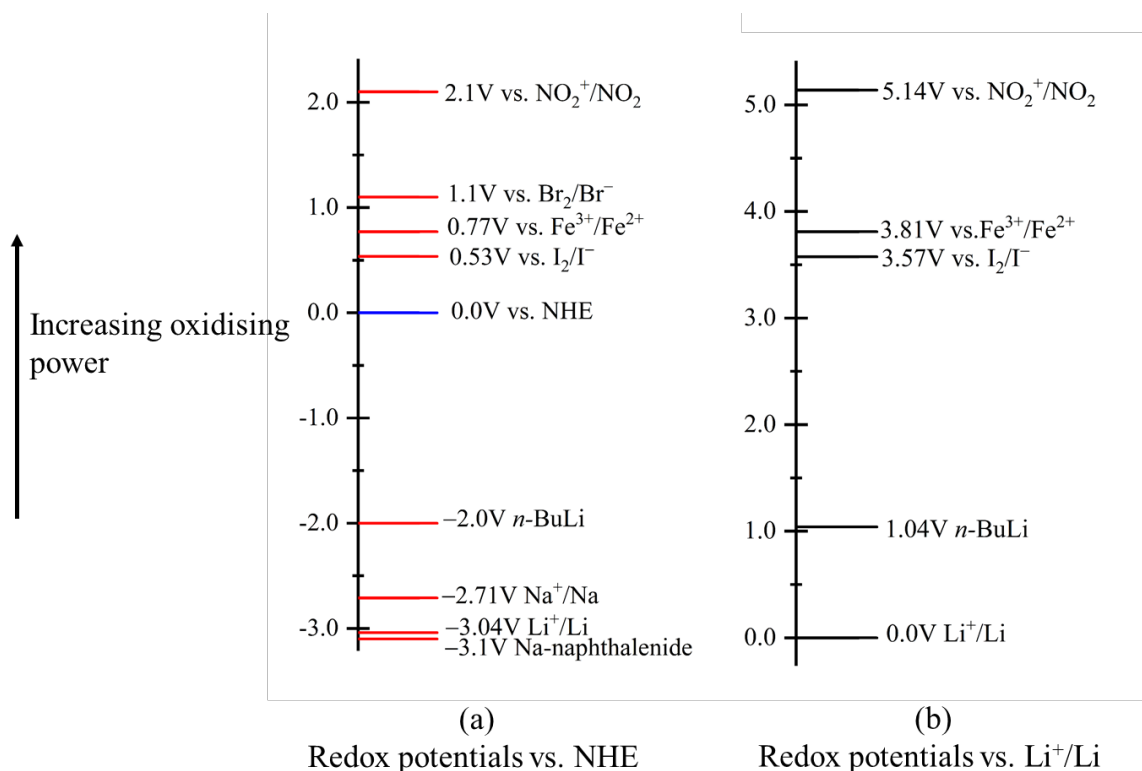
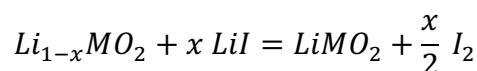
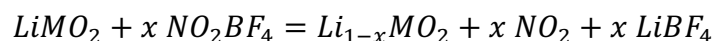
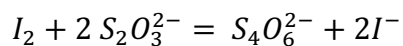
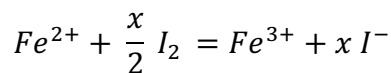
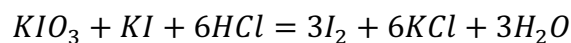
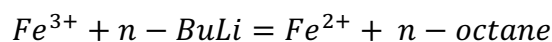


Figure 2.2 Redox potentials list; (a) Redox potentials vs. NHE. (b) Redox potentials vs. Li^+/Li

To achieve Li-intercalation, desired samples are treated with *n*-butyl lithium solution¹²¹ in a 1:5 molar ratio in N_2 gas environment inside a small Schlenk flask. The reaction usually takes 48 hours to complete, after that the lithiated sample is washed and filtered with excess toluene solution. After drying the sample in a dynamic vacuum, the black(usually) reduced powder is stored in an Ar-filled glove box. To check the reversibility, and determine the quantity of lithium inserted, the reduced sample is treated with a known quantity of I_2 in acetonitrile, and the I_2 consumed is calculated by titrating the remaining I_2 against a standardized thiosulphate solution. A simplified version of a few of the reactions involved are shown below.



For, Li-deintercalation, the desired sample is treated with nitroniumtetrafluoroborate¹²² in acetonitrile keeping the molar ratio of the reactants to 1:5 respectively in a small Schlenk tube with N₂ gas flowing. The Schlenk tube is sealed with a glass cap and the contents inside are stirred in an oil bath at 50 °C for 7 days. After 7 days the oxidized product is washed with acetonitrile and filtered in a Schlenk line. After drying in vacuum, the oxidized product is stored inside an Ar-filled glovebox. In order to check the reversibility, the oxidized sample is treated with LiI in acetonitrile at 50°C for 3 days and the released I₂ is estimated by titrating against a standardized thiosulphate solution. Samples (pristine/oxidized/reduced) with different lithium content at various stages of lithium intercalation and de-intercalation were characterized with various methods to check the undergoing change in the bonding and structural environment.

2.2.1. Powder diffraction

Powder diffraction is a widely used structural characterisation technique in academic and industrial laboratories for applications in solid-state chemistry. In this thesis X-ray powder diffraction and neutron powder diffraction methods were used for the structural analysis of the materials mentioned.

Solid crystalline materials have a periodic arrangement of its constituents. The periodic arrangement of the atoms constructs the lattice planes in the material. The array of lattice planes has a comparable spacing with the wavelength of the incident X-ray or Neutron radiations which when reflected, results in diffraction. The relationship between the wavelength (λ), the incident angle (θ) and the interplanar spacing (d) of the crystal lattice is given by Bragg's law^{123,124}. For constructive interference, the path difference should be an integral multiple of the wavelength of the incident radiation.

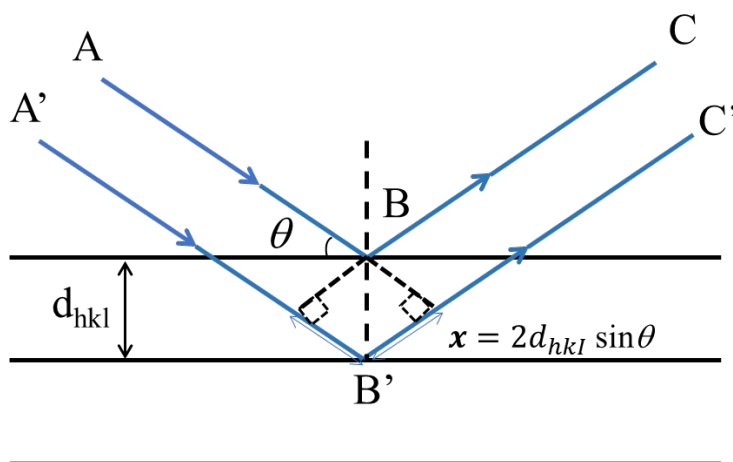


Figure 2.3 Schematics of diffraction techniques, Braggs Law

$$n\lambda = 2d_{hkl} \sin \theta$$

In the equation n is an integer, referred to as the order of diffraction, and is often unity. The intensity of the reflected radiations is defined as:

$$I_{hkl} \propto LmA|F_{hkl}|^2$$

In the equation, L is the Lorentz-polarisation function constant, m is the reflection multiplicity, A is the absorption factor and F_{hkl} is the structure factor. The structure factor F_{hkl} is expressed as

$$F_{hkl} = \sum_n f_n(\theta) \exp[2\pi i(hx_n + ky_n + lz_n)] \exp\left[\frac{-8\pi^2 U_{iso_n} \sin^2 \theta_{hkl}}{\lambda^2}\right]$$

Where, f_n is the atomic scattering factor, (x_n, y_n, z_n) are the fractional coordinates of the atoms in the unit cell and, U_{iso_n} is the isotropic thermal displacement factor.

2.2.1.1. X-ray powder diffraction

2.2.1.1.1. Bruker D8 eco diffractometer

Laboratory X-ray diffraction was performed on the powder samples obtained during the different stages of the reaction progression to monitor the structural change and to find out the extent of the reaction completed. A Bruker D8 eco diffractometer was used for such purpose. It operates at 40kV and 25mA, is equipped with a Bragg-Brentano focusing geometry, an LYNXEYE detector with $\text{Cu } K_{\alpha 1}$ and $K_{\alpha 2}$ wavelengths. Although Bruker data have spectral contamination, the high signal-to-noise ratio, X-ray absorption correction, and the ability for fast measurements with multiple samples in a single loading make it an ideal choice for Fe-based samples for a quick monitoring of the reaction progress and the associated structural change.

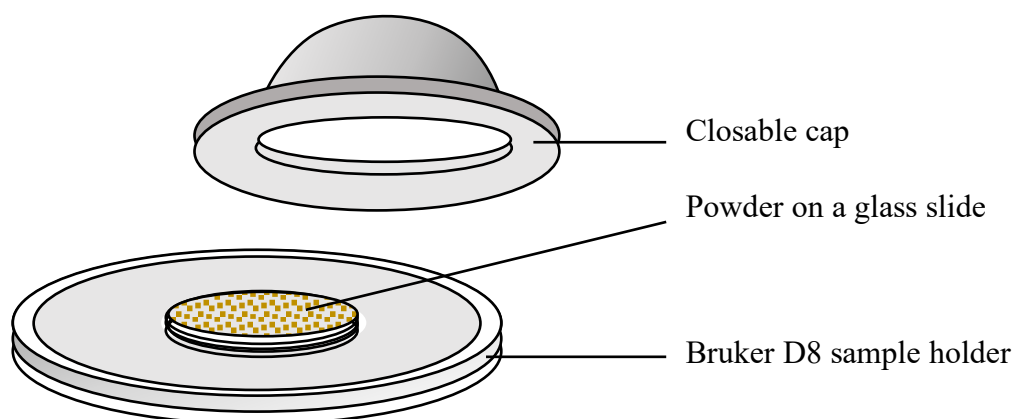


Figure 2.4 Bruker D8 eco sample holder

Powder samples were sprinkled on a thin-round glass slide coated with a very thin layer of high vacuum grease and the glass slide was fixed with grease to the sample holder, facing the powder to the top (as shown in Figure 2.4). For, air-sensitive diffraction measurement, a similar sample preparation method was carried out inside the glove box and then the cap was closed. After the sample preparation the sample holder was taken to the Bruker D8 eco instrument and X-ray diffraction was performed. The collected data was used for Rietveld refinement¹³² for structural analysis.

2.2.1.2. Synchrotron X-ray powder diffraction (SXRD)

A synchrotron is a type of circular particle accelerator which accelerates charged particles (electrons) through a sequence of magnets until they reach almost the speed of light. This produces X-ray radiation which is millions of times brighter than the light produced from conventional sources what can be used for powder diffraction resulting in a very high-resolution data. The synchrotron data in this thesis were collected from the I11 beamline at the Diamond Light Source Facility at Didcot, Oxford, U.K. A schematic of the I11 beamline is presented below¹²⁵.

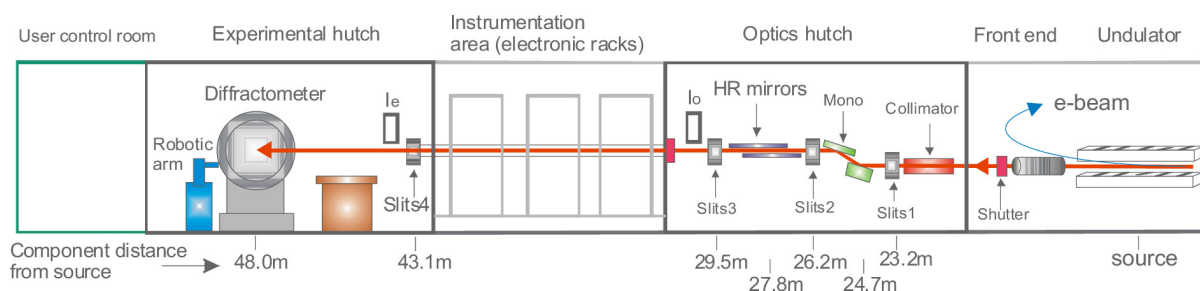


Figure 2.5 I11 beamline, Reprinted from Ref¹²⁵, with the permission from AIP Publishing

In the I11 beamline, a double-crystal monochromator composed of two liquid nitrogen-cooled Si (111) crystals; are used to select the wavelength of the incident beam. The produced X-rays have an energy range of 5-25 KeV (0.4-2.1 Å). The wide-angle Position Sensitive Detector (PSD) which uses Mythen-Si μ strip module¹²⁶, optimized for quick data collection (< 2 minutes) has been used for the SXRD data mentioned in this thesis.

Glass capillaries with diameter of 0.3 mm or 0.5 mm were filled with powder samples and sealed with a blowtorch maintaining the length of the filled capillary between 15-50 mm. For air-sensitive samples the powder was loaded into the capillary inside the glovebox and grease was applied to the open-end. After taking out the loaded capillary, it was immediately sealed. The capillary was mounted at a brass pin with a magnetic base that spins during the measurement. The collected SXRD data confirm the phase purity, often revealing tiny impurities and subtle splitting of the peaks for accurate unit cell determination. A detailed structural analysis is possible using Rietveld refinement. However, the location of light atoms and the distinction of similar scattering atoms (neighbouring atoms) in the periodic table could not be precisely determined using SXRD data.

2.2.1.3. Neutron powder diffraction (NPD)

Neutron powder diffraction is also a common characterisation technique for structure analysis of crystallized phases. While X-rays interact with the electron densities surrounding the atoms, neutron radiation interacts with the nuclei of atoms within the structure. A few comparisons of these two techniques are presented below.

Firstly, as the scattering of the X-rays is dependent on the electron density surrounding the atom, the contribution from the light atoms (e.g. lithium) is clouded by the contribution from heavier atoms (e.g. iron) making it difficult to locate the light atoms in the structure. The neutron scattering length is independent of the atomic number of the atom¹²⁷ and provides no linear relationship¹²⁸ (as shown in Figure 2.6). Thus, the neighbouring elements in the periodic table and the lighter atoms (e.g., lithium, oxygen ions) even in the presence of heavier atoms (e.g., iron, germanium cations) could be precisely located during the structure analysis. Table 2.2 shows the neutron scattering lengths of the relevant atoms discussed in this thesis.

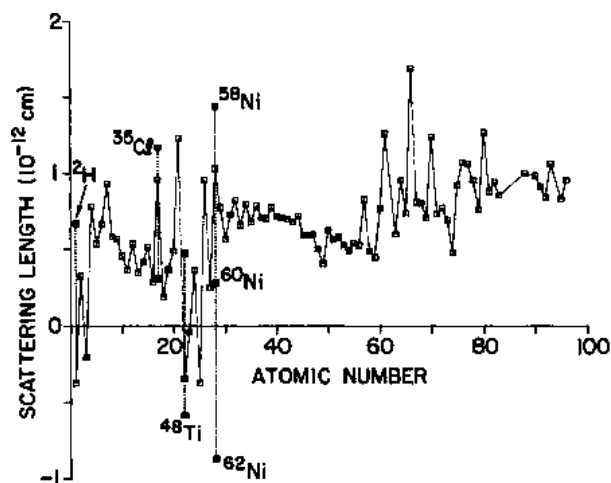


Figure 2.6 Neutron scattering factor dependence of the atomic number, Figure taken with permission from Ref¹²⁷.

Table 2.2. Table of neutron scattering lengths (taken from Ref¹⁷⁸)

Element	Neutron scattering lengths (fm)
Li	-1.90
O	5.803
Na	3.63
Al	3.449
Si	4.1491
Fe	9.45
Ga	7.288
Ge	8.185

Secondly, the intensity from the X-ray measurement diminishes with a higher scattering angle, whereas for neutron scattering the form factor is almost independent of the scattering angle. Thus, the intensity of the high angle diffraction is maintained in neutron, providing a more accurate structural analysis compared to X-ray diffraction.

Thirdly, the interaction of the neutrons and the atomic nuclei is very weak, thus a large sample is required for the diffraction experiment. Neutrons are also very penetrating, which further allows accurate bulk characterization and facile use of complex sample environments. Finally, Neutrons are spin $\frac{1}{2}$ particles, thus they are also scattered by a lattice of ordered magnetic moments. This allows the determination of long-range ordered magnetic structures in the materials. The interactions of neutrons with the outer shell electrons result in magnetic scattering. The magnetic form factor of the diffraction has an angular dependence that decays

fast (faster than x-rays). The magnetic structure factor $F_{hkl,mag}$ of an unpolarized neutron source can be defined as¹²⁹:

$$F_{hkl,mag} = \sum_j q_j p_j \exp [2\pi i(hx_j + ky_j + lz_j)]$$

Where q_j is the magnetic interaction vector, p_j is the magnetic scattering length, and (x_j, y_j, z_j) is the atomic coordinate of the j^{th} magnetic atom in the unit cell. The observed intensity of a magnetic reflection $I_{hkl,mag}$ is proportional to the square of the projection of the magnetic structure factor onto the scattering vector¹²⁹.

$$I_{hkl,mag} = |F_{hkl,mag}|^2 \cos^2 \alpha$$

Where α is the angle between the magnetic scattering structure and the relevant lattice plane.

For the final structure determination, a combined structural analysis using, powder X-ray and neutron diffraction data is carried out. Prior to the experiment, the powdered samples are loaded into vanadium cans and sealed with steel lids. For the air-sensitive samples, the powdered samples were sealed inside the Ar-filled glovebox. Vanadium has a very low coherent scattering length of -0.3824 fm¹²⁸, providing a negligible contribution to the collected diffraction pattern making it an ideal choice as a sample container for neutron diffraction.

The NPD data presented in this thesis are collected from the following neutron sources: POLARIS diffractometer at ISIS neutron facility, Rutherford Appleton Laboratory in Oxfordshire, UK; and D2B diffractometer at the Institut Laue-Langevin (ILL) in Grenoble, France. The assistance of Dr. R. Smith and Dr. E. Suard during the NPD data collection is greatly acknowledged.

2.2.1.3.1. Polaris (ISIS)

The Polaris powder diffractometer¹³⁰ is a high-intensity, medium-resolution time-of-flight diffractometer at ISIS Facility pulsed neutron and muon source. The high incident neutron flux enables faster and shorter time data collection with comparatively small sample volumes. In ISIS, the source of neutrons is a spallation reaction, which is moderated to the desired wavelength of the time of flight experiment. In the TOF technique, the initial position and the velocity of a pulse of neutrons are fixed and the final position and the time taken for the neutron to the final position are detected. De Broglie's relationship can be illustrated as:

$$\lambda = \frac{h}{mv} = \frac{h}{m} \times \frac{t}{L} = 2d \sin \theta$$

$$\text{Or, } d = \frac{h}{2m} \times \frac{t}{L \sin \theta}$$

Where h is the Plank's constant, m is the mass, v is the velocity of the neutron and t is the time taken to travel L distance. θ is the fixed angle where the different detectors are located and, it is generally known/unchanged. The Polaris diffractometer has a number of detectors for data collection which could be divided into five separate banks covering an overlapping d-spacing range. The resolution and d-spacing range varies with different detectors. Bank 1 at a very low angle, and bank 2 and 3 at low angles cover a wider d-spacing range but the resolution is poorer. Bank 4 at 90° and bank 5 at backscattering angles produce high resolution data and sharper diffraction but the d-spacing coverage is limited. The complementary data from the different banks are combined for structure analysis. In this thesis, the Polaris diffractometer is

utilized to characterize the lithium content and the structural change in different systems. (Chapters 3-9)

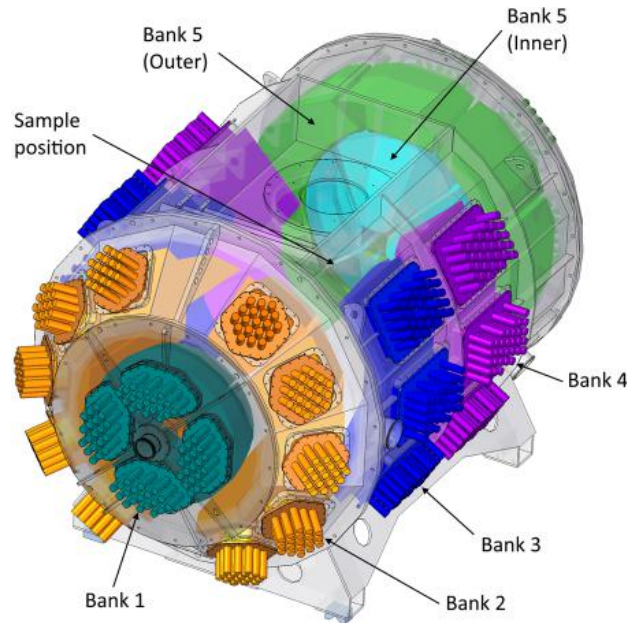


Figure 2.7 Polaris detector, picture reprinted with permission from ref¹³⁰

2.2.1.3.2. D2B (ILL)

The D2B¹³¹ instrument at the ILL neutron source in Grenoble, France is a high-resolution powder diffractometer used globally for structure analysis. In ILL the neutrons are produced from the nuclear fission reaction of ^{235}U and the desired energy range for the diffraction experiment is achieved by channelling the neutrons through moderators filled by D_2O . The data presented in this thesis from the D2B instrument is collected with a fixed wavelength of $\lambda = 1.59432 \text{ \AA}$ over the angle range of $4^\circ < 2\theta < 160^\circ$ with multiple scans which are summed together to yield data with high signal to noise ratio. The NPD data from D2B was used to determine the iron-gallium ordering in $\text{Na}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ and $\text{Na}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ phases as discussed in Chapters 9. A figure of the D2B¹³¹ diffractometer is presented below.

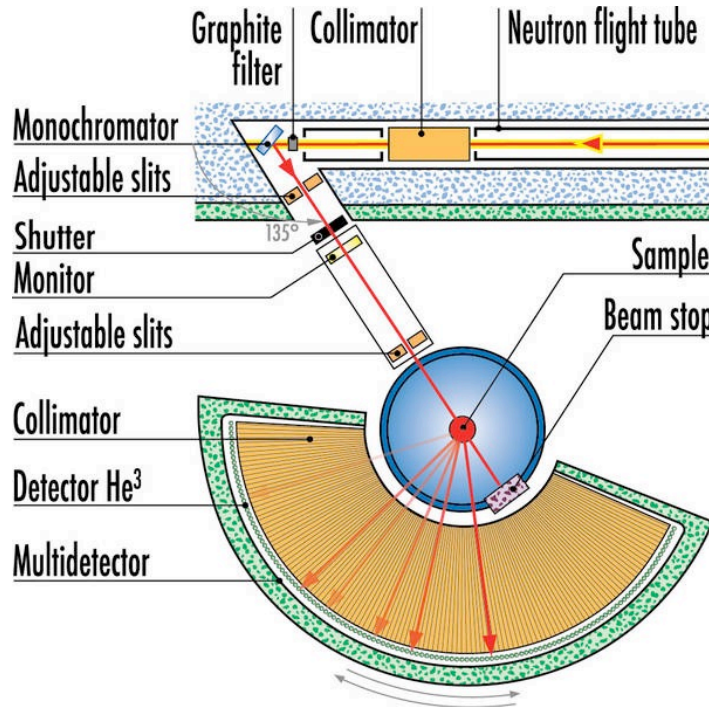


Figure 2.8 D2B diffractometer, Picture reprinted with permission from ref¹³¹

2.2.1.4. Rietveld Refinement

The Rietveld refinement¹³² method was used to refine the structural models with the experimentally collected SXRD or NPD data during the structural analysis. The method employs the matching of the experimentally observed intensity of the collected data and the calculated intensity of the structural model through a least-squares algorithm until a best-fit is achieved. During the refinement, the entire pattern and the background are considered instead of individual peaks, which excludes the de-convolution of the overlapping reflections. Being a quantitative method, it also precisely determines the atomic/phase weight percentage between multiple phases present in the sample. Both the structural and the instrumental parameters are refined during the analysis in order to minimize the difference (S) between the experimental and the simulated pattern from the input structural model using a least squares equation:

$$S = \sum_i w_i \{y_i^{obs} - y_i^{cal}\}^2$$

Where w_i is the weighting factor, y_i^{obs} , y_i^{cal} are the observed and calculated intensity at point i . During the refinement, an approximate structural model (.cif file) is incorporated and the atomic position, fractional occupancy, and the thermal parameter is refined to obtain the best fit. Also, the background, the unit cell parameters, zero shift, and peak shape parameters are refined to obtain the best fit. To account for the asymmetry of the observed peak intensity, refinement of the anisotropic peak broadening/sharpening along a certain direction is performed using Stephens model¹³³ for the lithium-exchanged phases (Chapters 3-5). The refinement is judged with the fitting statistics: goodness of fit χ^2 , profile factor R_p , and weighted profile factor wR_p .

$$\chi^2 = \frac{\sum_i w_i (y_i^{obs} - y_i^{cal})^2}{n_{obs} - n_{var}}$$

$$R_p = \frac{\sum_i |y_i^{obs} - y_i^{cal}|}{\sum_i y_i^{obs}} \times 100\%$$

$$wR_p = \sqrt{\frac{\sum_i w_i (y_i^{obs} - y_i^{cal})^2}{\sum_i w_i (y_i^{cal})^2}} \times 100\%$$

Where n_{obs} is the number of observations and n_{var} is the number of variables used during the refinement process. After obtaining the best fit, the refined model is used to calculate the final atomic positions, bond angles, bond distances, and bond-valence sum parameters. The Rietveld refinement was carried out using the GSAS¹³⁴ and TOPAS-V7¹³⁵ programs.

2.2.1.5. Profile fit (Pawley fit)

Pawley fit¹³⁶ is a fitting tool for indexing the collected XRD, SXRD, and NPD data using a crystallographic unit cell without any atoms. The method involves the refinement of the unit cell parameter by matching the observed intensity only through the constraints of the symmetry of the crystal system with allowed reflections coming from the Miller planes (hkl) with a peak shape parameter. The peak shape in the profile fit can be defined with different

mathematical functions like Gaussian, Lorentzian or a combined pseudo Voigt^{137,138} functions. This method is very useful for determining the cell parameters, the correct crystal symmetry, and the space group of a newly synthesized phase. Also, often during the Rietveld refinement the algorithm collapses due to vast differences in the observed and the simulated pattern originating from the differences between the inserted model and the actual structure. Thus to get the closest approximated unit cell parameters, Pawley method¹³⁶ is also helpful.

2.2.2. Electrochemical measurements

To obtain the cyclic voltametric profile and the charge-discharge capacity profiles a coin cell battery was prepared. The pristine lithium material (LiMO_2) was used as a cathode, a lithium metal chip as an anode, and lithium hexafluorophosphate as an electrolyte. A standard coin cell was prepared as described below.

A powder sample of the desired active lithium material, carbon black, and polyvinylidene fluoride (PVDF) was weighed and ground together with a mortar and pestle maintaining the mass ratio of 80:10:10 respectively. After grinding the mixture for 15 minutes the mixture is transferred to a 12 mL Thinky/planetary pot which is further transferred to a glove box. 0.3 mL of 1-methyl-2-pyrrolidone (NMP) was added to the mixture and the Thinky pot was taken out of the glove box and mixed using a Thinky ARE-250 mixer at 2000 rpm for 5 minutes. The pot was transferred back into the glovebox to visually check the consistency of the mixture, and if required more NMP solution was added and mixing was continued until a homogeneous viscous mixture was obtained. Once the right consistency was achieved it was poured into a carbon-coated aluminium foil inside a fume hood and casted into a slurry using a blade. Once dry, the slurry was heated overnight at 80 °C in a vacuum oven. The dry slurry cast was taken in a disc cutter apparatus and 12 mm disc cathodes were punched out from it which were transferred inside the glovebox. The coin cell was assembled using Cambridge Energy Solutions SS316 CR2032 coin cell cases, a lithium chip (15.6 mm diameter, 0.25 mm

thick), a Whatman glass fiber membrane separator (16mm diameter), and the cathode. A schematic of the coin cell assembly is presented below (Figure 2.9). During the coin cell assembly, the separator was placed between the positive and the negative electrode and was soaked with 10 μL of electrolyte.

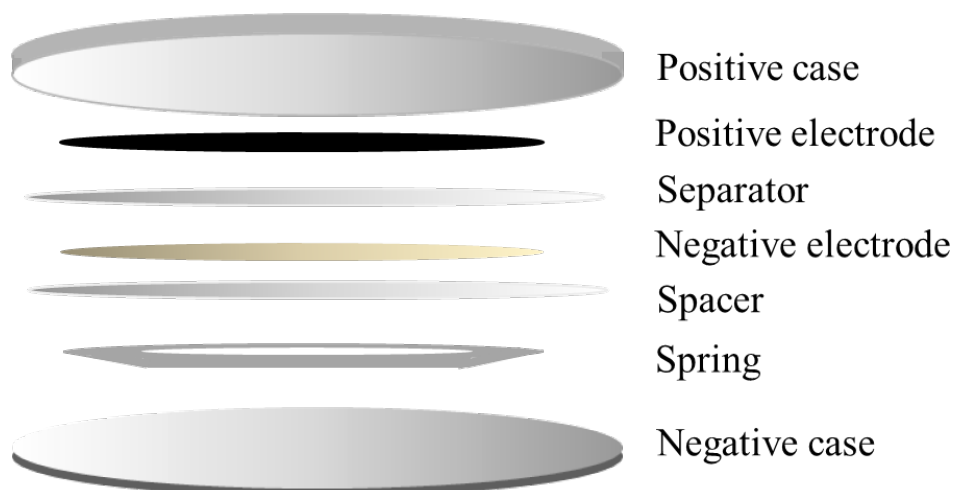


Figure 2.9 Schematics of coin cell preparation

The prepared coin cell was used for various electrochemical measurements. Cyclic voltammetry and galvanostatic testing were carried out at various voltage ranges from 1.0 V to 4.8 V. The testing was done at room temperature and it took approximately 7 days to complete the cyclic voltammetry testing and approximately 30 days for the galvanostatic testing. The open circuit voltage was measured and recorded before cycling to ensure the analysis was not carried out on short-circuited cells. The collected data was analysed with EC-Lab and Maccor software. All the electrochemical data presented in this thesis were collected at the University of Sheffield with the help of Dr. Samuel Booth, Heather Grievson, Anamaria Illinca and Josie-May Mortimer.

2.2.3. ICP-MS measurement

Inductively coupled plasma mass spectrometry¹³⁹ (ICP-MS) is a technique that can accurately determine the mass of different elements present in a sample. The elements present, when discharged at a very high temperature (~ 10000 K) are separated by producing a positively charged ion which is then directed into the mass spectrometer via the interface region. Based on the unique mass/charge ratio the elements are detected and the final mass is recorded. A set of known standards is required to calibrate the instrument before the measurement. During the sample preparation, accurately weighed powder of the desired sample is dissolved in 19 mL HNO_3 and 1 mL HCl solution followed by the addition of 180 mL deionized water and mixing well. Then, 2 mL of the mixture is taken into a 15 mL centrifuge tube and 8 mL of deionized water is added. The centrifuge tube was closed and sealed with paraffin films which were given to Trang. The measurements were carried out with the help of Trang To from the School of Geography and the Environment, University of Oxford. During the data processing mass of one element had to be fixed as per the stoichiometry of the sample. To maintain consistency, in all the samples, the concentration of iron was fixed as per the initial composition.

2.2.4. X-ray Absorption Spectroscopy (XANES and EXAFS)

X-ray absorption spectroscopy¹⁴⁰ is a powerful tool to determine the oxidation state and the local environments around the excited central atom. Depending on the energy range the XAS could be divided into two subcategories: X-ray absorption near edge structure (XANES) and Extended x-ray absorption fine structure (EXAFS).

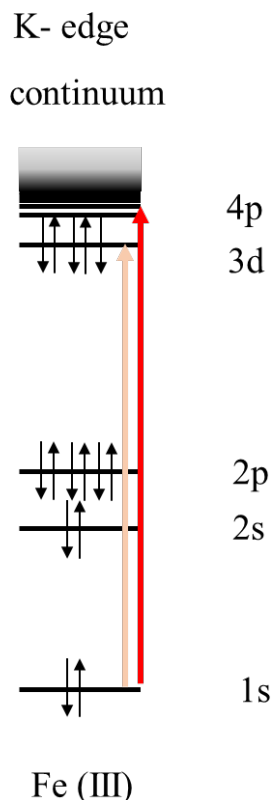


Figure 2.10 Schematics of Fe K-edge XANES; pre-edge ($1s \rightarrow 3d$): cream coloured line

In XANES, one electron from the core is excited to the lowest unoccupied molecular orbital (LUMO) state. For higher oxidation state metal cation, the edge shifts towards higher energy which could be explained due to stronger attraction between the nuclei and the $1s$ electron due to the lesser number of electrons in the valence orbital than in the unoxidised state. In the K-edge spectrum, the major contribution comes from $1s \rightarrow np$ transition, where np is the lowest unoccupied p orbital of the absorbing atom. For transition metal with a partially filled d orbital, a transition from $1s \rightarrow nd$ state could also take place, resulting in a pre-edge feature before the K-edge. This transition is forbidden by the selection rules. However, these selection rules are relaxed either in the presence of $s-p$ orbitals overlapping or the absorbing atom being in a tetrahedral environment. As the tetrahedral geometry is non-centrosymmetric it allows the excitation of $1s$ electron to nd state. The materials analysed in this thesis exhibit FeO_4 coordination, thus a pre-edge feature was observed for the XANES spectra collected from all the materials. The transmission observed can be expressed as:

$$\mu = \log \frac{I_o}{I_t}$$

where μ is the normalised transmission and I_o , I_t are the incident and transmitted intensities. The Athena¹⁴¹ software package was used during the analysis for the collected data. Iron K-edge XANES data for the samples discussed in this thesis are presented in Chapter 3-9.

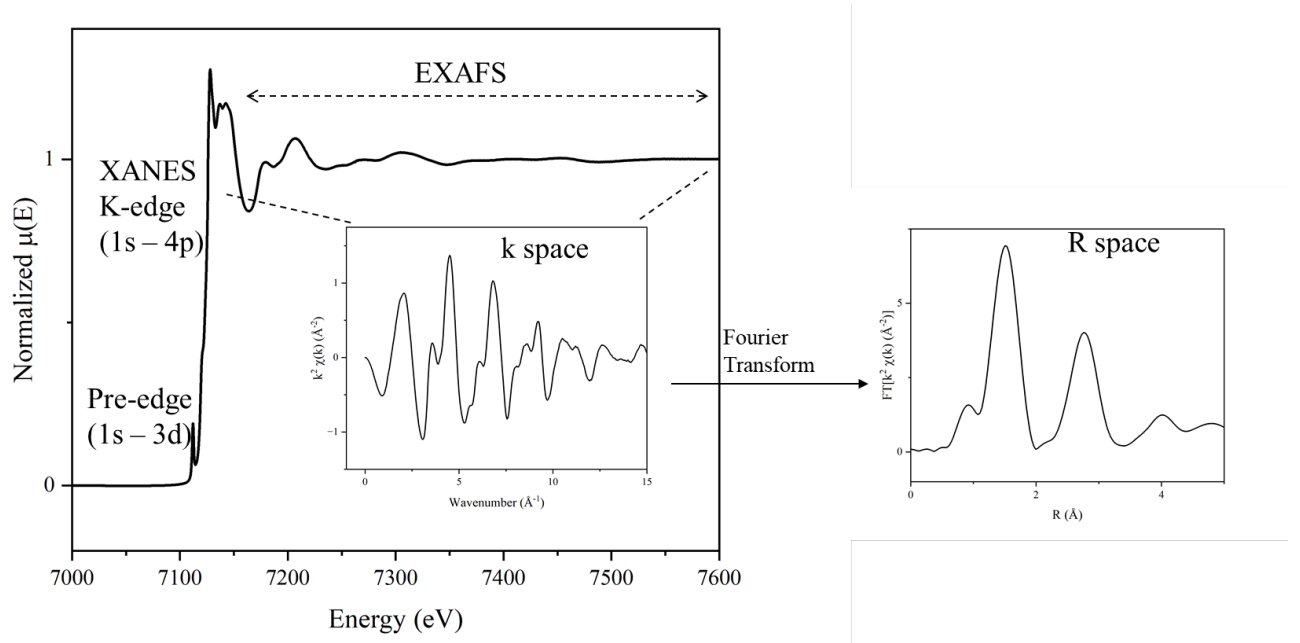


Figure 2.11 Fe-K edge XANES and EXAFS spectrum for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ sample

In EXAFS, when the core 1s electron is excited with further energy than the LUMO level, the electron is released by the absorbing atom and the excess energy is transmitted as kinetic energy. Due to the wave-particle duality of electrons, the interaction of the released electron with the backscattered electron wave from the neighbouring atoms could give rise to a series of constructive and destructive interferences. A quantitative modulation $\chi(k)$ of EXAFS interactions can be expressed as follows:

$$\chi(k) = \sum_j \frac{N_j S_0^2 |f_j(\pi, k)|}{k R_{aj}^2} e^{-2\sigma_{aj}^2 k^2} e^{\frac{-2R}{\lambda}} \sin [2kR_{aj} + \delta_{aj}(k)]$$

Where R_{aj} is the static disorder term, $e^{-2\sigma_{aj}^2 k^2}$ is the Debye-Waller factor; dynamic disorder term, σ_{aj} is the root-mean-square deviation, N_j is the number of paths, S_0^2 passive electron reduce factor, $|f_j(\pi, k)|$ is the effective scattering amplitude, k is the wave vector ($k = 2\pi/\lambda$), $\delta_{aj}(k)$ is the phase shift and λ is the electron mean free path. The Artemis software¹⁴¹ package was used during the fitting of the EXAFS data. The XAS data shown in this thesis were collected in B18¹⁴² beamline in the Diamond facility, UK, or with the help of Dr. Ashok Menon at the University of Warwick, UK.

2.2.6. Resonance In-elastic X-ray Scattering (RIXS)

Resonance in-elastic X-ray scattering¹⁴³ (RIXS) is an analytical tool that is a combination of X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES). It is element selective and can accurately determine the different species involved in the process. RIXS is a two-photon process and it could be considered as the X-ray equivalent of resonance Raman spectroscopy. During the XAS process, a core hole at the $1s$ orbital is generated, leaving the system in a very unstable, excited state which decays fast. The decaying of the excited state to the ground state via electron transfer from the outer shell to core $1s$ shell takes place with various possibilities^{93,144}. (1) During the decaying process when the energy of the excitation and the emission is the same, an elastic peak is observed. (2) The valence shell electron filling the hole at $1s$ orbital without any internal transition, generating element sensitive XES signal (usually takes place at higher excitation energy ~ 545 eV) (3) Before the decaying, low energy excitations (≤ 10 eV) as lattice excitations, spin flips, charge transfer excitations, $d-d$ transitions, magnons excitations, non-divalent oxygen state excitations taking place resulting an energy loss in the system which can be attributed to different characteristic excitations^{93,144}. Although at this stage the fundamental mechanism of the process is not clear, different energy loss phenomena are explained with the different processes involved⁹³.

Sharp and broad features in the XAS spectra of the O-K edge can be classified as: excitation energy range 528-534 eV is related with the excitation of O 1s to TM(3d)-O(2p) hybridised state, energy higher than 535 eV is related with the excitation of O 1s to the mixed TM(4s,4p)-O(2p) bands. Both these two hybridisations are associated with emission at ~ 525 eV for O²⁻ species in TM oxides. For an energy loss of 2.4 eV TM *d-d* excitations could be observed. The aforementioned excitations are dominated by the TM orbital contributions. However, there are two more features in the RIXS spectra that are believed to be the fingerprint of the oxidised oxygen species produced during the oxygen redox. A sharp feature with an excitation energy of 531 eV and emission energy of 523.7 eV (energy loss of 7.3 eV), while the other is a weak periodic feature close to the elastic line at the same excitation energy. Energy spacing between two adjacent periodic feature is associated with the vibrational energy level of the species under investigation which is further confirmed by Birge-Sponer plot¹⁴⁵.

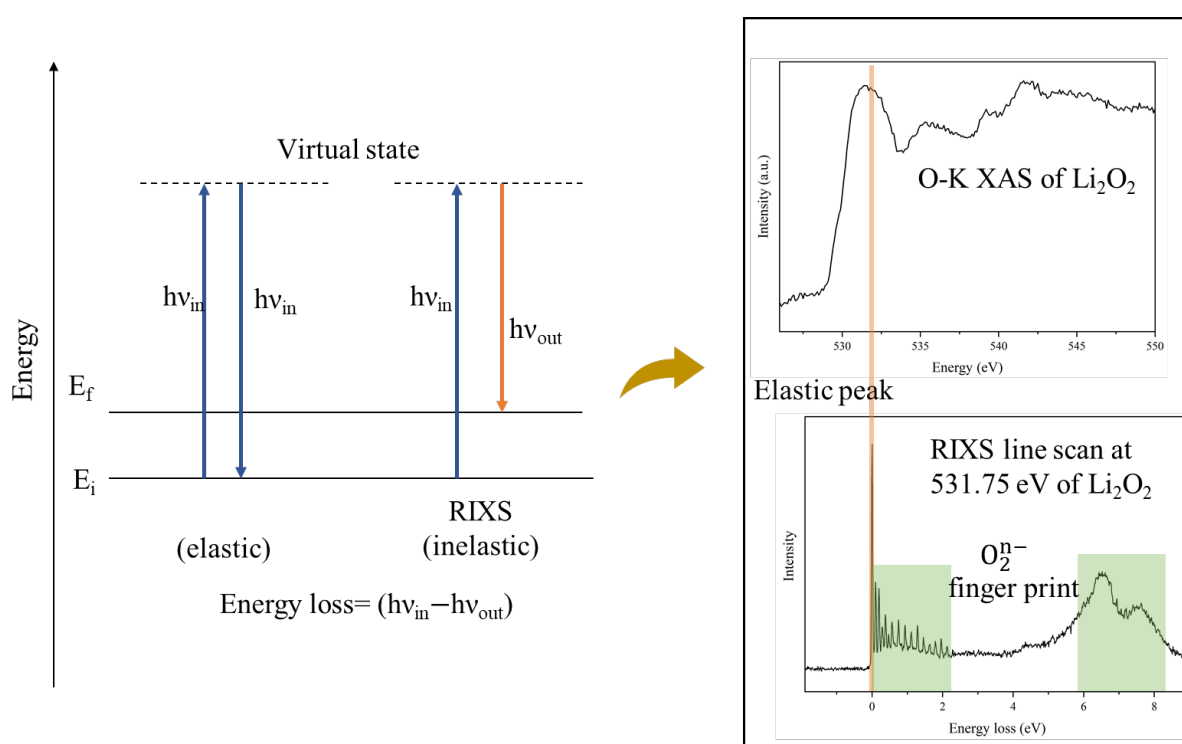


Figure 2.12 Schematics of RIXS (left), O K-edge XAS and RIXS line scan of Li_2O_2 at an excitation energy of 531.75 eV (right). Green region at energy loss 0-2 eV and 6-8 eV indicates features associated with oxygen oxidation

Due to such distinct features in RIXS (mapping and line scans) for molecular O₂, superoxide and peroxide species, it is becoming a useful tool for determining the oxygen species involved during the oxidation of the cathode at a very high voltage i.e. ≥ 4.2 V⁸⁴. However, there are some systems (Li₂MnO₃, Li₃IrO₄)^{146,147} which involve reversible oxygen species during cycling, but no RIXS feature is observed which raises some questions about the technique being universal. Nevertheless, to identify the oxygen species produced during the chemical oxidation of the materials mentioned in this thesis, O-K edge XAS and RIXS (line scans and mapping) were performed in I21 beamline in the Diamond light source, Oxford, UK. The data collection process was assisted by Dr. Xabier Martinez, Dr. Ashok Menon, Dr. Samuel Booth, and Dr. Stefano Agrestini.

2.2.7. Mössbauer Spectroscopy

⁵⁷Fe Mössbauer spectroscopy^{148,149} is a technique in which the interaction between the electromagnetic moment of the nuclear charge and the electromagnetic field produced by the extra-nuclear electrons are studied. This interaction gives rise to the splitting or shifting of nuclear energy levels. The technique involves absorption of γ -rays, from ⁵⁷Co to Fe atom, which initially decays to an excited ⁵⁷Fe populating the 136 and 14.4 keV nuclear level with nuclear spin quantum numbers I=5/2, and I=3/2 respectively, eventually decaying to the ground state. The 14.4 keV nuclear state has a half-life of 100 ns, making it ideally suited for Mössbauer spectroscopy. The distribution of energies about the energy E₀ (= transition probability as a function of transition energy E) is given by the Breit-Wigner formula¹⁴⁹:

$$I(E) = \frac{\left(\frac{\Gamma}{2}\right)^2}{(E - E_0)^2 + \left(\frac{\Gamma}{2}\right)^2}$$

Where Γ is the natural line width and is related to the mean half-life time (τ) via the uncertainty principle as $\Gamma \cdot \tau = h/2\pi$. The value of τ and Γ for Fe makes it suitable for

Mössbauer spectroscopy. Due to the absorbance of γ -rays the absorbing atom suffers a recoil effect that is 5-6 orders of magnitude larger than the natural line width Γ , which makes no possible resonance between free atoms or molecules, thus the Mössbauer effect could not be observed for freely moving atoms or molecules, i.e., in a gaseous or liquid state. Although the translational and rotational motions are restricted in solids, the vibrational motion is allowed which leads to the thermal broadening of the emission and absorption lines. In the solid state, crystalline or non-crystalline, recoilless resonant absorption produces maximum overlap of the emission and absorption line for identical materials. For non-identical materials, the resonance effect may be perturbed due to electric and magnetic hyperfine interactions between the nuclei and the electric and magnetic fields by the electrons. This hyperfine shift, shifts the energy level as well as split the degenerate nuclear lines into multiple transitions. The perfect overlap could be restored, by moving the source with the Doppler effect. The hyperfine interaction energy ε is related to the Doppler velocity v via $\varepsilon = (\frac{v}{c})E_\gamma$. Where c is the speed of light and E_γ is the transition energy. The plot of the relative transmission of γ radiation as a function of the Doppler velocity is called the Mössbauer spectrum. The hyperfine interactions are classified into three categories:

Isomer shift δ (mm/s): It is an electric monopole interaction between the protons of the nucleus and the electrons (s electrons mainly). It gives information about the oxidation state, spin state, and bonding properties. The isomer shift δ is expressed as the difference between the transition energies of the source (E_S) and absorber (E_A):

$$\delta = E_A - E_S = \frac{2\pi Ze^2}{3}(\rho_A - \rho_B)(R_e^2 - R_g^2)$$

Where R_e and R_g are the radii of the excited state and the ground state respectively, ρ_A and ρ_B are the electronic densities of the absorber and source respectively. The isomer shift of

Fe compounds with different oxidation states and spin states are well reported¹⁴⁹ and a comparison of the new data to the old reports can be used for accurate identification of its electronic and chemical behaviour.

Quadrupole splitting ΔE_Q (mm/s): It is an electric quadrupole interaction between the nuclear quadrupole moment and an inhomogeneous electric field, in absence of magnetic dipole interaction. The splitting is sensitive to the oxidation state, spin state, and coordination environment. It is worth mentioning that the quadrupole splitting is sensitive to the anisotropy present in the system and is normally suppressed for the symmetric cubic system where only a single line is observed instead of a doublet. The details of quadrupole splitting are presented in Figure 2.13 below.

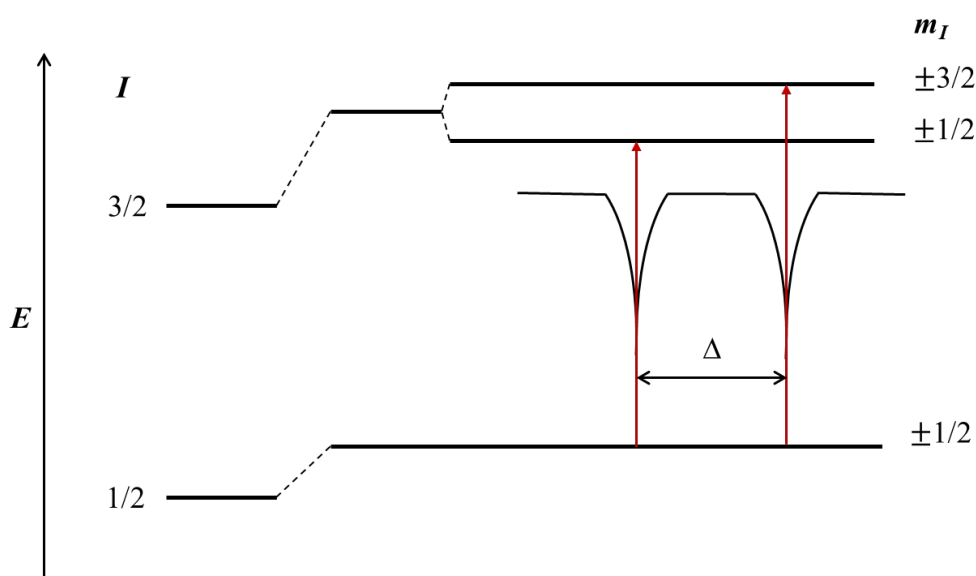


Figure 2.13 Quadrupole splitting from I 1/2 to 3/2 transition. The magnitude of the quadrupole splitting is Δ .

Magnetic splitting ΔE_M (mm/s): It is a magnetic dipole interaction between the nuclear magnetic dipole moment and the magnetic field at the nucleus. This property gives information about the magnetic properties of the material. Due to the magnetic field perturbation, the degenerate states are split into $2I+1$ states. For magnetic dipole transitions the selection rule is given as $\Delta I = \pm 1$, $\Delta m_I = 0, \pm 1$ which makes up for the six allowed transitions (Figure 2.14).

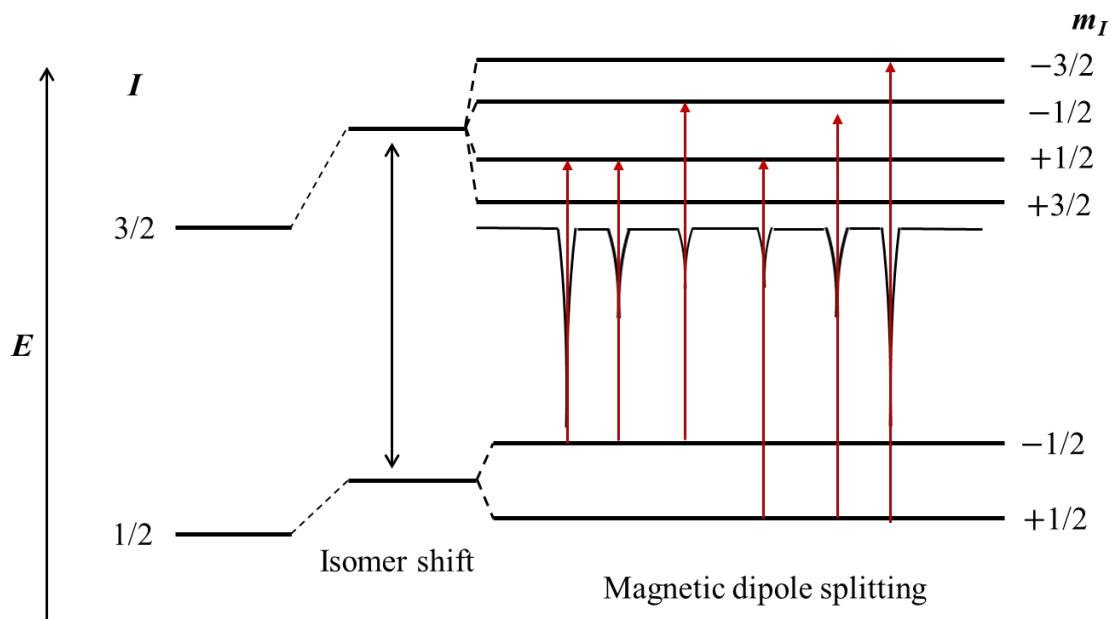


Figure 2.14 Schematics of magnetic splitting in Mössbauer spectroscopy

All the different shift and splitting values were calculated and recorded for the $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples mentioned in the thesis. Based on the value obtained, the change in the oxidation state of iron, and coordination environment change was assessed which is further supported by other characterizations data. During the sample preparations: prior to the measurement, the samples were ground with graphite and sealed in acrylic absorber discs. The collected spectra were normalized with an $\alpha\text{-Fe}$ standard using a 36 mCi ^{57}Co in Rh source. The data was collected over a velocity range of ± 12 mm/s. All spectra mentioned in this thesis were collected and fitted by Dr. Paul A. Bingham from Sheffield Hallam University.

2.2.8. Bond Valence Sum (BVS)

Bond valence sum (BVS) calculation¹⁵⁰ is a method for estimating the valence of an ion based on the bond lengths, surrounding atoms, and the coordination sphere. This method compares the bond length of all the reported compounds of the desired ion in similar environments with the calculated bond length of the desired ion in the structural model with an equation as follows:

$$V_i = \sum_j v_{ij} = \sum_j e^{(R_0 - R_{ij})/b}$$

Where, v_{ij} is the bond valence of a single bond between i and j ion, R_{ij} is the calculated bond length between i and j ion in the structural model, R_0 is the averaged, reported bond length between i and j ion in similar environments as R_{ij} and b is an empirical constant, usually considered to be 0.37. The calculation was performed in Vesta software and the value of R_0 is taken from the list of references, reported by David Brown¹⁵⁰. The calculated BVS parameter was used to describe the change in charge with respect to best-fit structural information.

Chapter 3 – Synthesis and characterization of β -NaFe_{1-x}M_xO₂ and T-LiFe_{1-x}M_xO₂ materials (M =Al, Ga)

3.1. Introduction

The synthesis, and characterization along with the electrochemical performance of T-LiFeO₂ (tetrahedral-LiFeO₂) as a cathode for the lithium ion batteries, was reported by Armstrong et al⁵⁵. T-LiFeO₂ material undergoes a transformation to a LiFe₅O₈ spinel phase during the electrochemical charging process, releasing oxygen gas irreversibly from the lattice. In an attempt to prevent conversion to LiFe₅O₈ on lithium extraction, the Al-for-Fe and Ga-for-Fe cation substitution of T-LiFeO₂ was investigated. The synthesis and characterization of β -NaFe_{1-x}M_xO₂ and T-LiFe_{1-x}M_xO₂ samples (M = Al and/or Ga) are presented in this chapter.

3.2. Experimental section

3.2.1. Synthesis of NaFe_{1-x}M_xO₂ and LiFe_{1-x}M_xO₂ sample

Samples of NaFe_{1-x}M_xO₂ (where M = Al and/or Ga) were synthesized by a high-temperature ceramic method as mentioned in Section 2.1.1. Suitable ratios of Na₂CO₃ (>99%, BDH chemicals), Fe₂O₃ (99.85%, Alfa Aesar), Ga₂O₃ (99.99% Alfa Aesar), and Al₂O₃ (99.9%, Alfa Aesar) were weighed, ground and calcined in air at 750 °C for 12 hours. The powders were then reground and pressed into 13 mm pellets and heated at 1100 °C for 12 hours. Samples of NaFe_{1-x}Al_xO₂ were then heated at 1100 °C for periods of 12 hours. Samples of NaFe_{1-x}Ga_xO₂ were heated at 900 °C for periods of 12 hours. Samples of NaFe_{0.5}Al_{0.5-y}Ga_yO₂ were heated at 950 °C for periods of 12 hours. The addition of an extra 5-10 mol percent of Na₂CO₃ during the later heating cycles seemed to facilitate the preparation of the pure samples.

After obtaining the pure $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$ samples a two-step, low-temperature topochemical cation exchange was performed to obtain the corresponding $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ phases. Initially ten mole equivalents of LiCl (98+%, Alfa Aesar) or LiBr (99%, Alfa Aesar) was added to a 250 mL round bottom flask containing ~ 150 mL of *n*-hexanol, then the $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$ sample was added. A water condenser was attached to the flask and the apparatus was heated at 165 °C for 48 hours using an oil bath with constant stirring of the *n*-hexanol suspension. After heating, the contents of the flask were filtered and then washed with methanol.

Following this procedure, the partially exchanged sample was ground with 10 mole equivalents of LiBr , and transferred to an open-end Pyrex tube, which was heated at 200 °C in a vertical furnace for 48 hours. The mixture was then washed with methanol to remove the LiBr and the Li-exchanged sample was collected by vacuum filtration.

Attempts to prepare Li-exchanged samples directly by the molten salt method by mixing the Na-precursor with a ten-fold excess of LiNO_3 (99.98% Alfa Aesar) and heating at 300°C for 48 hours resulted in the formation of LiFe_5O_8 and LiFeO_2 (cubic, disordered rock salt structure type, $Fm\bar{3}m$) impurities along with the main $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ phase.

3.3 Results

3.3.1. Structural characterisation of $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$

Synchrotron X-ray diffraction (SXRD) data was collected from powdered $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$ samples. A series of crystallographic models were constructed based on the reported structure of $\beta\text{-NaFeO}_2$ ¹⁵¹, described in space group $Pna2_1$, with the $4a$ site containing a combination of Fe/Al/Ga cations appropriate to the sample composition. These models were refined against the data to achieve good fits as shown for $\text{NaFe}_{0.5}\text{Al}_{0.5}\text{O}_2$, $\text{NaFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{NaFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ in Figures 3.2, 3.3 and 3.4 respectively with crystallographic details in Tables 3.2, 3.3 and 3.4 respectively. Details of the structural refinements of the remaining

NaFe_{1-x}M_xO₂ phase are given in Appendix-I Figures (and Tables) 3a.1-3a.10. A plot of the lattice parameters of the NaFe_{1-x}M_xO₂ phases as a function of composition are shown in Figure 3.5, with the parameters exhibiting a monotonic change as a function of composition consistent with Vegard's law¹⁵². Bond valance sums for the Na and Fe/M cation sites are given in Tables 3.5, 3.6, 3.7 and plotted in Figure 3.6.

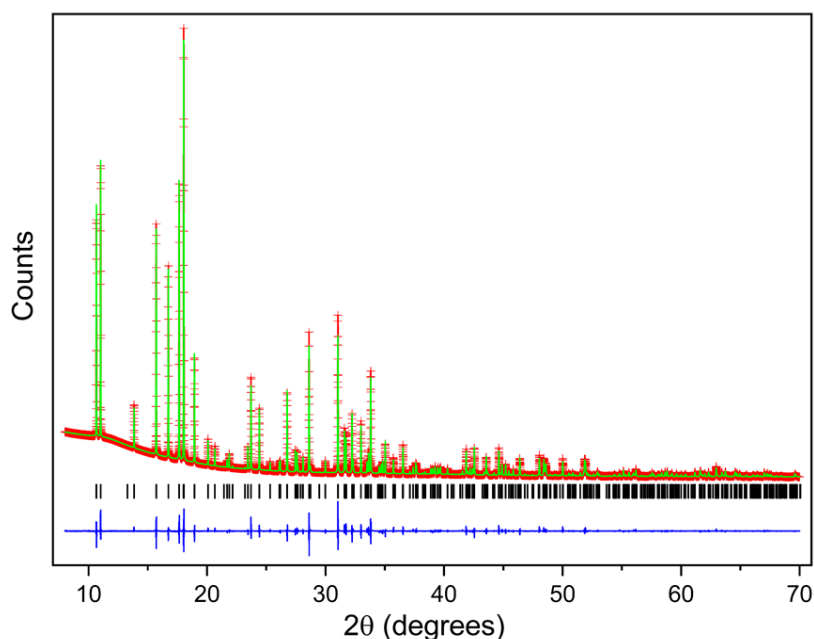


Figure 3. 1 Observed (red), calculated (green) and difference plots(blue) from the structural refinement of β -NaFeO₂ against SXRD data at room temperature

Table 3.1 Parameters from the structural refinement of β -NaFeO₂ sample against synchrotron x-ray powder diffraction (SXRD) data

Atom	site	x	y	z	Fraction	B _{eq} (Å ²)
Na	4a	0.4258(2)	0.1212(4)	0.4846(6)	1	1.28(3)
Fe	4a	0.0678(1)	0.1268(1)	0	1	0.40(1)
O(1)	4a	0.0410(4)	0.0885(4)	0.3429(3)	1	0.88(5)
O(2)	4a	0.3826(3)	0.1678(3)	0.9242(4)	1	0.88(5)
NaFeO ₂ – space group <i>Pna</i> 2 ₁ (#33)						
$a = 5.6814(1) \text{ Å}$, $b = 7.1463(1) \text{ Å}$, $c = 5.3909(1) \text{ Å}$						
volume = 218.882(1) Å ³						
Formula weight = 110.835 g mol ⁻¹ , Z = 4						
Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ Å}$						
Temperature: 298 K						
$R_p = 1.57 \%$, $wR_p = 3.20 \%$, $R_{Bragg} = 1.63$						

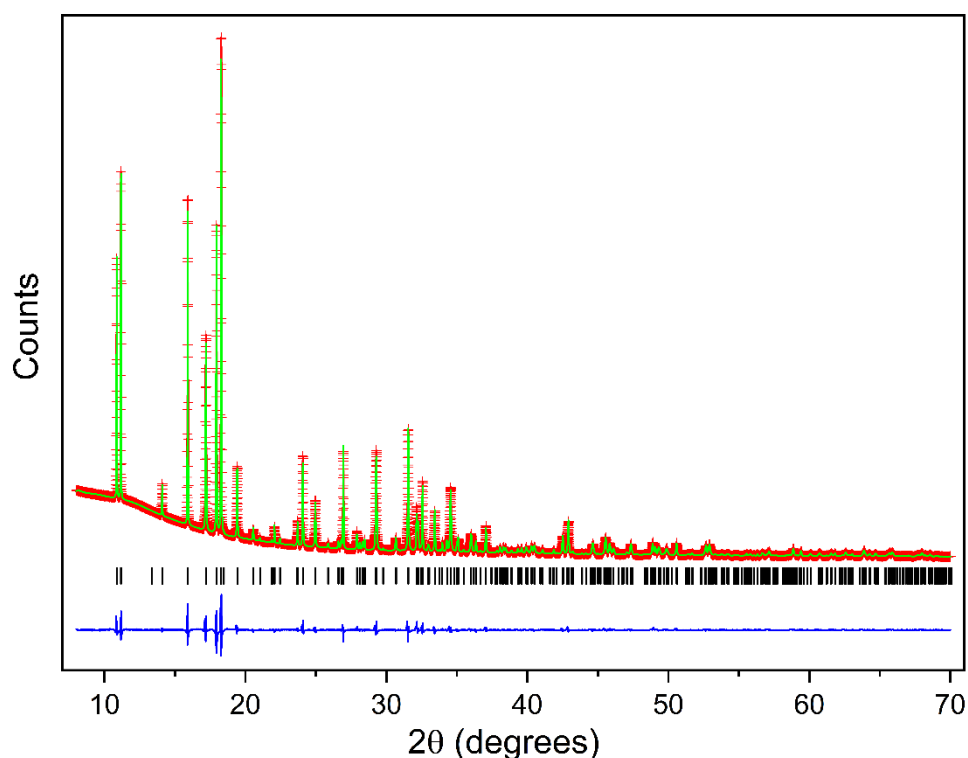


Figure 3. 2. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ against SXRD data.

Table 3.2 Parameters from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4295(1)	0.1231(2)	0.4863(3)	1	1.34(2)
Fe/Al	$4a$	0.0643(1)	0.1260(1)	0	0.5/0.5	0.62(1)
O(1)	$4a$	0.0366(3)	0.0799(2)	0.3297(2)	1	0.92(3)
O(2)	$4a$	0.3820(2)	0.1687(2)	0.9281(2)	1	0.92(3)
$\text{NaFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.5286(1) \text{ \AA}$, $b = 7.0970(1) \text{ \AA}$, $c = 5.2998(1) \text{ \AA}$ volume = $207.95(1) \text{ \AA}^3$ Formula weight = $96.4015 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.65 \%$, $wR_p = 2.98 \%$, $R_{\text{Bragg}} = 1.21$						

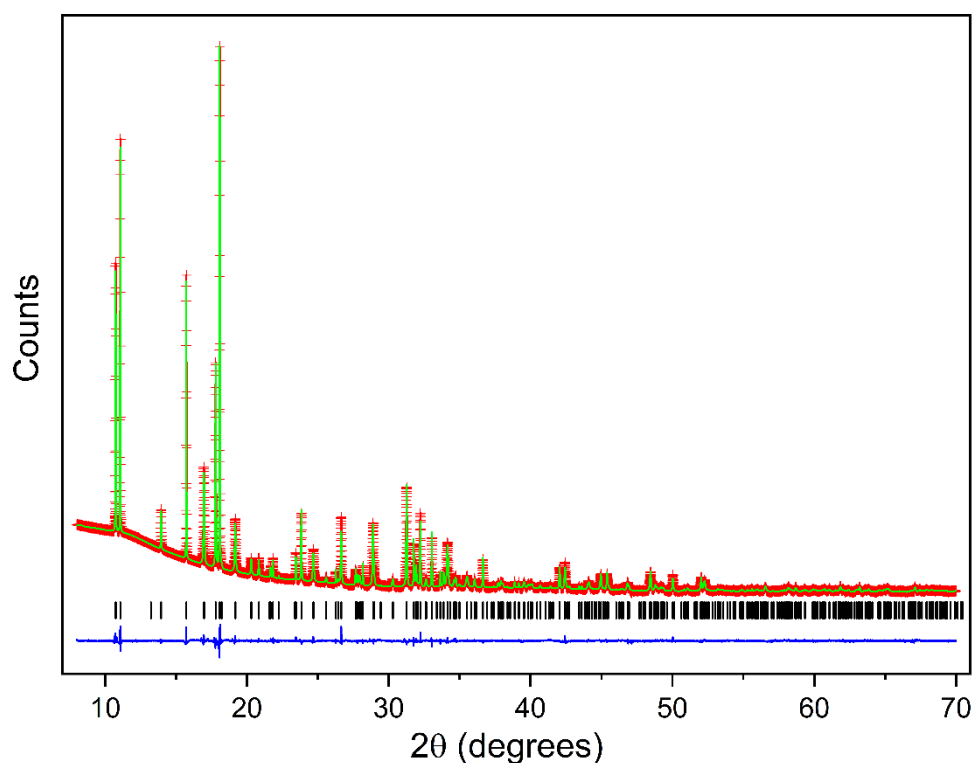


Figure 3.3. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ against SXRD data.

Table 3.3. Parameters from the structural refinement of $\text{NaFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4297(2)	0.1262(4)	0.4831(7)	1	0.84(3)
Fe/Ga	$4a$	0.0655(1)	0.1273(1)	0	0.5/0.5	0.47(1)
O(1)	$4a$	0.0353(4)	0.0879(3)	0.3409(3)	1	0.79(4)
O(2)	$4a$	0.3865(3)	0.1597(3)	0.9201(3)	1	0.79(4)
$\text{NaFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.6044(1) \text{ \AA}$, $b = 7.1761(1) \text{ \AA}$, $c = 5.3445(1) \text{ \AA}$ volume = $214.97(1) \text{ \AA}^3$ Formula weight = $117.7720 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.19 \%$, $wR_p = 1.80 \%$, $R_{\text{Bragg}} = 1.02$						

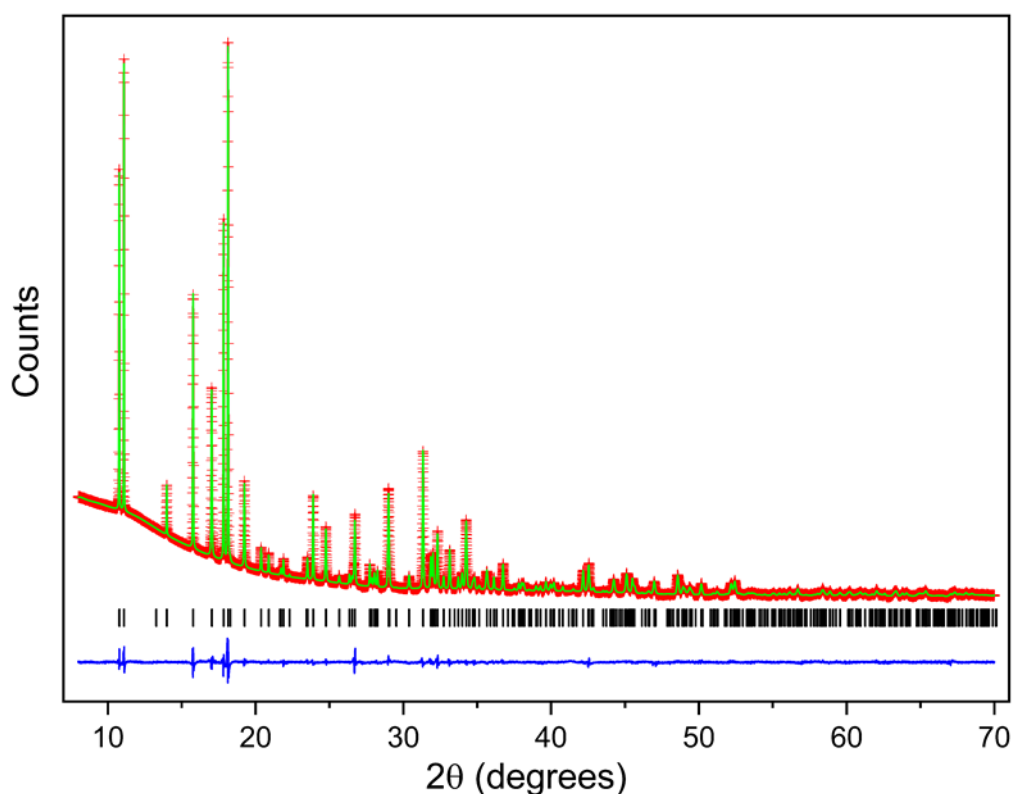


Figure 3. 4. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ against SXRD data.

Table 3.4. Parameters from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	4a	0.4291(2)	0.1221(5)	0.4826(6)	1	1.01(3)
Fe/Al/Ga	4a	0.0646(1)	0.1263(2)	0	0.5/0.125/0.375	0.53(1)
O(1)	4a	0.0393(4)	0.0843(4)	0.3379(3)	1	0.79(5)
O(2)	4a	0.3826(3)	0.1653(3)	0.9232(4)	1	0.79(5)
$\text{NaFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.5831(1) \text{ \AA}$, $b = 7.1573(1) \text{ \AA}$, $c = 5.3324(1) \text{ \AA}$ volume = $213.082(3) \text{ \AA}^3$ Formula weight = $96.40275 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.17 \%$, $wR_p = 1.88 \%$, $R_{\text{Bragg}} = 0.65$						

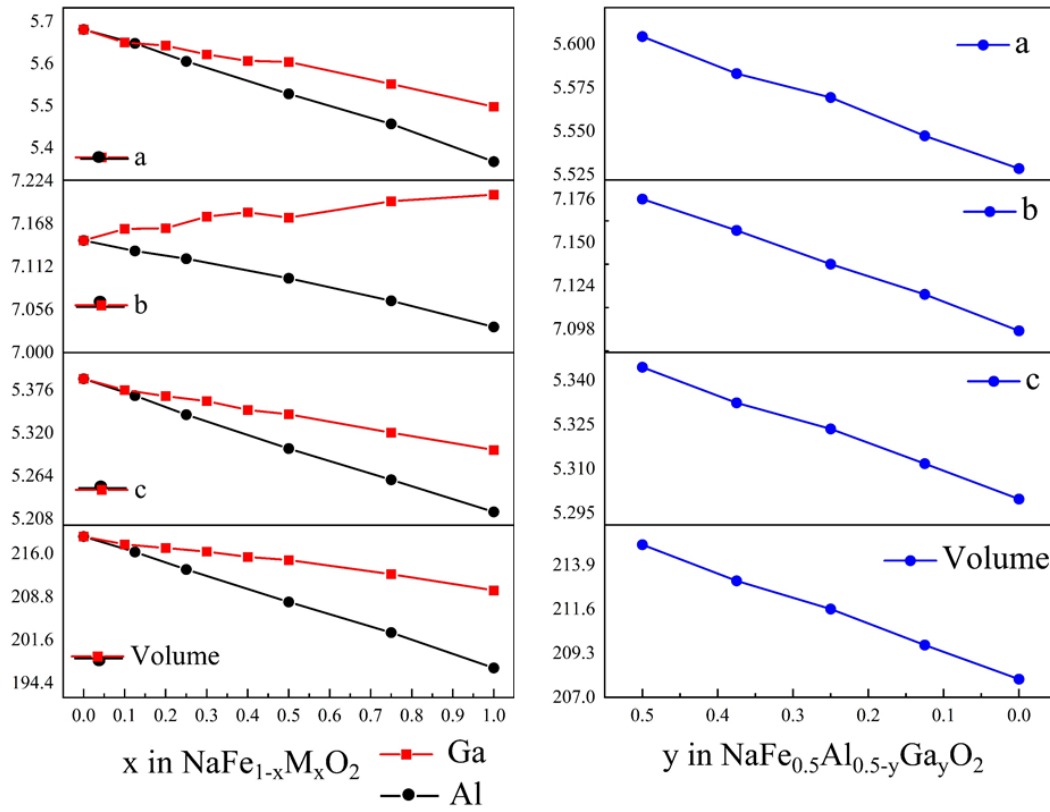


Figure 3. 5. Plot of lattice parameters as a function of composition for $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$ phases (left) and $\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ phases (right); Error bars are smaller than the plotted points

Table 3.5. Bond lengths and BVS parameter of $\text{NaFe}_{1-x}\text{Al}_x\text{O}_2$ sample determined from structural refinement against SXRD data

x	$\text{NaFe}_{1-x}\text{Al}_x\text{O}_2$			
	$\langle\text{Na-O}\rangle$ (Å)	Na-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	2.348(4)	0.919	1.861(3)	3.033
0.125	2.337(7)	0.948	1.856(5)	3.080
0.25	2.349(3)	0.914	1.832(3)	3.285
0.5	2.350(3)	0.911	1.800(2)	3.521
0.75	2.348(2)	0.918	1.783(2)	3.744

Table 3.6. Bond lengths and BVS parameter of $\text{NaFe}_{1-x}\text{Ga}_x\text{O}_2$ sample determined from structural refinement against SXRD data

x	$\text{NaFe}_{1-x}\text{Ga}_x\text{O}_2$			
	$\langle\text{Na-O}\rangle$ (Å)	Na-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	2.348(4)	0.919	1.861(3)	3.033
0.1	2.351(5)	0.911	1.851(5)	3.116
0.2	2.341(4)	0.935	1.856(4)	3.078
0.3	2.335(3)	0.950	1.858(3)	3.063
0.4	2.333(4)	0.956	1.857(4)	3.066
0.5	2.325(5)	0.980	1.861(3)	3.037
0.75	2.328(8)	0.969	1.847(5)	3.155

Table 3.7. Bond lengths and BVS parameter of $\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ sample determined from structural refinement against SXRD data

y	$\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$			
	$\langle\text{Na-O}\rangle$ (Å)	Na-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0.5	2.350(3)	0.911	1.800(2)	3.521
0.125	2.344(2)	0.930	1.821(2)	3.382
0.25	2.331(3)	0.967	1.838(3)	3.225
0.375	2.340(5)	0.939	1.839(3)	3.217
0.5	2.325(5)	0.980	1.861(3)	3.037

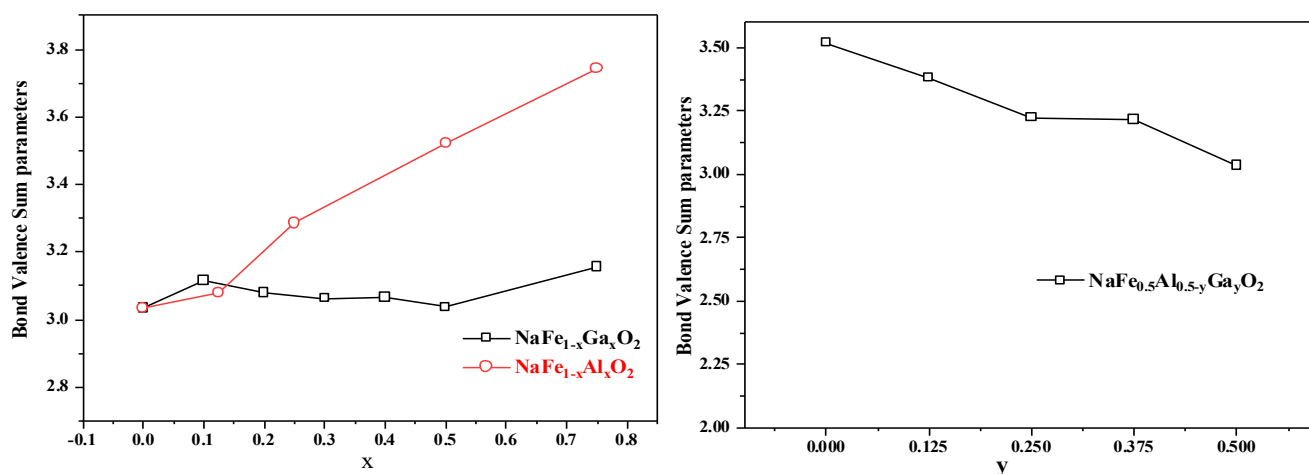


Figure 3. 6. Plot of Fe-Bond Valence Sum parameters as a function of composition for $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Al}, \text{Ga}$) phases (left) and $\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ phases (right) determined from the structural refinement against SXRD data (left); Error bars are smaller than the plotted points

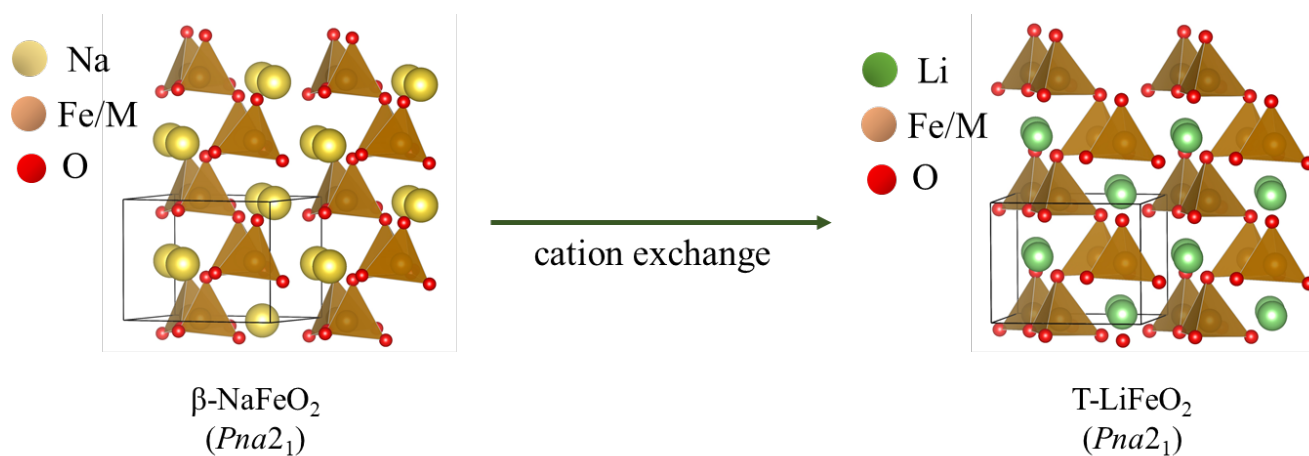


Figure 3. 7. Cation exchange schematics

3.3.2. Structural characterisation of $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$

Synchrotron X-ray diffraction (SXRD) and Neutron powder diffraction (NPD)

SXRD data were collected from the $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ phases prepared by cation exchange. A series of crystallographic models described in space group $Pna2_1$ were constructed based on the models of the corresponding $\text{NaFe}_{1-x}\text{M}_x\text{O}_2$ materials described above, but with sodium replaced with lithium. These models were then refined against the corresponding SXRD data. Close inspection of the SXRD data revealed a series of small diffraction peaks consistent with the presence of LiFe_5O_8 in the samples, so this was added to the structural model as a second phase. SXRD data (with $\lambda = 0.8268 \text{ \AA}$) collected from $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ samples reveal an additional unknown impurity with reflections at $2\theta = 6.258^\circ$, 12.547° and 16.281° which were excluded (black arrows, Figure 3.13) from the refinement process.

3.3.2.1. Structural refinement of Al doped T- LiFeO_2 samples

To assist with structural determination, neutron powder diffraction (NPD) data was collected from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$. The crystallographic model described above was refined against the NPD data to achieve a good fit as shown in Figures 3.9 and 3.10 with crystallographic details given in Table 3.9. The structural analysis confirms complete disordering of the Fe and Al cations in $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$. Crystallographic models refined against the SXRD data collected from the other $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ samples also show disorder between Fe and Al. Details of structural refinements of $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ phases (for $x = 0.125$, 0.25 and 0.75) are given in Appendix-I Figures (and Tables) 3a.11-3a.13.

3.3.2.2. Structural refinement of Ga doped T- LiFeO_2 samples

NPD data collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ revealed an additional peak at $d = 5.4575 \text{ \AA}$. This corresponds to the (010) reflection of the $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ lattice, but is systematically absent for the $Pna2_1$ space group. However, this reflection is allowed in a Ga/Fe cation ordered

model, analogous to the reported structure of $\text{Li}_2\text{ZnGeO}_4$ ¹⁵³ described in space group Pn . This model was refined against the NPD data to achieve a good fit as shown in Figures 3.11 and 3.12 with crystallographic parameters in Table 3.10. An ordering between Fe and Ga atoms in the structure of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ is observed.

The SXRD data collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ show no indication of Fe/Ga cation order with disordered ($Pna2_1$) and ordered (Pn) models refining to give statistically equivalent fits to the data, indicating the SXRD data are not sensitive to this feature of the structure. Refinement of ordered and disordered models against SXRD data collected from other $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ samples also gave equivalent fits as detailed in Appendix-I Figures (and Tables) 3a.14-3a.18. However, it is reasonable to assume that these other $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ phases also exhibit a degree of Fe/Ga order in their structures.

A plot of the cell parameters and the Fe-BVS parameters as a function of composition (x) of the $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ phases are shown in Figures 3.13 and 3.14 respectively, exhibiting a monotonic change as a function of composition consistent with Vegard's law.

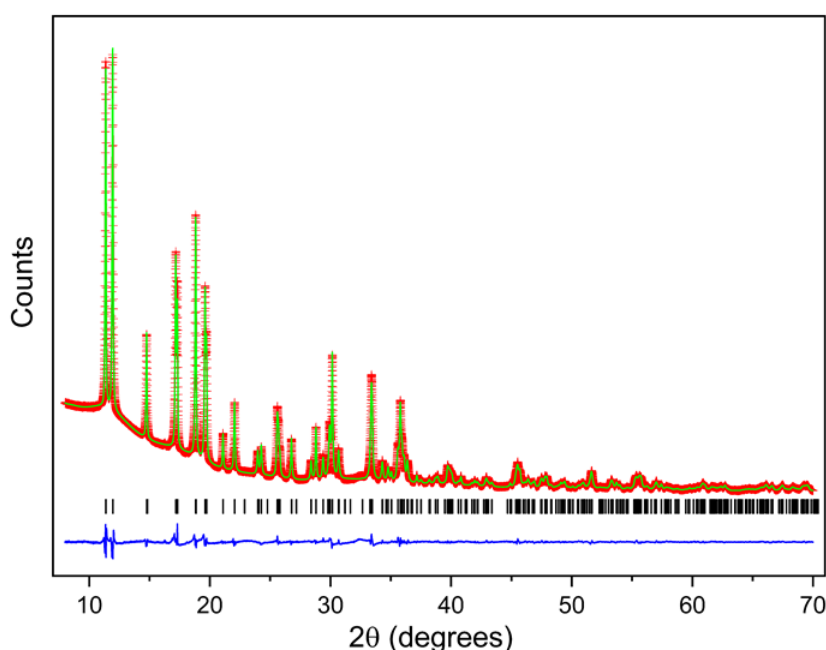


Figure 3. 8. Observed, calculated and difference plots from the structural refinement of $T\text{-LiFeO}_2$ against SXRD data.

Table 3.8. Parameters from the structural refinement of LiFeO_2 against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.4340(8)	0.1375(18)	0.5142(26)	1	0.81(9)
Fe	$4a$	0.0839(1)	0.1270(2)	0	1	0.22(1)
O(1)	$4a$	0.0756(4)	0.1118(8)	0.3760(3)	1	0.32(2)
O(2)	$4a$	0.4153(4)	0.1310(8)	0.8951(3)	1	0.32(2)

LiFeO_2 – space group $Pna2_1$ (#33)
 $a = 5.4916(1) \text{ \AA}$, $b = 6.4050(1) \text{ \AA}$, $c = 5.0547(1) \text{ \AA}$
 volume = $177.796 (1) \text{ \AA}^3$
 Formula weight = $94.78675 \text{ g mol}^{-1}$, $Z = 4$
 Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$
 Temperature: 298 K
 $R_p = 2.19 \%$, $wR_p = 3.11 \%$, $R_{\text{Bragg}} = 2.00$

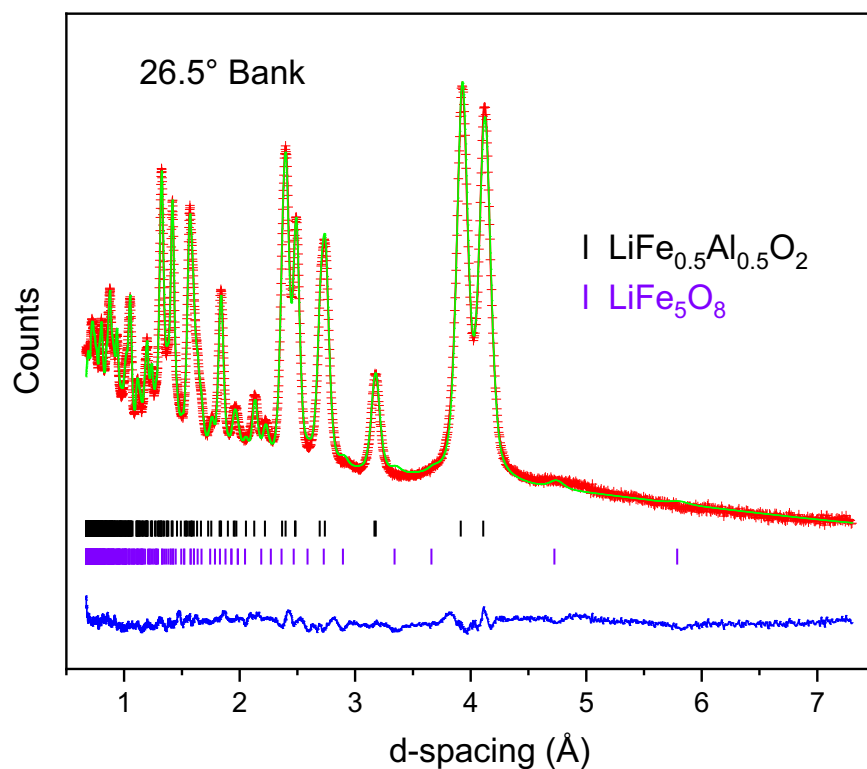


Figure 3. 9. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ against NPD data (26.5° bank).

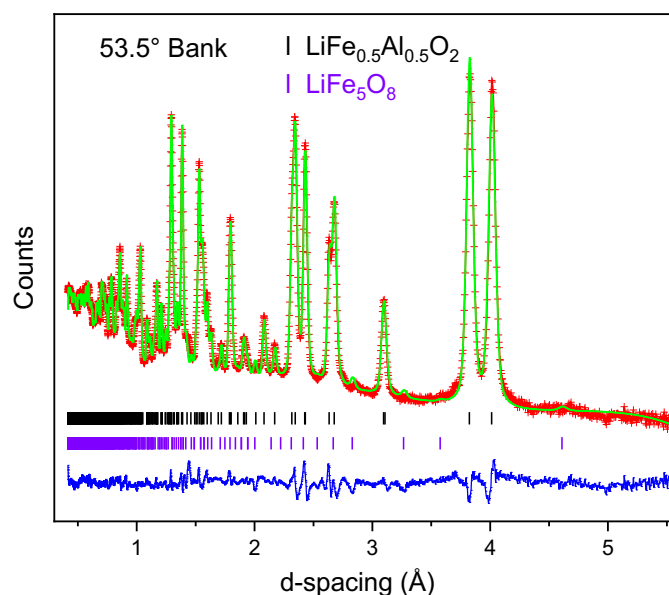


Figure 3. 10. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ against NPD data (53.5° Bank).

Table 3.9. Parameters from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction
Li1	$4a$	0.0969(9)	0.5947(9)	0.9877(9)	1
Fe1/Al1	$4a$	0.0778(2)	0.1306(3)	0	0.497(3)/0.503(3)
O1	$4a$	0.0688(2)	0.1004(3)	0.3704(3)	1
O2	$4a$	0.4050(3)	0.1369(3)	0.8999(3)	1
$\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ – space group $Pna2_1$ (#29) $a = 5.3852(1) \text{ \AA}$, $b = 6.3563(2) \text{ \AA}$, $c = 4.9686(1) \text{ \AA}$, volume = $170.078(9) \text{ \AA}^3$ Formula weight = $80.2385 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 2.07 \%$, $wR_p = 2.62 \%$					
Crystallographic parameters LiFe_5O_8 added as a secondary phase during the refinement LiFe_5O_8 – space group $P4_332$ (#212) $a = b = c = 8.1836(12) \text{ \AA}$, volume = $548.078(248) \text{ \AA}^3$ weight % = 5(2)					

Atom	U11	U22	U33	U12	U13	U23
Li1	0.0245(23)	0.176(26)	0.1297(17)	0.0225(25)	-0.0261(19)	-0.0217(20)
Fe1/Al1	0.0000(4)	0.0049(6)	0.0042(5)	0.0036(5)	0.0020(6)	0.0022(7)
O1	0.0065(4)	0.0109(6)	0.0081(4)	-0.0017(4)	0.0009(4)	-0.00637(5)
O2	0.0065(4)	0.0109(6)	0.0081(4)	-0.0017(4)	0.0009(4)	-0.00637(5)

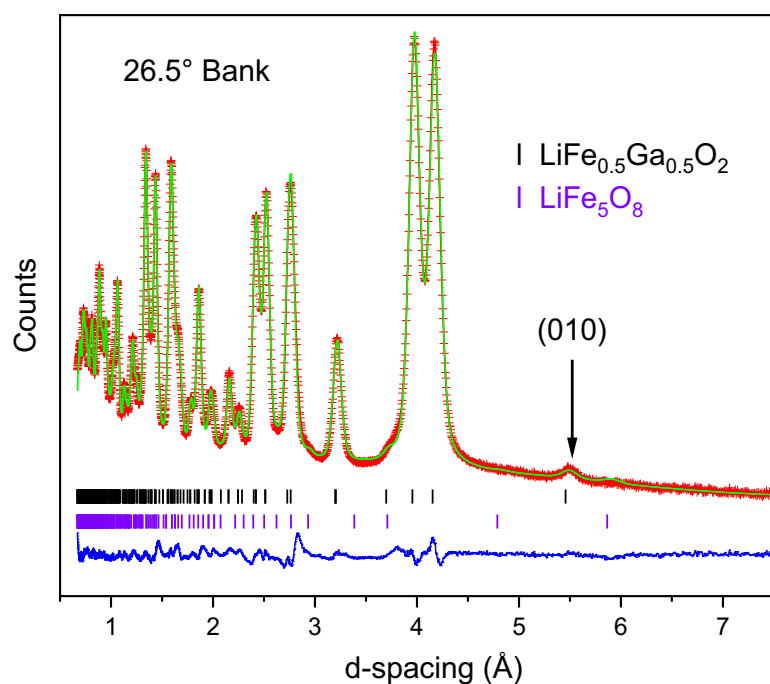


Figure 3. 11. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{FeGaO}_4$ ($\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$) against NPD data (26.5° Bank).

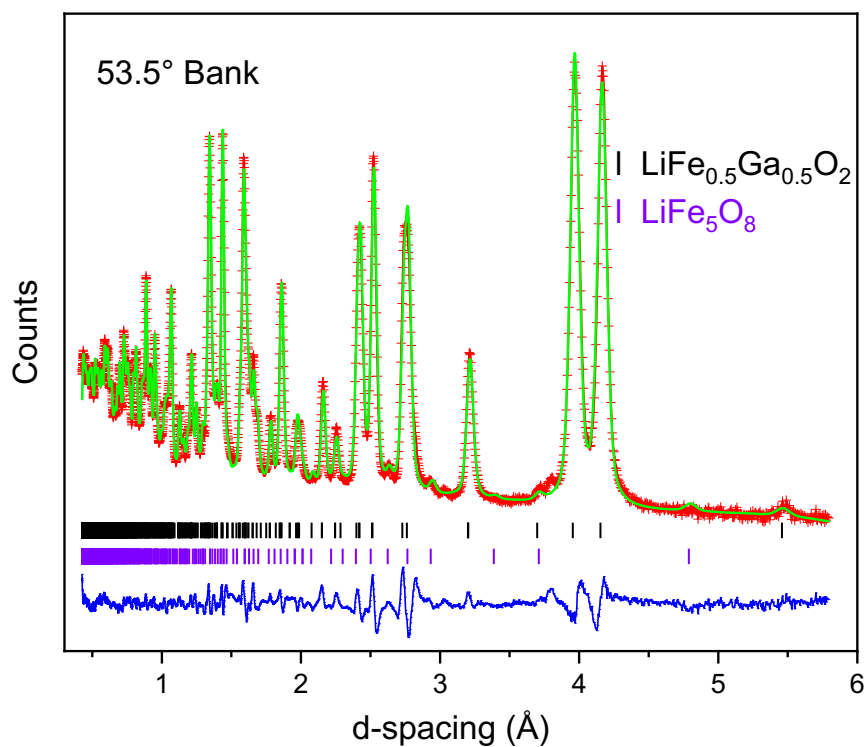


Figure 3. 12. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{FeGaO}_4$ ($\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$) against NPD data (53.5° Bank)

Table 3.10. Parameters from the structural refinement of $\text{Li}_2\text{FeGaO}_4$ ($\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$) sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	$2a$	0.5251(33)	0.1018(25)	0.9858(39)	1	0.93(26)
Li2	$2a$	0.7201(42)	0.3220(33)	0.5917(22)	1	0.93(26)
Fe1	$2a$	0.2510(4)	0.3264(7)	0.5085(7)	1	
Ga1	$2a$	0.9979(5)	0.1676(9)	0.0064(8)	1	
O1	$2a$	0.4983(9)	0.1593(9)	0.4159(7)	1	
O2	$2a$	0.2734(9)	0.6543(8)	0.3821(7)	1	
O3	$2a$	0.0140(7)	0.1881(7)	0.3594(7)	1	
O4	$2a$	0.2248(7)	0.3280(8)	0.8945(7)	1	
$\text{Li}_2\text{FeGaO}_4$ – space group Pn (#7) $a = 6.4015(3) \text{ \AA}$, $b = 5.4575(2) \text{ \AA}$, $c = 5.0296(2) \text{ \AA}$, $\beta = 89.999^\circ(4)$, volume = $175.718 (11) \text{ \AA}^3$ Formula weight= $203.4465 \text{ g mol}^{-1}$, $Z = 2$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 3.60 \%$, $wR_p = 2.72 \%$						
Crystallographic parameters LiFe_5O_8 added as a secondary phase during the refinement LiFe_5O_8 – space group $P4_332$ (#212) $a = b = c = 8.2948(11) \text{ \AA}$, volume = $570.716(233)$ weight % = 5(2)						

Atom	U11	U22	U33	U12	U13	U23
Fe1	0.0083(15)	0.0000(10)	0.0061(12)	-0.0028(12)	-0.0034(13)	0.0036(12)
Ga1	0.0095(19)	0.0000(13)	0.0000(11)	-0.0051(14)	0.0002(24)	-0.0022(13)
O1	0.0066(9)	0.0000(5)	0.0024(6)	-0.0022(7)	-0.0039(9)	0.0056(5)
O2	0.0066(9)	0.0000(5)	0.0024(6)	-0.0022(7)	-0.0039(9)	0.0056(5)
O3	0.0066(9)	0.0000(5)	0.0024(6)	-0.0022(7)	-0.0039(9)	0.0056(5)
O4	0.0066(9)	0.0000(5)	0.0024(6)	-0.0022(7)	-0.0039(9)	0.0056(5)

Table 3.11. Bond lengths and BVS parameter table for $\text{Li}_2\text{FeGaO}_4$ ($\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$)

$\langle \text{Fe-O} \rangle (\text{\AA})$	Average $\langle \text{Fe-O} \rangle (\text{\AA})$	Fe-BVS	$\langle \text{Ga-O} \rangle (\text{\AA})$	Average $\langle \text{Ga-O} \rangle (\text{\AA})$	Ga-BVS
1.852 (6)	1.897(6)	2.761	1.782 (6)	1.813(7)	3.202
1.886 (7)			1.786 (7)		
1.904 (6)			1.841 (8)		
1.949 (6)			1.845 (7)		

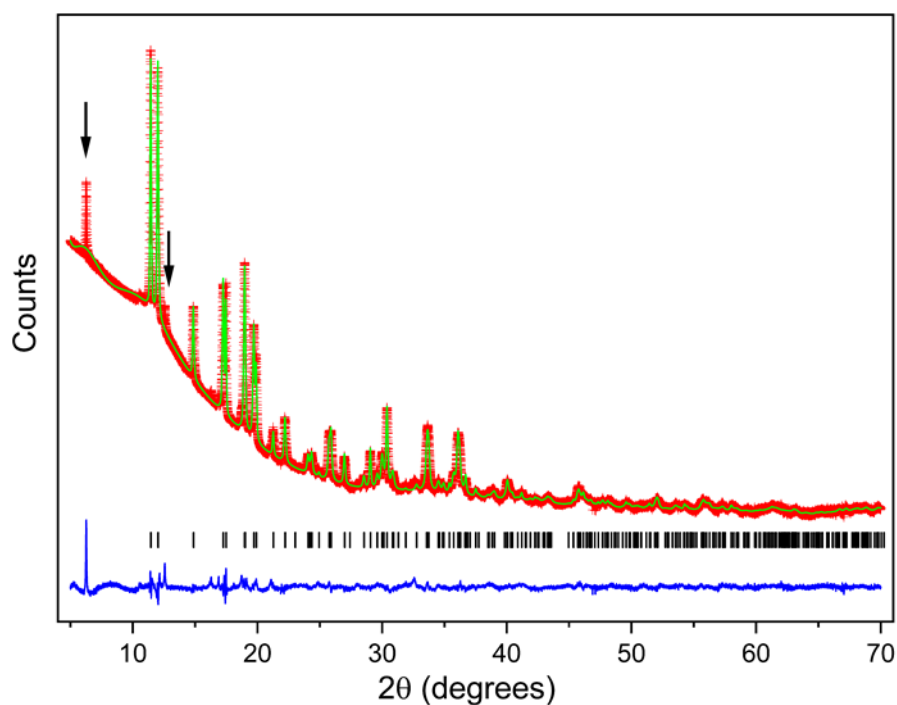


Figure 3.13. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ against SXRD data, Unindexed impurity phase (black arrows)

Table 3.12. Parameters from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.4519(12)	0.1598(16)	0.5024(12)	1	1.36(16)
Fe/Al/Ga	$4a$	0.0828(1)	0.1297(2)	0	0.5/0.125/0.375	0.23(2)
O(1)	$4a$	0.0840(7)	0.0960(9)	0.3805(10)	1	0.04(6)
O(2)	$4a$	0.4105(8)	0.1130(8)	0.8945(11)	1	0.04(6)
$\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4393(1) \text{ \AA}$, $b = 6.3870(1) \text{ \AA}$, $c = 5.0154(1) \text{ \AA}$ volume = $174.243(13) \text{ \AA}^3$ Formula weight = $96.381 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.13\%$, $wR_p = 1.56 \%$, $R_{\text{Bragg}} = 0.68$						

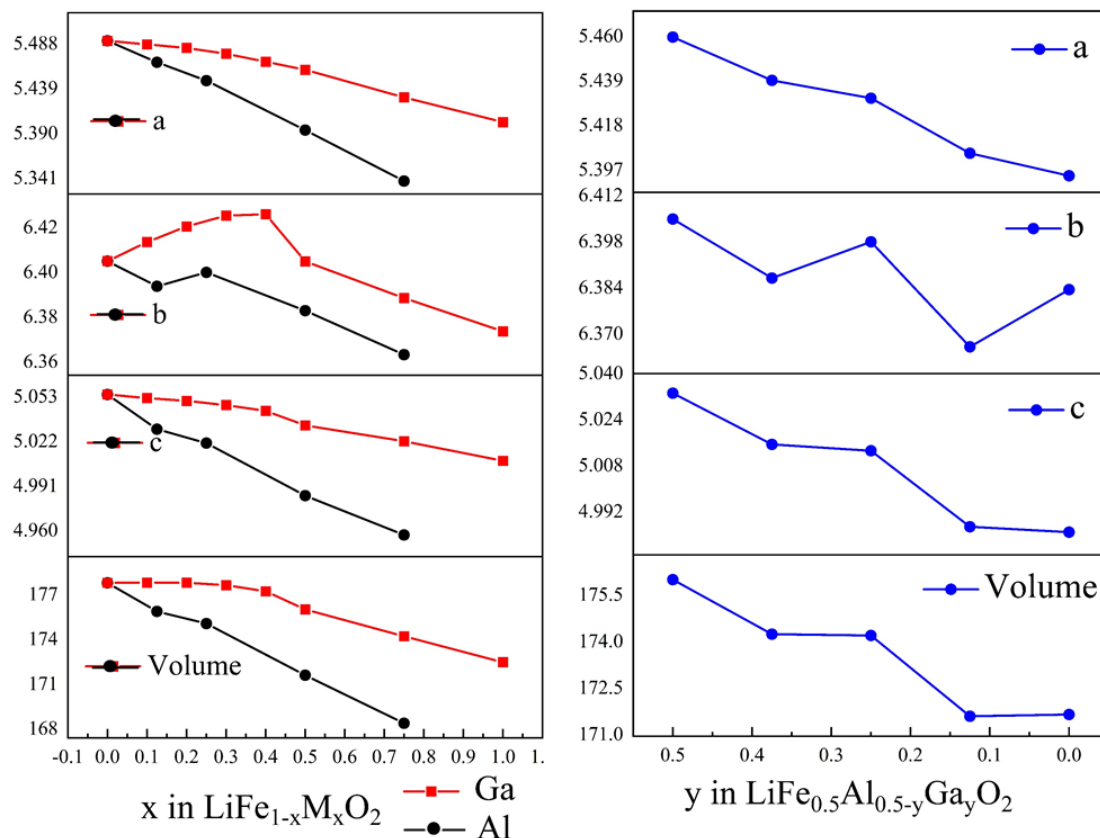


Figure 3. 14. Plot of lattice parameters as a function of composition for $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ phases (left) and $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ phases (right); Error bars are smaller than the plotted points

Table 3.12. Bond lengths and BVS parameters of $\text{NaFe}_{1-x}\text{Al}_x\text{O}_2$ and $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ samples determined from structural refinement against SXRD and NPD data

x	$\text{NaFe}_{1-x}\text{Al}_x\text{O}_2$		$\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$	
	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	1.861(3)	3.033	1.888(4)	2.824
0.125	1.856(5)	3.080	1.897(7)	2.762
0.25	1.832(3)	3.285	1.872(3)	2.975
0.5	1.800(2)	3.521	1.823(6)	3.3663
0.75	1.783(2)	3.744	1.827(4)	3.352

Table 3.13. Bond lengths and BVS parameters of $\text{NaFe}_{1-x}\text{Ga}_x\text{O}_2$ and $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ samples determined from structural refinement against SXRD and NPD data

x	$\text{NaFe}_{1-x}\text{Ga}_x\text{O}_2$		$\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$	
	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	1.861(3)	3.033	1.888(4)	2.824
0.1	1.851(5)	3.116	1.898(3)	2.765
0.1	1.856(4)	3.078	1.895(4)	2.810
0.3	1.858(3)	3.063	1.901(3)	2.802
0.4	1.857(4)	3.066	1.900(7)	2.822
0.5	1.861(3)	3.037	1.897(3)	2.761
0.75	1.847(5)	3.155	1.871(4)	3.069

Table 3.14. Bond lengths and BVS parameters of $\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ and $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ samples determined from structural refinement against SXRD and NPD data

y	$\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$		$\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$	
	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	2.350(3)	0.911	1.823(6)	3.3663
0.125	2.344(2)	0.930	1.848(2)	3.161
0.25	2.331(3)	0.967	1.893(3)	2.827
0.375	2.340(5)	0.939	1.884(4)	2.887
0.5	2.325(5)	0.980	1.897(3)	2.761

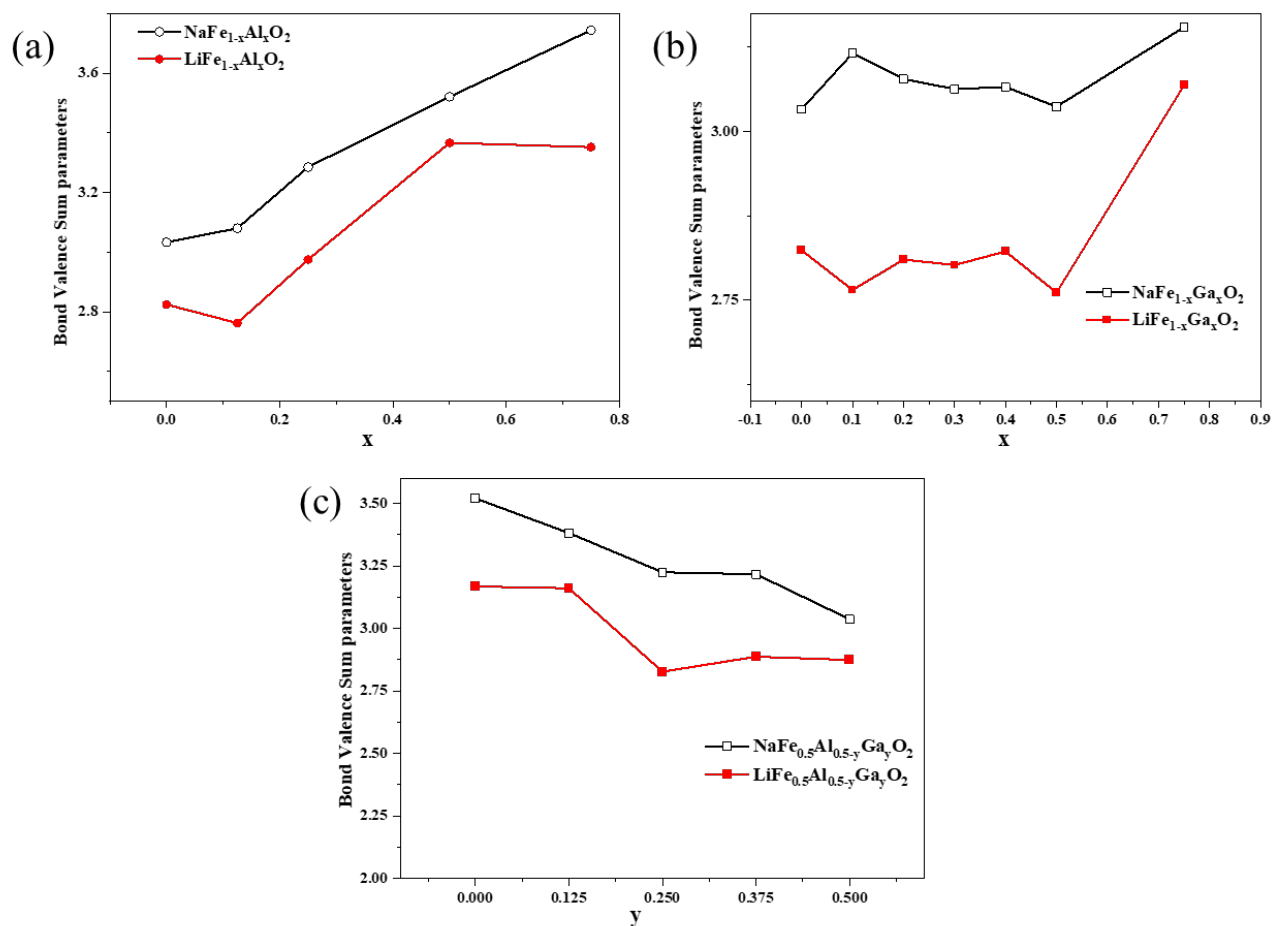


Figure 3. 15. Plot of Fe-Bond Valence Sum parameters as a function of composition for $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Al}, \text{Ga}$) phases (a,b) and $\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ phases (c) determined from the structural refinement against SXRD and NPD data (left); Error bars are smaller than the plotted points

3.4. Discussion for Al, Ga doped β -NaFeO₂ and T-LiFeO₂ material

Structural refinements against SXRD and NPD data of NaFe_{1-x}M_xO₂ and LiFe_{1-x}M_xO₂ phases reveal that complete solid solutions can be made of the NaFe_{1-x}M_xO₂ phases and that these can then be converted to the corresponding LiFe_{1-x}M_xO₂ phases. The lattice parameter of both the Al and Ga substituted phases decline with increasing substitution levels consistent with the smaller ionic radii of Al³⁺ (0.39 Å)¹⁵⁴ and Ga³⁺ (0.47 Å)¹⁵⁴ compared to Fe³⁺ (0.49 Å)¹⁵⁴.

As sodium cations in NaFe_{1-x}M_xO₂ are replaced by lithium cations in LiFe_{1-x}M_xO₂, the structure contracts around the lithium site which can be seen in the lattice parameters and this contraction around the lithium site also leads to the expansion around the iron site as shown in Tables 3.12, 3.13 and 3.14.

One striking difference between the LiFe_{1-x}Al_xO₂ and LiFe_{1-x}Ga_xO₂ series is the observation of Fe/Ga cation order in LiFe_{0.5}Ga_{0.5}O₂ but Fe/Al cation disorder in LiFe_{0.5}Al_{0.5}O₂. This difference is hard to explain on the basis of lattice strain, as the radii of Fe³⁺ and Ga³⁺ are more similar than Fe³⁺ and Al³⁺, suggesting other subtle bonding interaction are at play in these structures.

Chapter 4 – Reduction of Al, Ga doped T-LiFeO₂ phases

4.1. Introduction

n-butyl lithium (BuLi) has an electrode potential of 1.04 V vs the Li⁺/Li redox couple¹⁵⁵. Hence, reductive lithium insertion reactions with *n*-BuLi can be considered as chemical equivalents of the electrochemical discharge processes of a cathode in a lithium ion battery¹⁰⁷. To achieve reductive lithium insertion, LiFe_{1-x}M_xO₂ samples were treated with *n*-BuLi in hexane. The resulting products were characterized using SXRD, NPD, XAS, and iodometric titrations techniques. The outcomes derived from these analyses are detailed within this chapter. Furthermore, the electrochemical behaviour of a few selected LiFe_{1-x}M_xO₂ samples are also discussed.

4.2. Experimental section

4.2.1. Lithium intercalation in LiFe_{1-x}M_xO₂ samples

Approximately 200 mg of each LiFe_{1-x}M_xO₂ sample was placed in a small Schlenk tube under a nitrogen atmosphere. Then, 6-8 mL of a 1.6 M solution of *n*-BuLi in *n*-hexanes (Merck Life Sciences) was added to achieve a 1:5 molar ratio of LiFe_{1-x}M_xO₂ : *n*-BuLi. The tube was sealed with a glass cap, and the contents inside were stirred at room temperature for 48 hours. A colour change of the powder from orange/dark brown to black was observed. The black suspension was filtered and washed with excess toluene under nitrogen. Finally, the black powder was dried using a vacuum line and transferred into an argon-filled glove-box.

To evaluate the reversibility of lithium intercalation, the samples were treated with a known concentration of iodine in acetonitrile. Following the reaction, the remaining iodine was titrated against a standardized thiosulphate solution.

4.2.2. Galvanostatic measurements

Motivated by the findings of Armstrong et al¹⁰². on the improved electrochemical properties of T-LiFeO₂ derived from ball-milled NaFeO₂, NaFe_{1-x}M_xO₂ samples were ball milled for 30 minutes with a program of 20 Hz (cycles/second). From the ball milled samples, lithium exchange was performed to prepare the corresponding LiFe_{1-x}M_xO₂ phases which were subjected to electrochemical measurements. The coin cell preparation was conducted using the following approach.

A mixture with a 80:10:10 mass ratio of LiFe_{1-x}M_xO₂ : carbon black : polyvinylidene fluoride (PVDF) was weighed and ground into a fine powder. 0.3 mL of 1-methyl-2-pyrrolidone (NMP) was then added and the mixture was mechanically shaken until a homogeneous viscous slurry was obtained. The slurry was poured onto a carbon-coated aluminium foil and first dried in air and then heated for 12 hours at 80°C in a vacuum oven. The dry slurry cast was cut into 12 mm disc cathodes and transferred into the glovebox. A coin cell was assembled using Cambridge Energy Solutions SS316 CR2032 coin cell cases, a lithium chip (15.6 mm diameter, 0.25 mm thick), a Whatman glass fiber membrane separator (16mm diameter), and the cast cathode. The separator was soaked with 10 µL of electrolyte and the coin cell was sealed. Cyclic voltammograms and charge-discharge capacity profile measurements were conducted after assembling the coin cell.

4.3. Results and discussion for Al doped T-LiFeO₂ samples

4.3.1. Structural characterization (SXRD data)

SXRD data collected from lithiated LiFe_{1-x}Al_xO₂, henceforth referred to as Li_{1+δ}Fe_{1-x}Al_xO₂, are shown in Figures 4.1 and 4.2. The diffraction data collected for the $x = 0$ and $x = 0.125$ samples could be indexed on the basis of orthorhombic unit cells, to yield lattice parameters which are unchanged from the analogous unlithiated phases. Close inspection of

the data reveals a broad diffraction feature at $2\theta \sim 23.4^\circ$ which coincides with the strongest diffraction feature of elemental iron (Figure 4.1). Detail of structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ is given in Appendix-I Figure (and Table) 4a.1.

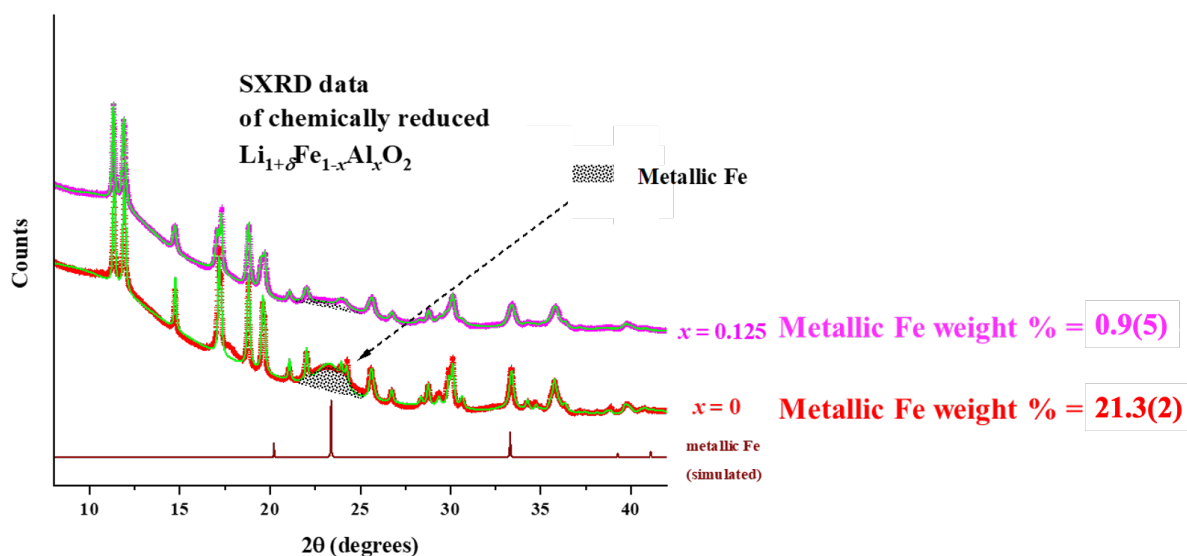


Figure 4. 1. Plot of fitted SXRD data from $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ samples for $x = 0$ and 0.125 with simulated pattern of metallic iron, Green line: calculated intensity; Shaded box: broad peaks associated with metallic iron

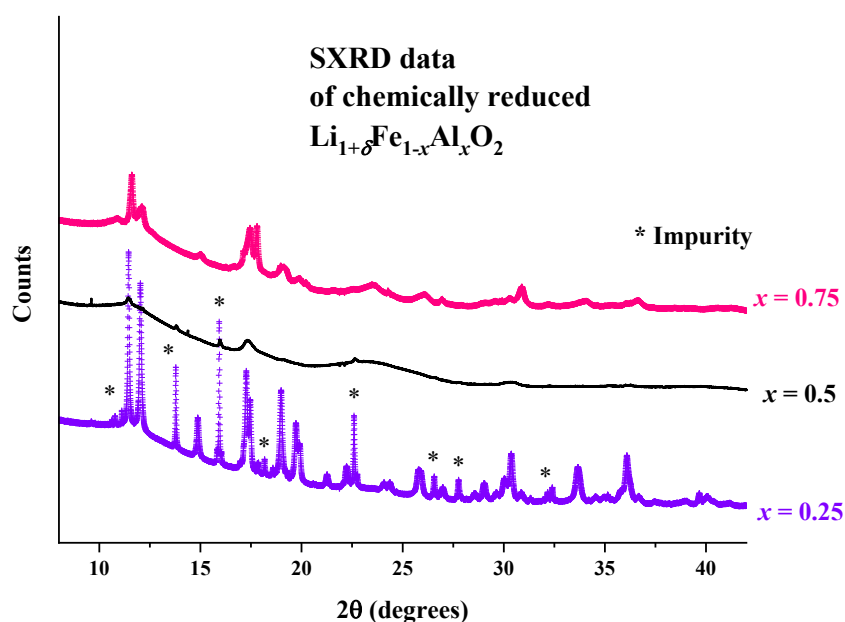


Figure 4. 2. SXRD patterns collected from $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ samples for $x = 0.25, 0.5$ and 0.125 ; * indicates peaks from impurity phase formed during reduction of $\text{Li}_{1+\delta}\text{Fe}_{0.75}\text{Al}_{0.25}\text{O}_2$

SXRD data collected from $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{M}_x\text{O}_2$ samples (Figure 4.2) with $x > 0.125$ exhibit broad diffraction features which can be assigned to the $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{M}_x\text{O}_2$ phases. These data also exhibit a series of additional diffraction features assigned to unidentified phases. Together these features show that $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{M}_x\text{O}_2$ phases with $x > 0.125$ have decomposed on reaction with *n*-BuLi.

4.3.2. XANES characterisation of the chemically reduced $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ sample

To determine the oxidation state of the iron centres in $\text{Li}_{1+\delta}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$, XANES data were collected from $\text{Li}_{1+\delta}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ along with data from FeO and Fe_2O_3 to act as references for Fe (II) and Fe (III) K-edges respectively.

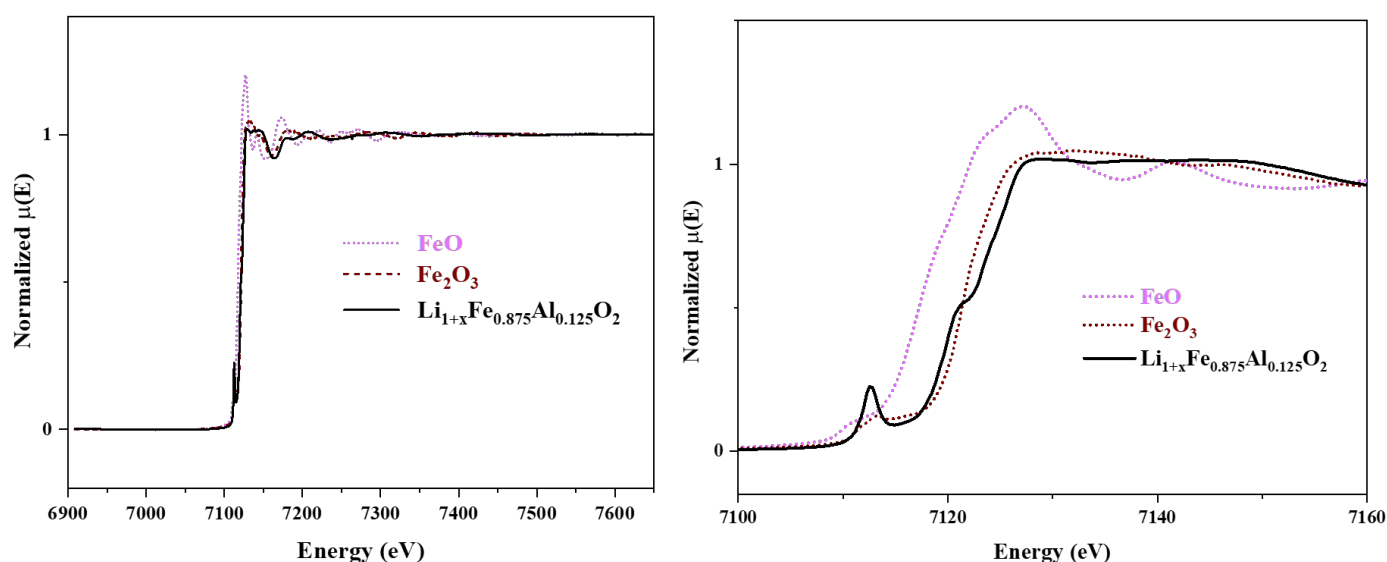


Figure 4. 3. XANES data of $\text{Li}_{1+x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ with references (dotted lines); normalization(left), Fe K-edge comparison(right).

XANES data from the Fe K-edge of $\text{Li}_{1+x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ (black line in Figure 4.3) was found to match with the K-edge of Fe_2O_3 indicating the oxidation state of iron in the $\text{Li}_{1+x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ sample is close to +3 and thus the degree of reduction due to lithium insertion is minimal.

4.3.3. Discussion for the chemically reduced $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ sample

SXRD data collected from T- LiFeO_2 shows no change in lattice parameters after exposure to $n\text{-BuLi}$, and signs of elemental iron formation. This indicates that lithium cannot be easily topochemically inserted into the material, with the only reaction observed being the partial decomposition of the phase and the formation of elemental iron. Likewise, SXRD data from $\text{LiFe}_{0.875}\text{Al}_{0.125}\text{O}_2$ after exposure to $n\text{-BuLi}$ also show no signs of lithium insertion, confirmed by XANES data which show no signs of reduction of the Fe^{3+} cations in the material.

Exposure of $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ phases with $x \geq 0.25$ to $n\text{-BuLi}$ results in the formation of unidentified secondary phases, indicating $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ framework decomposes under these conditions.

4.4. Results and discussion for Ga doped T- LiFeO_2 samples

4.4.1 Structural characterization (SXRD)

SXRD data collected from samples of $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ ($0 < x < 0.75$) which had been exposed to $n\text{-BuLi}$, could be indexed using orthorhombic unit cells and the data fitted by structural models based on the Fe/Ga disordered structures of $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ described in Chapter 3. However, close inspection of the SXRD data from $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ phases with $x \leq 0.2$ (Figure 4.4) revealed a broad diffraction feature at $2\theta \sim 23^\circ$, attributed to elemental iron, indicating the materials, like undoped T- LiFeO_2 , partially decompose on exposure to $n\text{-BuLi}$. However, the data from lithiated $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ samples with $x \geq 0.3$ show no indication of decomposition (Figure 4.4), revealing this level of substitution is sufficient to stabilize T- LiFeO_2 under reductive conditions.

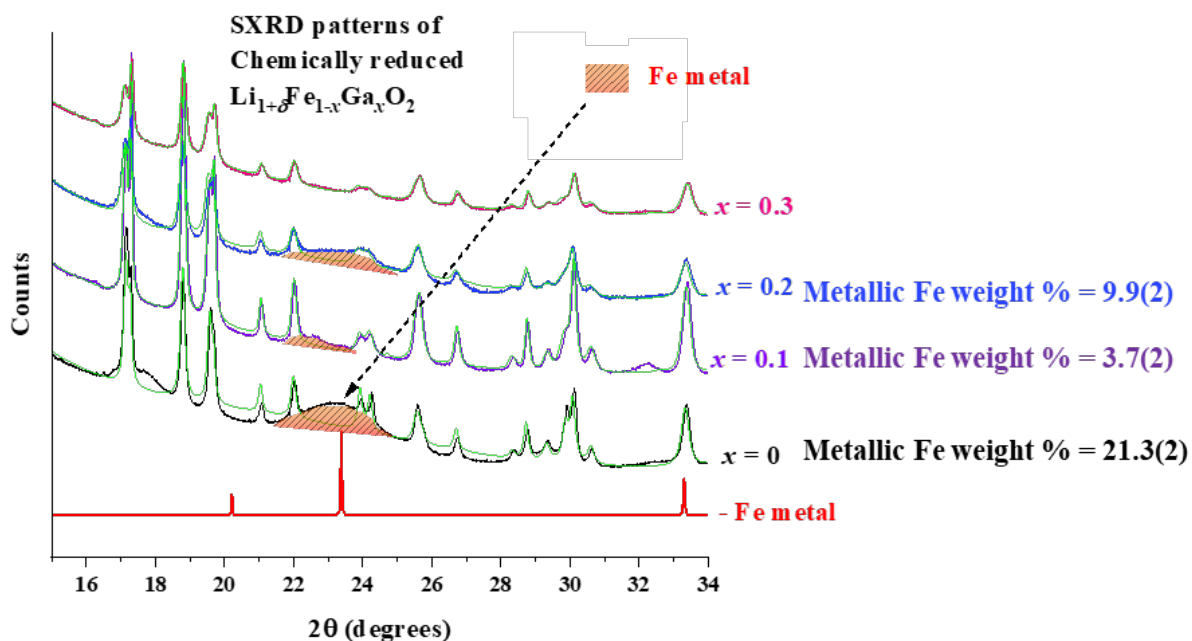


Figure 4. 4. Overlay of SXRD analysis (green line represents calculated intensities) of $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ samples for $x = 0, 0.1, 0.2$ and 0.3 with simulated XRD pattern of Fe-metal in 2θ range of $15\text{--}34^\circ$

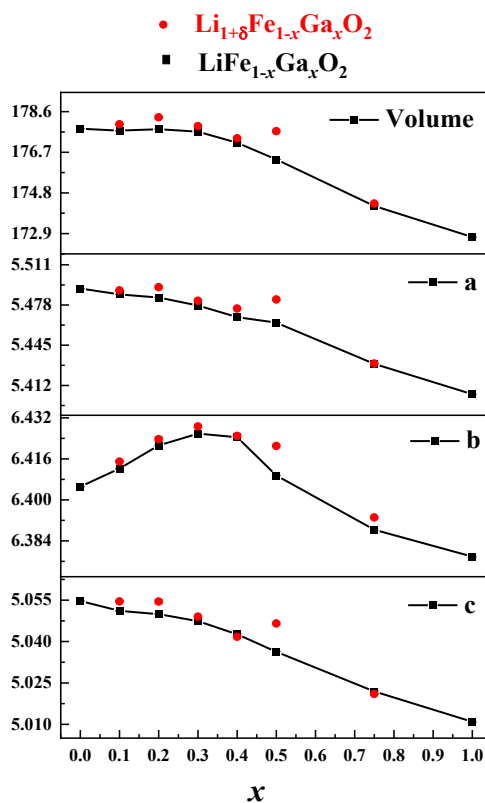


Figure 4. 5. Plot of lattice parameters of $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ (red circle) and $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ (black square) as a function of gallium concentration determined from the structural refinement against SXRD data; error bars are smaller than the plotted points

Figure 4.5 shows the variation of lattice parameters of lithiated $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ phases (red circles) and corresponding pristine $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ phases (black squares) as a function of gallium concentration. An increase in the lattice parameters of $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ phases are observed in comparison to $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$. Although an increase in the cell parameter is observed for the reduced samples, SXRD analysis does not reveal any information about the concentration or location of the inserted lithium, thus iodometric titrations were performed on $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ phases in the composition range $0.5 \geq x \geq 0.3$, and NPD data was collected from the $x = 0.5$ material.

4.4.2. Neutron powder diffraction (NPD) data

Room temperature NPD data was collected from lithiated $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$. Similar to $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, an ordered Fe/Ga structural model ($\text{Li}_2\text{ZnGeO}_4$ type¹⁵³, space-group: Pn , as mentioned in Section 3.3.2.) was refined against the data, which yielded a good fit as shown in Figure 4.9 with crystallographic parameters given in Table 4.1. The location of additional lithium ions was determined from the highest negative scattering density in a Fourier difference map calculated from the data (Figure 4.6). This reveals the lithium ions are located in a diffuse manner around the centre of octahedral sites ($2a$) which share faces with nearby Fe-O and Li-O tetrahedra.

During the structural determination, the additional lithium ions were initially placed in the $2a$ octahedral sites, and their positions and occupancy parameters were refined. This resulted in a final refined model with a composition of $\text{Li}_{1.49}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, which is in good agreement with the lithium content determined by iodometric titration (Appendix-I, Table 4a.9). From the refined model, calculated $\langle\text{Fe-O}\rangle$, $\langle\text{Ga-O}\rangle$, and Fe-BVS revealed an elongation of $\langle\text{Fe-O}\rangle$ bond lengths and a decrease in Fe-BVS in $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ compared to $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ (see Table 4.3. and Figure 4.8). These findings are consistent with the reduction of Fe-site due to lithium insertion.

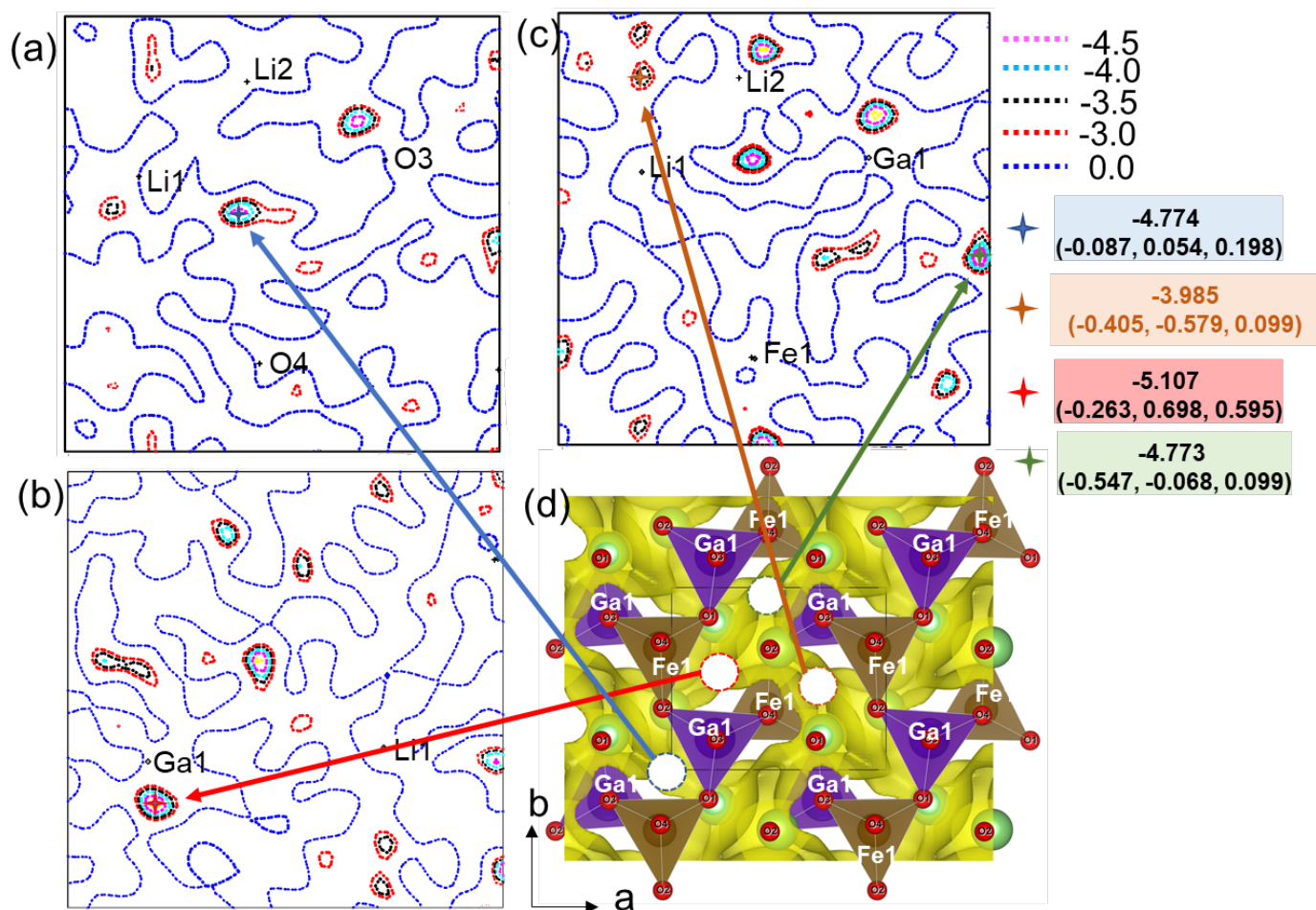


Figure 4. 6. Plot of selected Fourier difference maps [centre of reference (0,0,0), with height above the centre 0.5Å (a), 1Å(b) and 3Å (c)] calculated from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ against NPD data (a,b, and c). Arrows and "+" signs indicate the positions of the highest negative scattering densities. Four distinct minima are marked by different arrows, denoted with blue, dark brown, green and red "+" signs.

(d) displays the Bond Valance Energy Landscape (BVEL) map for lithium ions within $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ structure. Yellow isosurfaces represent a constant Bond Valence Sum (BVS) value for lithium ions, calculated with a percolation energy of 3 eV. The empty octahedral sites, shown by dotted circles, exhibit the highest density of lithium percolation channels.

The correlation between the four empty octahedral sites, characterised by both the highest percolation channel density and the highest negative scattering density in the Fourier difference maps, is visually emphasised with arrows in the plot (a,b,c, and d).

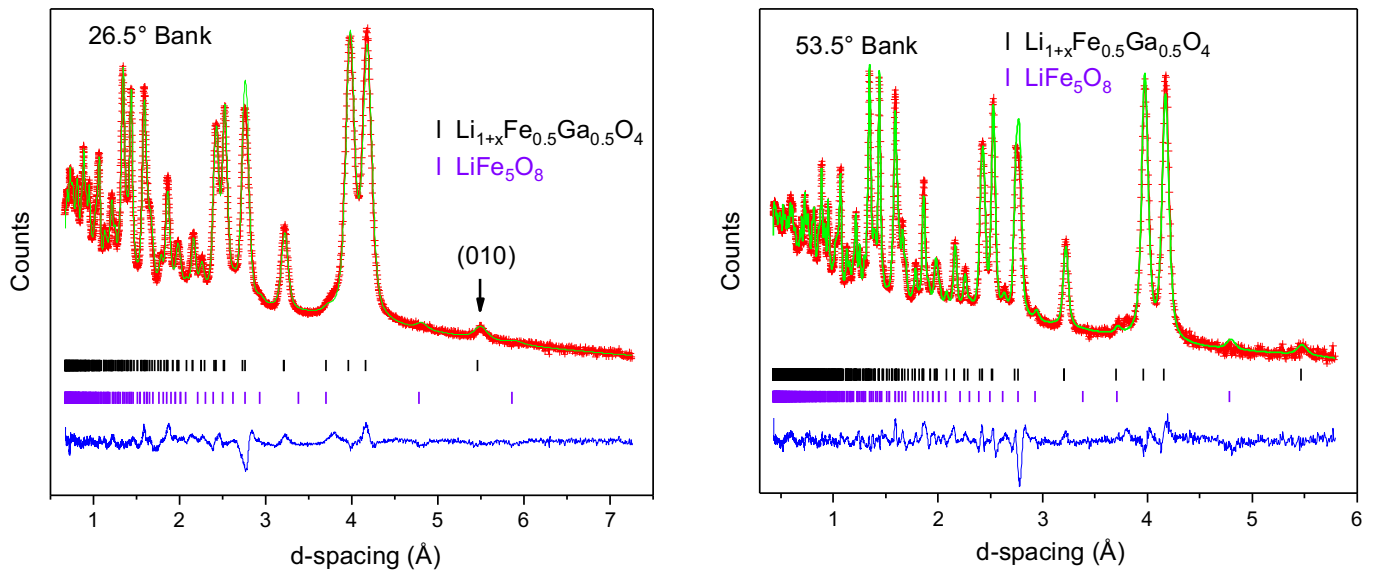


Figure 4. 7. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ against NPD data, bank 26.5° (left), 53.5° (right)

Table 4.1. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	$2a$	0.5615(64)	0.0759(17)	0.9872(58)	1	0.3(1)
Li2	$2a$	0.8053(62)	0.3018(28)	0.5593(58)	1	0.3(1)
Li3	$2a$	0.7902(51)	0.0589(74)	0.6593(58)	0.21(2)	0.9(3)
Li4	$2a$	0.2901(50)	0.0589(74)	0.6593(58)	0.25(1)	0.9(3)
Li5	$2a$	$\frac{1}{2}$	$\frac{1}{2}$	0.0589(74)	0.23(1)	0.9(3)
Li6	$2a$	$\frac{1}{2}$	$\frac{1}{2}$	0.5589(74)	0.25(1)	0.9(3)
Fe1	$2a$	0.2901(51)	0.3210(7)	0.4862(50)	1	0.15(3)
Ga1	$2a$	0.0543(49)	0.1660(9)	0.9775(51)	1	0.18(1)
O1	$2a$	0.5387(51)	0.1569(11)	0.3769(52)	1	0.19(2)
O2	$2a$	0.3258(51)	0.6623(10)	0.3678(51)	1	0.19(2)
O3	$2a$	0.0508(53)	0.1897(9)	0.3273(51)	1	0.19(2)
O4	$2a$	0.2786(51)	0.3294(10)	0.8638(50)	1	0.19(2)
$\text{Li}_{2.98}\text{FeGaO}_4$ ($\text{Li}_{1.49}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$) – space group Pn (#7) $a = 6.4139(4) \text{ \AA}$, $b = 5.4649(2) \text{ \AA}$, $c = 5.0371(2) \text{ \AA}$, $\beta = 89.9999^\circ(5)$, volume = $176.562 (16) \text{ \AA}^3$ Formula weight = $210.11 \text{ g mol}^{-1}$, $Z = 2$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 2.12 \%$, $wR_p = 2.77 \%$						
Crystallographic parameters LiFe_5O_8 added as a secondary phase during the refinement LiFe_5O_8 – space group $P4_332$ (#212) $a = 8.3147(14) \text{ \AA}$, volume = $574.850(296)$ weight % = 9(2)						

Table 4.2. Bond lengths and BVS parameter table for $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$

$\langle\text{Fe-O}\rangle$ (Å)	Average $\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Ga-O}\rangle$ (Å)	Average $\langle\text{Ga-O}\rangle$ (Å)	Ga-BVS
1.87(5)	1.915(7)	2.633	1.76(4)	1.804(7)	3.281
1.91(4)			1.79(4)		
1.91(4)			1.82(4)		
1.971(14)			1.840(13)		

Table 4.3. $\langle\text{Fe-O}\rangle$ bond lengths and Fe-BVS parameter table of $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ and $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$

$x\text{Ga}_x\text{O}_2$ phases determined from structural refinements against NPD and SXRD data

x	$\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$		$\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$	
	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0.1	1.888(4)	2.824	1.974(3)	2.731
0.2	1.898(3)	2.765	1.967(3)	2.534
0.3	1.895(4)	2.810	1.985(2)	2.730
0.4	1.901(3)	2.802	1.946(2)	2.587
0.5	1.897(6)	2.761	1.915(7)	2.633
0.75	1.897(3)	2.761	1.986(3)	2.919

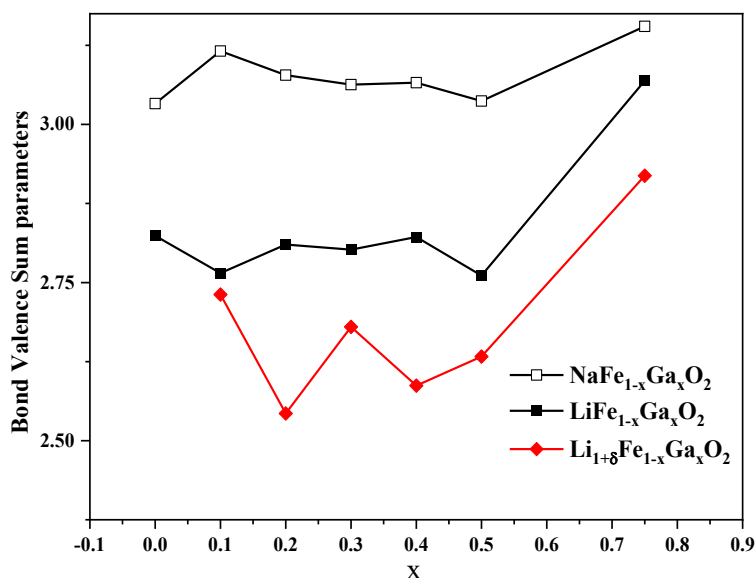


Figure 4. 8. Plot of Fe-BVS as a function of gallium concentration for $\text{NaFe}_{1-x}\text{Ga}_x\text{O}_2$, $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$, and $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ determined from structural refinement against SXRD and NPD data

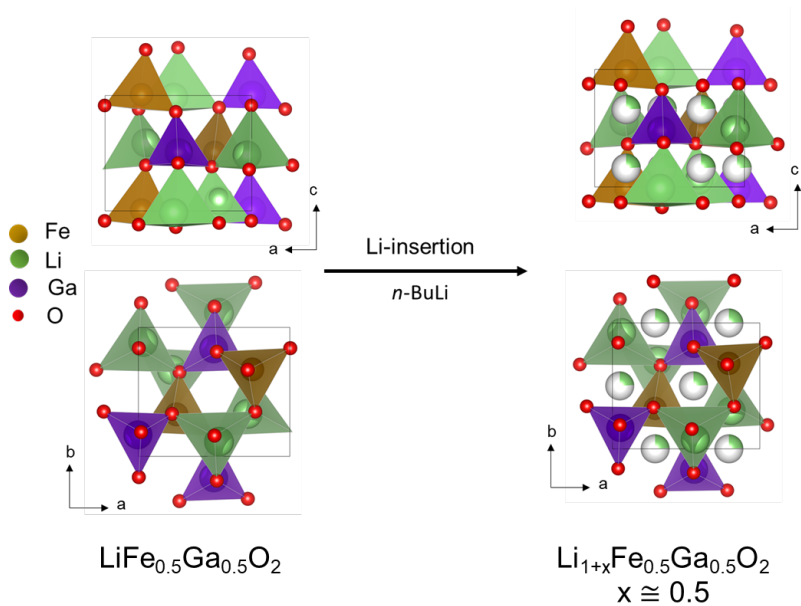


Figure 4. 9. Structural description for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ (pristine) and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ (reduced)

4.4.3. X-ray absorption spectroscopy (XAS) data

X-ray absorption spectroscopy (XAS) data were collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ along with data from FeO and Fe_2O_3 to investigate not only the change in iron oxidation state but also the change in the local structure of iron in $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ after exposure to $n\text{-BuLi}$. During the XANES analysis the Fe K-edge data of FeO and Fe_2O_3 were used as references for Fe (II) and Fe (III) K-edges respectively. Results from the XANES and EXAFS analysis are presented below.

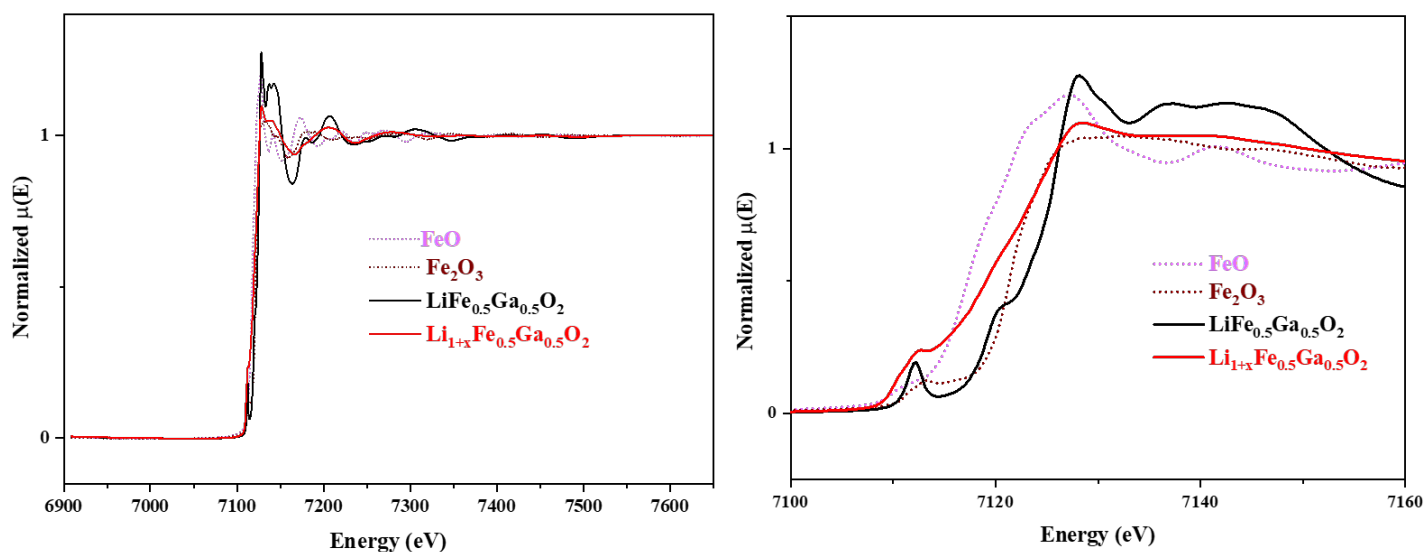


Figure 4. 10. XANES data of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ with references (dotted lines); normalization(left), Fe K-edge comparison(right).

As illustrated in Figure 4.10, the pristine $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ sample displays a pre-edge feature at 7112 eV, characteristic of a tetrahedral coordination environment of iron. A noticeable shift of the Fe K-edge to lower energy is observed for the reduced $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ material (red line, Figure 4.11), resulting in an overlap of the Fe K-edge with that of FeO (Fe(II) standard). These findings are consistent with the reduction of Fe in $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ due to lithium insertion

XAS data at energies above the absorption edge were extracted and processed as EXAFS data. The EXAFS data from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ were fitted with a structural model derived from the structural determination against NPD data. During the fitting process, oscillations in the first and second coordination shells of the absorber atom were calculated and converged with the observed oscillations, as shown in Figure 4.11. The refined EXAFS parameters are detailed in Table 4.4

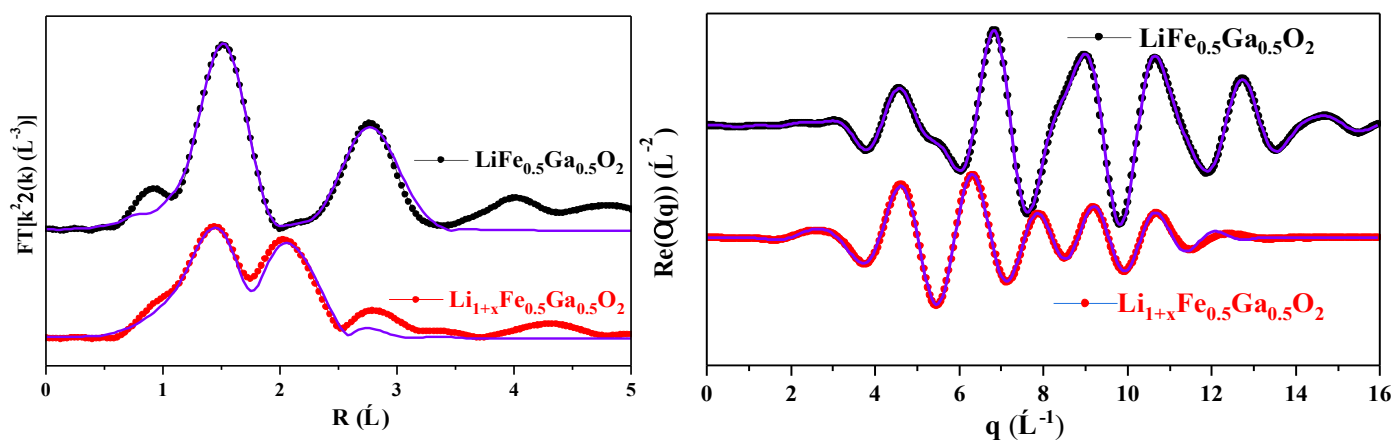


Figure 4. 11. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 4.4. Refined EXAFS parameters of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD (Å)
$\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ ($\text{Li}_2\text{FeGaO}_4$)	Fe-O	4	1.88(4)	3.7(4)	0.6	2.824	1.897(6)
	Fe-Fe	2	3.26(1)	6.9(3)			
	Fe-Ga	2	3.13(1)	5.2(1)			
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ ($\text{Li}_3\text{FeGaO}_4$)	Fe-O	4	1.916(5)	8.2(3)	5.3	2.6168	1.915(7)
	Fe-Ga	2	2.479(4)	8.4(3)			
	Fe-Fe	2	2.64(1)	4.9(1)			

During the EXAFS analysis, data obtained from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ were fitted, with a first coordination shell of tetrahedral $\langle\text{Fe-O}\rangle$ and the second coordination shell comprising of $\langle\text{Fe-Fe}\rangle/\langle\text{Fe-Ga}\rangle$ with a ratio of 1:1 due to Fe-Ga ordering in the structure. This fitting yielded a good fit in both R and q space, as shown in Figure 4.12. The $\langle\text{Fe-O}\rangle$ and Fe-BVS parameters, obtained from the EXAFS fitting of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, are in good agreement with those determined from structural refinement against the neutron powder diffraction (NPD) data.

The EXAFS data from $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ was fitted with first shell of Fe-O tetrahedra similar to $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, with slight increase in $\langle\text{Fe-O}\rangle$ bond length. However, the second shell of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ is found to be distinct from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and was fitted with Fe-Ga/Fe-Fe bonds with bond distances 2.749(4)-2.64(1) Å. Which suggests the formation of elemental iron or gallium secondary phases during the lithium intercalation reaction.

4.4.4. Discussion of the reduced $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ samples

SXRD data collected from the reduced $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ phases reveals that a gallium concentration of 30% effectively prevents the formation of crystalline metallic iron upon exposure to *n*-BuLi. Iodometric titrations and neutron powder diffraction (NPD) analyses confirm the presence of an additional ~ 0.5 lithium ions within the structure of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$. Furthermore, NPD data specifies the location of this additional lithium in the octahedral sites that share faces with Fe-O and Ga-O tetrahedra.

The Fe-BVS values, derived from a combined analysis of SXRD and NPD data, demonstrate a decrease in bond-valence sum parameters (as depicted in Figure 4.6) for the reduced samples. This reduction is consistent with the Fe-site becoming slightly larger and experiencing a decrease in oxidation state.

X-ray absorption spectroscopy (XAS) data confirms the reduction of Fe^{3+} to Fe^{2+} in $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ upon exposure to *n*-BuLi. The first shell fit of the extended X-ray absorption fine structure (EXAFS) data closely aligns with the NPD analysis. However, an analysis of the second coordination shell in the reduced $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ sample reveals the formation of elemental iron or gallium due to lithium insertion. This suggests that while gallium doping effectively suppresses the crystalline elemental iron formation in the average structure (as observed in the SXRD and NPD data), it is still noticeable in the local structure (as observed in the EXAFS data).

4.5. Results and discussion for both Al and Ga doped T-LiFeO₂

4.5.1. Structural characterization of the reduced LiFe_{0.5}Al_{0.5-y}Ga_yO₂ samples (SXRD)

SXRD data were collected from lithiated Li_{1+δ}Fe_{0.5}Al_{0.5-y}Ga_yO₂ samples with $y = 0.125$, 0.25, and 0.375 and are shown in Figure 4.12. These data exhibit broad peak at $2\theta \sim 23.4^\circ$ which are associated with the presence of metallic iron.

SXRD data collected from reduced Li_{1+δ}Fe_{0.5}Al_{0.5-y}Ga_yO₂ phases could be indexed using orthorhombic unit cells with reflection conditions consistent with $Pna2_1$ space group symmetry. The structural models based on the corresponding LiFe_{0.5}Al_{0.5-y}Ga_yO₂ phases were refined against the SXRD data to achieve good fits as shown in Figure 4.13 and crystallographic parameters given in Table 4.9. The same for samples with $y = 0.25$ and 0.375 are given in Appendix-I Figures (and Tables) 4a.7-4a.8

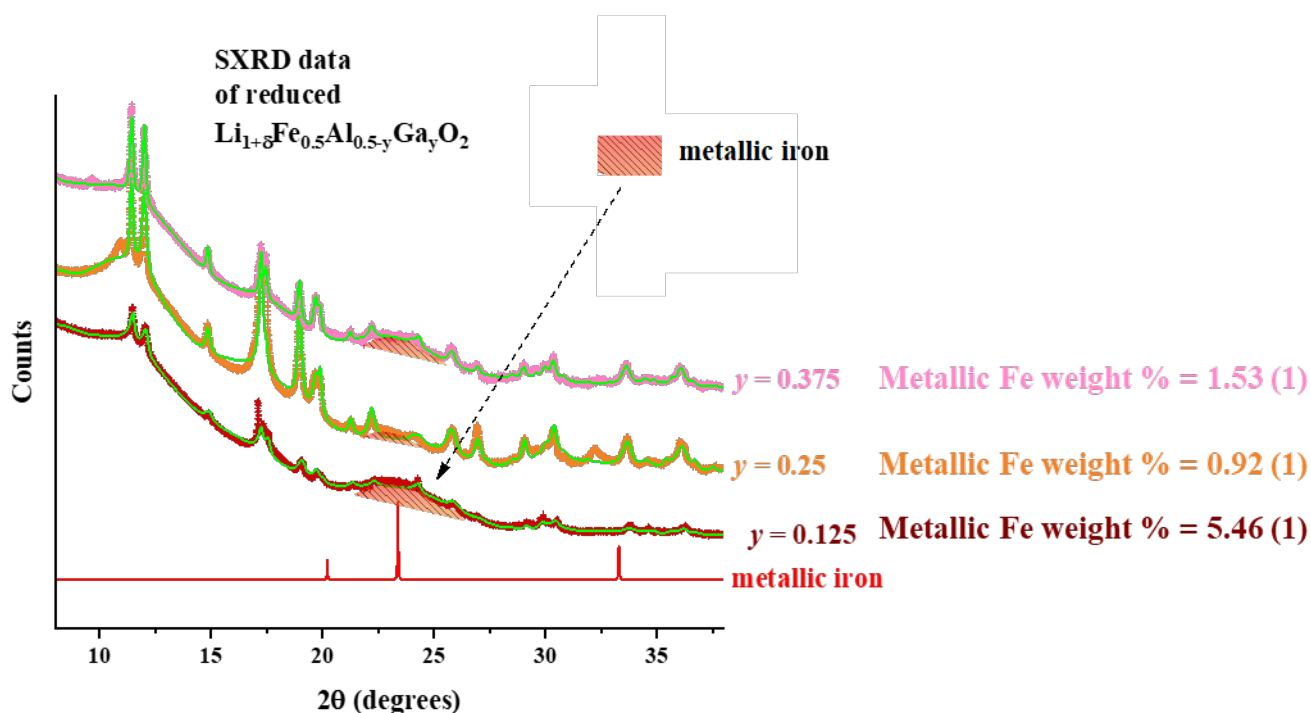


Figure 4. 12. Plot of SXRD analysis of Li_{1+δ}Fe_{0.5}Al_{0.5-y}Ga_yO₂ samples for $y = 0.125$, 0.25 and 0.375 with simulated pattern of metallic iron, Green line: calculated intensity; Shaded box: broad peaks associated with metallic iron

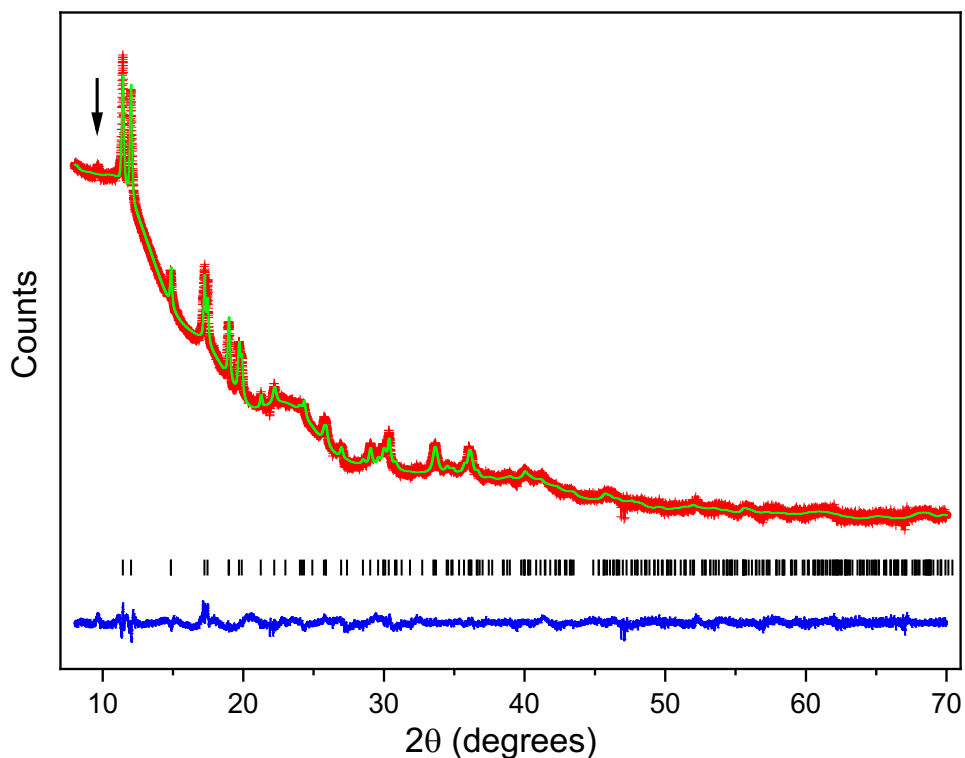


Figure 4. 13. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ against SXRD data (black arrow indicates unidentified impurity)

Table 4.5. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.359(4)	0.118(10)	0.530(10)	1	0.1
Fe/Al/Ga	$4a$	0.0810(5)	0.1223(8)	0	0.5/0.125/0.375	0.45(6)
O(1)	$4a$	0.013(20)	0.1313(57)	0.3631(16)	1	0.1
O(2)	$4a$	0.4151(28)	0.1332(51)	0.8852(16)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4488(4) \text{ \AA}$, $b = 6.3980(6) \text{ \AA}$, $c = 5.0216(4) \text{ \AA}$ volume = $175.064 (27) \text{ \AA}^3$ Formula weight = $96.381 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.02\%$, $wR_p = 1.35 \%$, $R_{\text{Bragg}} = 0.67$						

B_{eq} of lithium and oxygen ions were set to $0.1 \text{ \AA}^2$ due to absorption issues

Table 4.6. Bond lengths and BVS parameter table of pristine $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ and chemically reduced $\text{Li}_{1+\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ determined from structural refinements against SXRD data

y	$\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$		$\text{Li}_{1+\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$	
	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	1.823(6)	3.366	--	--
0.125	1.848(2)	3.161	1.916(6)	2.62
0.25	1.893(3)	2.827	2.021(5)	2.109
0.375	1.884(4)	2.887	1.882(6)	2.871
0.5	1.897(3)	2.761	1.915(7)	2.633

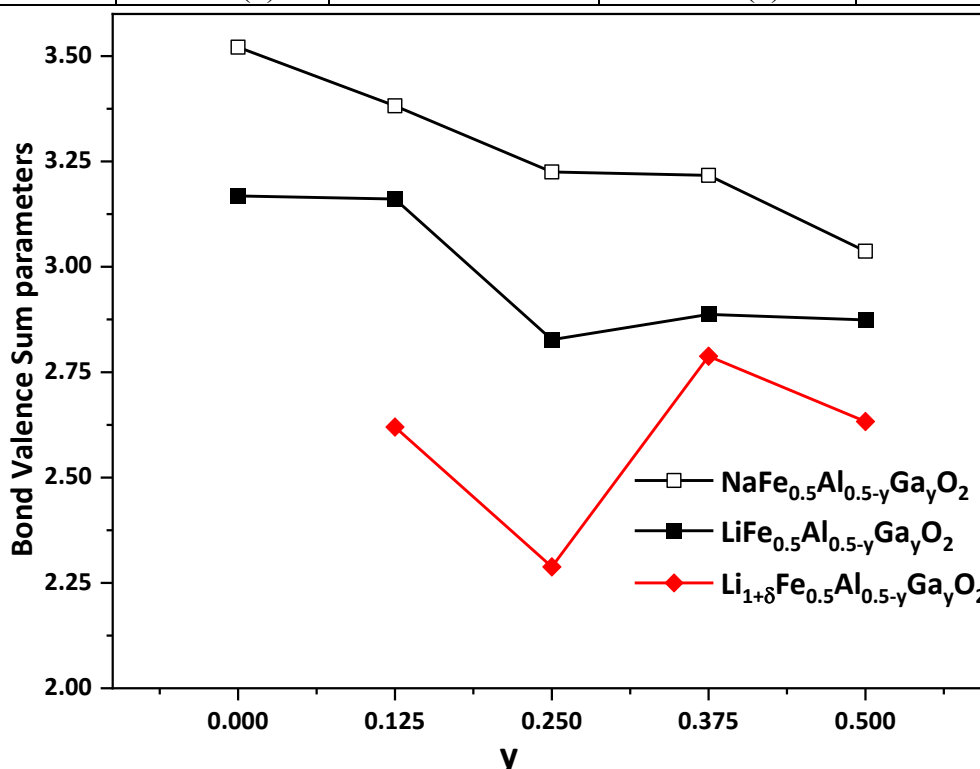


Figure 4. 14. Plot of Fe-BVS as a function of gallium concentration for $\text{NaFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$, $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$, and $\text{Li}_{1+\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ determined from structural refinement against SXRD data

The bond-valence sum calculated for the reduced $\text{Li}_{1+\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ samples (red line Figure 4.14) shows a decrease in the Fe-BVS value in comparison to the pristine $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ (black line Figure 4.16). Additionally, the bond distance of $\langle\text{Fe-O}\rangle$ bond in $\text{Li}_{1+\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ is found to have increased compared to the corresponding $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ phases (Table 4.6). Both these observations are consistent with the Fe-site being chemically reduced when lithium is inserted.

4.5.2. X-ray absorption spectroscopy (XAS) data

Similar to $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, XAS data were collected from $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$, $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ along with data FeO and Fe_2O_3 . During the XANES analysis Fe K-edge data from FeO and Fe_2O_3 were used as references for Fe (II) and Fe (III) respectively. Results from the XANES and EXAFS analysis are presented below.

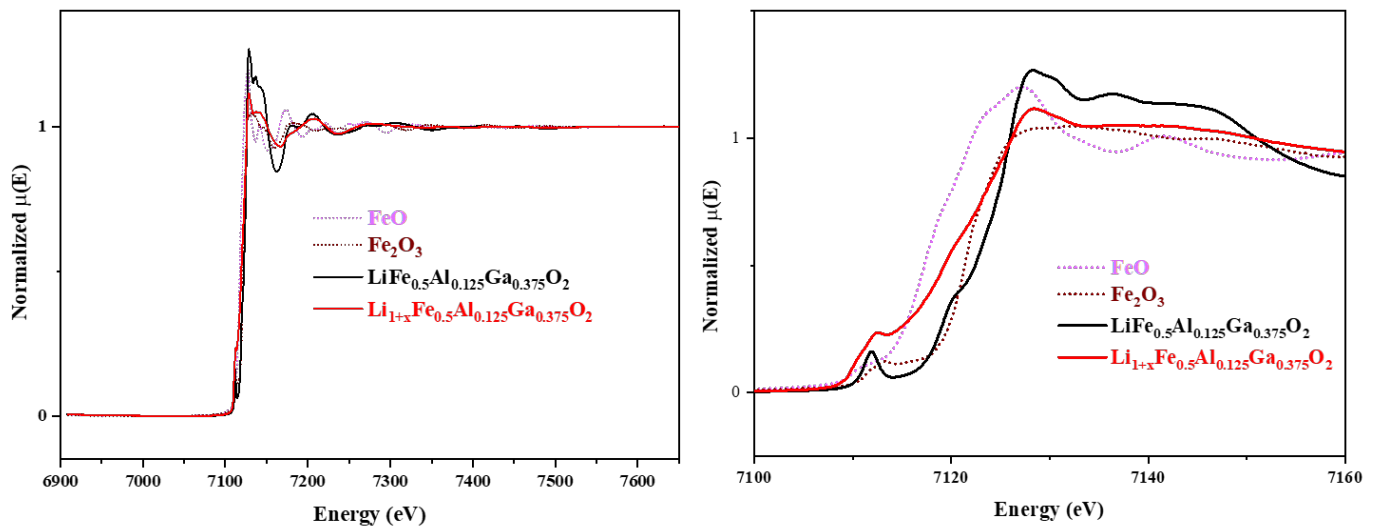


Figure 4. 15. XANES data of $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$, and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$, with references (dotted lines); normalization(left), Fe K-edge comparison(right).

As depicted in Figure 4.15, the pristine $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ material exhibits a pre-edge feature at 7112 eV, indicative of its characteristic tetrahedral iron environment. A comparison of the XANES data between the pristine and reduced materials reveals a shift of the Fe-K edge to lower energy in the reduced sample. The XANES data of the reduced sample (red line) partially aligns with the Fe (II) standard in specific regions, but a complete overlap is not observed.

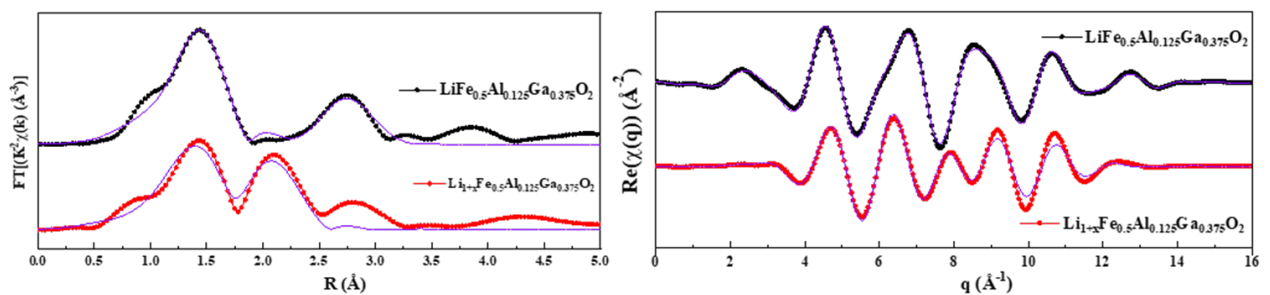


Figure 4. 16. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 4.7. Refined EXAFS parameters of $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from XRD (Å)
$\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$	Fe-O	4	1.875(6)	4.29(1)	0.8	2.857	1.8846
	Fe-Fe	2	3.12(4)	8.48(3)			
	Fe-Ga	1	2.76(3)	8.48(3)			
	Fe-Al	1	3.14(7)	8.48(3)			
$\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$	Fe-O	4	1.88(3)	6.4(3)	6.8	2.837	1.8828
	Fe-Fe	2	2.65(4)	4.9(1)			

The XAS data, collected from $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ and $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ at energies beyond the absorption edge were converted into EXAFS data. The calculated oscillations in the first and second coordination shells of the absorber atom were matched with the observed oscillations during the fitting process as shown in Figure 4.16. The first coordination shell was fitted with a tetrahedral iron site, for the pristine $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ material, displaying a $\langle\text{Fe-O}\rangle$ bond length of 1.875(6) Å, which closely aligns with the $\langle\text{Fe-O}\rangle$ bond length obtained from synchrotron X-ray diffraction (SXRD) data. The second coordination shell of the pristine material was fitted with $2 \times \text{Fe-Fe}$, $1 \times \text{Fe-Ga}$, and $1 \times \text{Fe-Al}$ bond lengths, reflecting the Fe-Al-Ga disorder around the iron site.

In the case of the reduced $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ sample, the first shell closely resembles that of the pristine material. However, an intense peak adjacent to the first shell is observed at a slightly higher R-value than the first shell (Figure 4.16, similar to $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, as discussed in Section 4.4.4). Thus, the first shell was fitted with $\langle\text{Fe-O}\rangle$ bond lengths of 1.88(3) Å, while the second shell was fitted with $\langle\text{Fe-Fe}\rangle$ bond length of 2.65(4) Å consistent with the presence of elemental iron. Such refinement strategy led to a good fit of the data as shown in in Figure 4.16 with the refined parameters in Table 4.7.

4.5.3 Electrochemical data

To assess the electrochemical performance of both aluminium and gallium doped T-LiFeO₂ samples, a cyclic voltammogram (CV) was collected from LiFe_{0.5}Al_{0.25}Ga_{0.25}O₂ as shown in Figure 4.17.

The CV profile collected from LiFe_{0.5}Al_{0.25}Ga_{0.25}O₂ during the first discharge cycle exhibits a small reduction feature at ~ 1.4 V and, at a lower voltage of 1 V, another reduction feature is observed. On oxidation, a single broad feature is evident at ~ 2 V. In the subsequent voltage cycles, the area under the reduction feature diminishes rapidly, indicating repeated cycling is not possible for LiFe_{0.5}Al_{0.25}Ga_{0.25}O₂.

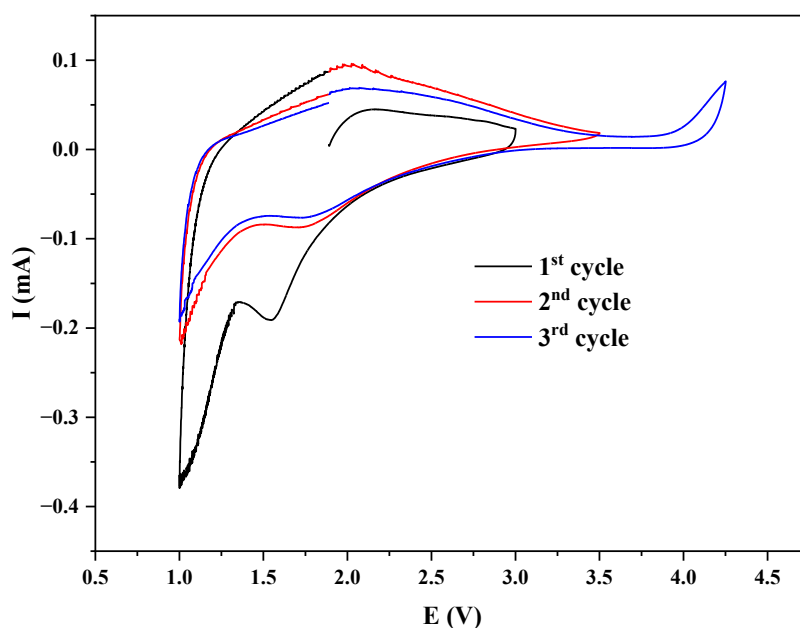


Figure 4. 17. Plot of cyclic voltammogram data of LiFe_{0.5}Al_{0.25}Ga_{0.25}O₂

4.5.4 Discussion of the reduced $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ samples

Structural refinements of lithiated $\text{Li}_{1+\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ phases against the SXRD data revealed that, despite the retention of overall crystallinity, the reduction process leads to the formation of metallic iron and other impurity phases. This indicates that the presence of simultaneous gallium and aluminium doping does not stabilize the T- LiFeO_2 structure with respect to reduction, resulting in the decomposition of the structure, similar to the behaviour observed with only aluminium doped samples ($\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$).

XANES data collected from $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ confirm the reduction of iron from Fe^{3+} to Fe^{2+} , while analysis of the EXAFS data reveal the reduction of some Fe^{3+} to elemental iron. Consequently, it can be inferred that samples containing both aluminium and gallium suffer from the limitations observed to aluminium doped samples ($\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$), which fail to stabilize the tetrahedral framework of iron during chemical reduction.

4.6. Conclusion

Based on the comprehensive analysis involving SXRD, NPD, titration, XAS, and electrochemical characterization of $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ under reductive conditions, several significant conclusions can be drawn:

1. Aluminium doping fails to stabilize the T- LiFeO_2 structure under reductive conditions and results in the production of additional unknown impurity phases.
2. The incorporation of gallium at a concentration of 30% or higher into T- LiFeO_2 effectively suppresses the formation of crystalline metallic iron and facilitates reversible lithium insertion. However, the formation of amorphous elemental iron in the case of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ suggests that gallium doping fails to fully stabilize the structure under reductive conditions.

3. When both aluminium and gallium are doped into T-LiFeO₂, the resulting material exhibits characteristics similar to those of singly aluminium-doped samples under reductive conditions. This includes the production of metallic iron and other decomposition products, signifying the limitations associated with aluminium doping.

The instability of LiFe_{1-x}Al_xO₂ under reductive conditions can be rationalized by considering the ionic radii of the constituent elements. Specifically, the large difference in ionic radii between Al³⁺ (0.39 Å)¹⁵⁴ and Fe²⁺ (0.63 Å in Td site)¹⁵⁴ results in significant strain on the structure when Fe³⁺ (0.49 Å in Td site)¹⁵⁴ is reduced to Fe²⁺, ultimately leading to a complete structural decomposition. In contrast, LiFe_{1-x}Ga_xO₂ exhibits better stabilization of the T-LiFeO₂ framework compared to aluminium-doped samples due to the more similar ionic radii of Ga³⁺ (0.47 Å)¹⁵⁴ and Fe²⁺ (0.63 Å)¹⁵⁴.

Chapter 5 – Oxidation of Al, Ga doped T-LiFeO₂ phases

5.1. Introduction

Nitronium tetrafluoroborate (NO₂BF₄) has an oxidation potential of 5.14 V vs the Li⁺/Li couple¹¹⁵. Thus, oxidative delithiation reactions with nitronium tetrafluoroborate^{115,116} can be considered as the chemical equivalent of the electrochemical charge process of a cathode in a lithium ion battery. To achieve oxidative lithium deintercalation, LiFe_{1-x}M_xO₂ samples were treated with nitronium tetrafluoroborate in acetonitrile. The products obtained were characterized by SXRD, ICP-MS, NPD, XAS, RIXS and titration techniques. The analysis of these results are described in this chapter. In addition, electrochemical performances of a few selected LiFe_{1-x}M_xO₂ samples are also discussed.

5.2. Experimental section

5.2.1. Chemical Li-deintercalation

In a small Schlenk tube under a nitrogen atmosphere, approximately 500 mg of NO₂BF₄ (95+%, Merck Life Science) was dissolved in 10 mL of acetonitrile. Maintaining a molar ratio of 1:5 of LiFe_{1-x}M_xO₂: NO₂BF₄, around 200 mg of LiFe_{1-x}M_xO₂ sample was added to the solution, and the tube was sealed with a glass cap. The tube was then transferred to an oil bath where the contents inside the tube were constantly stirred and heated at 50°C for 7 days. Following this period, the suspension obtained was filtered with excess acetonitrile solution, and the resulting powder was collected via vacuum filtration.

To check the reversibility of lithium deintercalation, the deintercalated sample (Li_{1-δ}Fe_{1-x}M_xO₂) was treated with LiI (99.999%, Alfa Aesar) in the following manner. In a controlled nitrogen atmosphere, about 300 mg of LiI (99.999%, Alfa Aesar) was dissolved in 10 mL of acetonitrile within a small Schlenk tube. Maintaining a molar ratio of 1:10 between Li_{1-δ}Fe_{1-x}

xM_xO_2 and LiI, approximately 50-70 mg of the $Li_{1-\delta}Fe_{1-x}M_xO_2$ sample was introduced into the solution, and the tube was then sealed with a glass cap. The sealed tube was placed in an oil bath where its contents were continuously stirred and heated at 50°C for 3 days. A noticeable change in the colour of the solution from colourless to yellow or dark brown was observed, indicating iodine release during the reaction. Following this reaction, the powder was collected through filtration. To quantify the released iodine, the filtrate was titrated against a standardized thiosulphate solution.

5.2.2. Galvanostatic measurements

Electrochemical cycling was performed to a coin cell assembled with $LiFe_{1-x}M_xO_2$ ($M=$ Al and/or Ga) as active cathode material, PVDF-carbon as binder, $LiFePF_6$ as electrolyte and Li chips as anode (described in detail in Section 3.2.1). Cyclic voltammogram up to six cycles and charge-discharge capacity profiles up to hundred cycles were measured.

5.3. Results and discussion for Al doped T-LiFeO₂ samples

5.3.1. Structural characterization (SXRD data)

SXRD data were collected from chemically oxidised $LiFe_{1-x}Al_xO_2$ phases after treatment with NO_2BF_4 , henceforth known as $Li_{1-\delta}Fe_{1-x}Al_xO_2$. SXRD data (Figure 5.1) show that oxidation of T-LiFeO₂ results in complete structural decomposition. Annealing the resultant T- $Li_{1-x}FeO_2$ sample at 600°C under vacuum resulted in the formation of the spinel phase $LiFe_5O_8$ (Appendix-I Figure 5a.1). Previous reports of T-LiFeO₂ by Armstrong et al⁵⁵ describe the transformation of T-LiFeO₂ to $LiFe_5O_8$ during the electrochemical charging process, which is consistent our observation of chemical deintercalation of T-LiFeO₂.

As shown in Figure 5.1, the SXRD data collected from $Li_{1-x}Fe_{0.75}Al_{0.25}O_2$ exhibit broad features at low 2θ angles ($<8^\circ$), which were assigned to be some organic-borate-fluoride complex that formed during the nitronium tetrafluoroborate decomposition (* in Figure 5.1).

A series of crystallographic models based on the disordered Fe/Al structure (described in Section 3.3.2.1) were prepared, which were refined against the SXRD data collected from $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ phases for $x \geq 0.125$. The SXRD pattern collected from $\text{Li}_{1-x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ was found to exhibit a series of unindexed peaks, which are attributed to the slight decomposition of the phase upon chemical delithiation. For other $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ samples with $x = 0.25, 0.5$, and 0.75 no such additional peaks were observed. The structural refinement plots and crystallographic parameters from $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ are given in Appendix-I Figures (and Tables) 5a.2-5a.4. In Figure 5.2, a plot comparing of the cell parameter of $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ and $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ phases are given as a function of composition, which shows modest change of cell parameters for $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ phases, after the chemical oxidation.

A detailed structural characterization of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ was performed by neutron powder diffraction and will be discussed in Section 5.3.2.

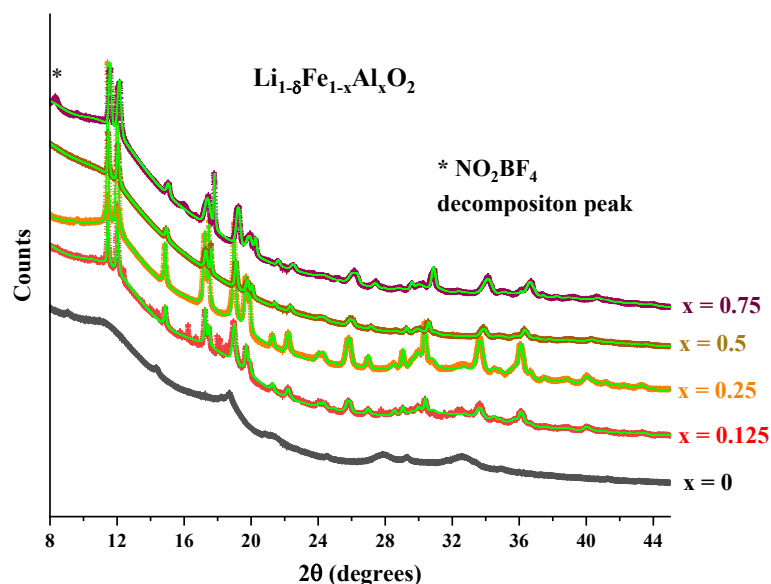


Figure 5. 1. Plot of observed and calculated intensity fit (green line) from $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ phases obtained after the structural refinement against SXRD data

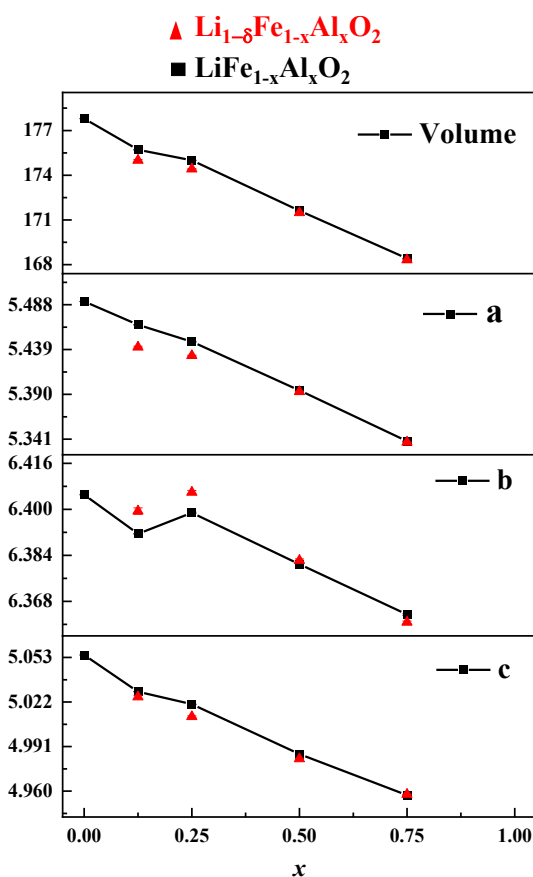


Figure 5. 2. Plot of lattice parameters of $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ (red triangles) and $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ (black squares) as a function of composition determined from the structural refinement against SXRD data; error bars are smaller than the plotted points

5.3.2. Neutron diffraction (NPD) data

Neutron powder diffraction (NPD) data were collected from chemically de-lithiated $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ sample. A crystallographic model based on the disordered T- LiFeO_2 ($Pna2_1$) structure was refined against the data which converged rapidly to achieve a good fit as shown in Figure 5.3 with crystallographic parameters given in Table 5.1.

During the structural refinement, the lithium occupancy parameter was refined, resulting in the determination of the final composition of the delithiated sample as $\text{Li}_{0.8}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$, which is consistent with the lithium content determined from ICP-MS analysis (Appendix-I Table 5a.8). The structural model derived from this refinement were used to calculate $\langle\text{Fe-O}\rangle$ bond lengths and Fe-BVS parameters (detailed in Table 5.2). Table 5.3

and Figure 5.4 present a comprehensive comparison of $\langle\text{Fe-O}\rangle$ and Fe-BVS values for all $\text{Li}_{1-x}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ alongside their corresponding pristine $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ phases, obtained from structural refinement against SXRD/NPD data. These results indicate a reduction in the $\langle\text{Fe-O}\rangle$ bond length and an increase in Fe-BVS after chemical delithiation, indicating oxidation of the Fe site due to oxidative delithiation.

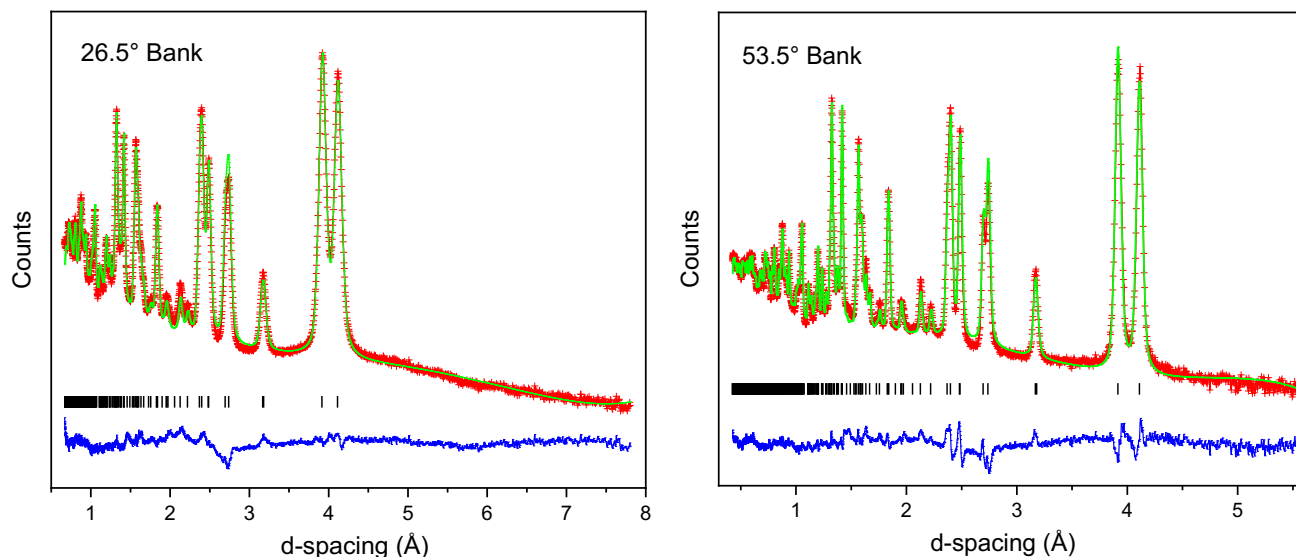


Figure 5. 3. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ against NPD data. bank 26.5°(left), bank 53.5° (right)

Table 5.1. Parameters from the structural refinement of $\text{Li}_{0.80}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	4a	0.1016(11)	0.6037(14)	0.9788(14)	0.80(1)	0.08(5)
Fe1/Al1	4a	0.0764(2)	0.1266(3)	0	0.5/0.5	0.21(1)
O1	4a	0.0688(3)	0.0990(3)	0.3669(3)	1	0.53(2)
O2	4a	0.4025(3)	0.1401(4)	0.9031(4)	1	0.53(2)
$\text{Li}_{0.80}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ – space group $Pna2_1$ (#29) $a = 5.3876(2) \text{ \AA}$, $b = 6.3591(2) \text{ \AA}$, $c = 4.9686(2) \text{ \AA}$, volume = 170.248 (11) $\text{\AA}^3$ Formula weight= 79.0075 g mol $^{-1}$, Z = 4 Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 1.94 \%$, $wR_p = 2.58 \%$						

Table 5.2. Bond lengths and BVS parameter table for $\text{Li}_{0.80}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$

$\langle\text{Fe-O}\rangle/\langle\text{Al-O}\rangle$ (Å)	Average $\langle\text{Fe-O}\rangle/\langle\text{Al-O}\rangle$ (Å)	Fe-BVS	Al-BVS
1.779(3)	1.818(3)	3.4104	2.5470
1.823(3)			
1.832(2)			
1.8413(16)			

Table 5.3. Bond lengths and Fe-BVS parameter of $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ and oxidised $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ sample estimated against NPD and SXRD data

x	$\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$		$\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$	
	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	1.888(4)	2.824	--	--
0.125	1.897(7)	2.762	1.910(7)	3.027
0.25	1.872(3)	2.975	1.875(4)	2.936
0.5	1.823(6)	3.3663	1.818(3)	3.4140
0.75	1.827(4)	3.352	1.806(3)	3.568

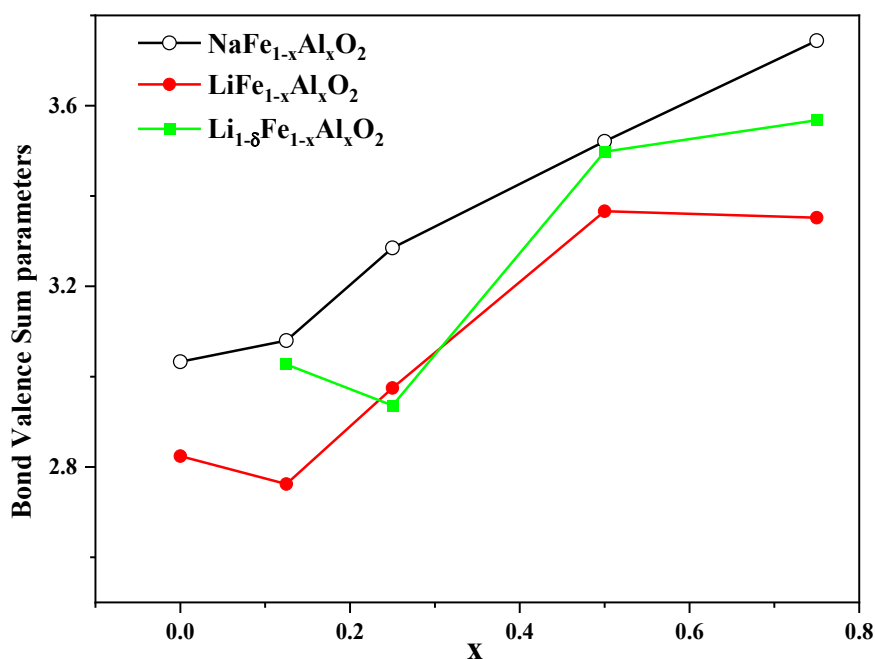


Figure 5. 4. Fe-BVS plot as function of composition for $\text{NaFe}_{1-x}\text{Al}_x\text{O}_2$, $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$, and $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ determined from structural refinement against SXRD and NPD data

5.3.3. X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) data were collected from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$, and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ ($\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2 + \text{LiI}$), alongside Fe_2O_3 and SrFeO_3 . The collected XAS data was processed separately as X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data. XANES data was specifically examined to ascertain the iron oxidation state change in $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ following chemical delithiation.

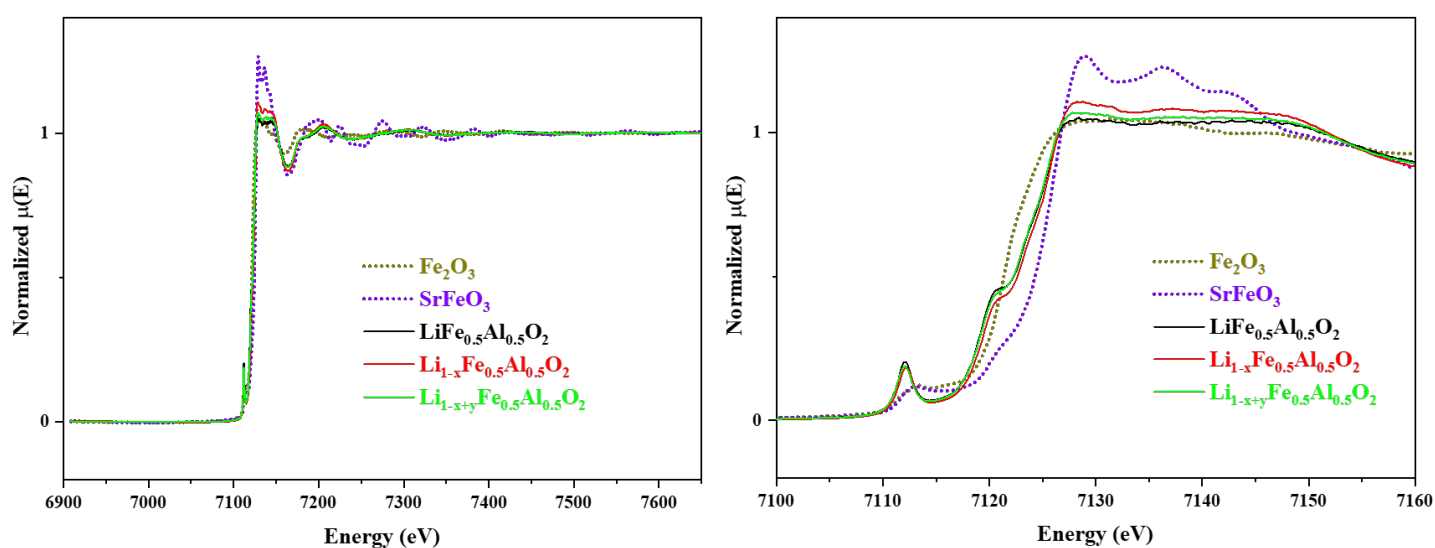


Figure 5. 5. XANES data of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ with references (dotted lines); normalization(left), Fe K-edge comparison(right).

As shown in Figure 5.5, Fe K-edge XANES data of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$, and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ ($\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2 + \text{LiI}$) exhibit a distinct pre-edge feature followed by a sharp K-edge feature. The pre-edge feature is attributed to the characteristic of the tetrahedral Fe-O coordination environment in $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ structure. A small shift in the Fe K-edge to higher energy was observed for the oxidized $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$. For the reversibly intercalated sample ($\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$), a shift towards lower energy in comparison to $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ is observed, indicating iron is mildly oxidised on treatment with NO_2BF_4 and this chemical oxidation is reversible.

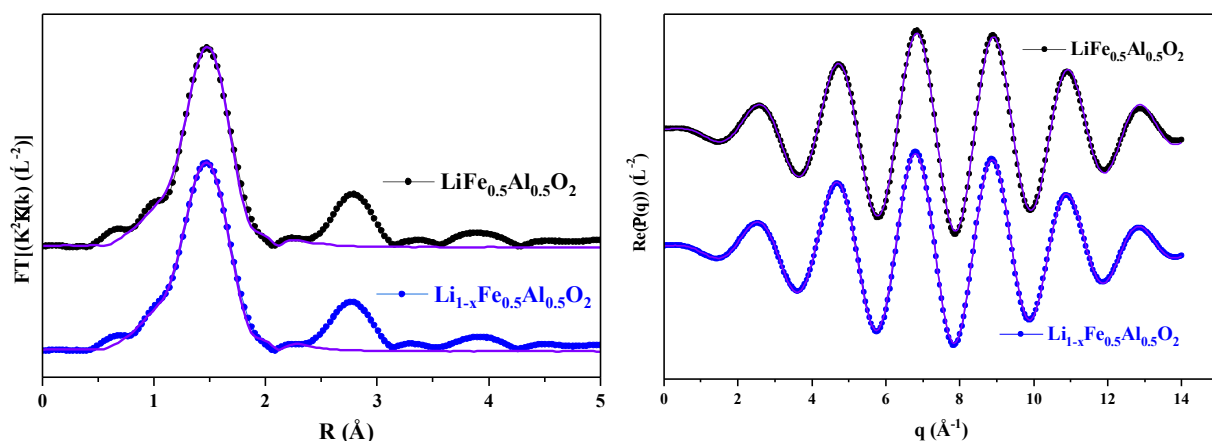


Figure 5.6. EXAFS data and fit (purple line) for $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$, Fourier transform of the k^2 weighted EXAFS oscillations (left), Corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 5.4 Refined EXAFS parameters of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD (Å)
$\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$	Fe-O	4	1.871(4)	3.36(6)	0.4	2.9552	1.823(6)
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$	Fe-O	4	1.874(3)	3.6(5)	0.25	2.9314	1.818(3)

XAS data collected from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$, at energies above the absorption edge were transformed to EXAFS data which were fitted with crystallographic model obtained from the structural refinement against the NPD data. The first shell fit of the EXAFS data from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ in R and q space is shown in Figure 5.6. The fitted Fe-O tetrahedral bonds revealed the similarity of $\langle \text{Fe-O} \rangle$ bond length being 1.871 (4) Å in both $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$, indicating minimal change in the local structure of iron in $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ post-chemical delithiation. Slight difference in the $\langle \text{Fe-O} \rangle$ bond lengths determined by EXAFS and NPD is noticed. This disparity may be explained by the presence of Fe/Al disorder within the $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ structure. It is notable that while NPD identifies the average Fe-O/Al-O bond length changes, EXAFS specifically detects alterations in pure Fe-O bond lengths.

5.3.4. O K- edge X-ray absorption spectroscopy

O K-edge XAS data were collected from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ in fluorescence yield (FY) mode. The normalized data are presented below.

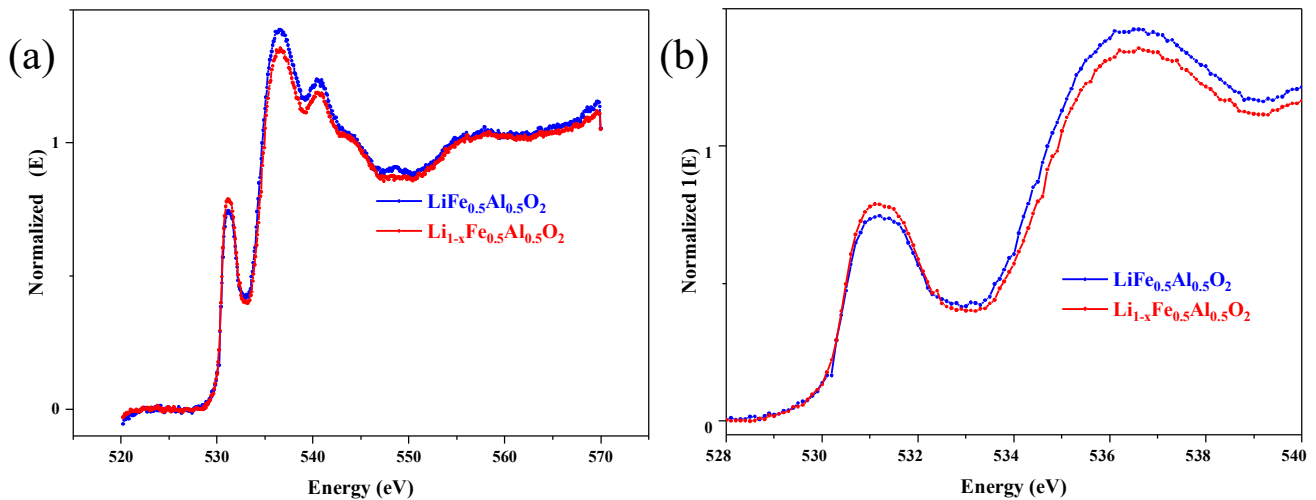


Figure 5. 7. Plot of O K-edge XAS data collected from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ in fluorescence yield mode (a,b), Normalization: (a), enlarged comparison (b)

As shown in Figure 5.7, the O K-edge XAS data collected from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (pristine) and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (oxidised) show a sharp feature at 531 eV which is assigned to the excitation of Oxygen 1s electron to Fe(3d)-O(2p) hybridised band⁸³. At energies higher than 534 eV the spectra exhibit broad features which are assigned to the excitation of Oxygen 1s electron to Fe(4s,4p)-O(2p) hybridised band⁸³.

Comparison of XAS data from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ in FY mode [(a,b) Figure 5.7] show no shift in K-edge energy (for the sharp feature at 531 eV) however, a small increase in intensity can be noticed. For the broad feature in the O-K edge spectra [(b) in Figure 5.8] a shift towards higher energy is noticed for the oxidised material in comparison to the pristine $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ sample.

The intensity enhancement at an energy of 531 eV and movement of the broad feature to higher energies in O K-edge XAS data is consistent with oxygen oxidation in $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ according to recent reports with the oxidation of other cathode materials^{89,156–159}.

5.3.5. RIXS data

Resonant inelastic X-ray scattering (RIXS) data were collected from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ to further investigate the oxidised oxygen species generated after chemical delithiation. The RIXS energy map was calculated with multiple RIXS line scans with excitation energies ranging from 529 to 535 eV with a step size of 0.25 eV. In addition, RIXS line scan data were collected at an excitation energy of 531.75 eV.

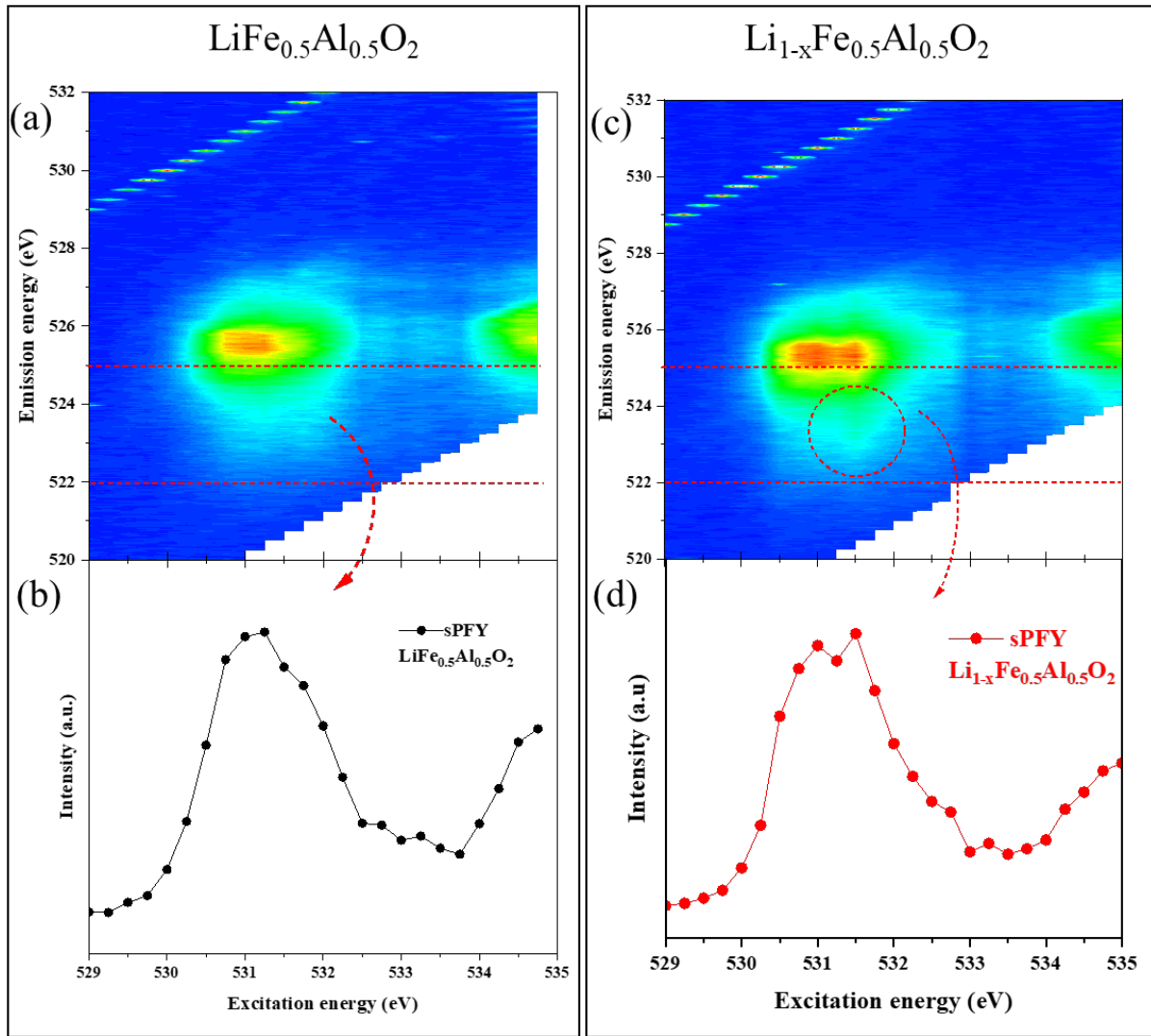


Figure 5. 8. Plot of mRIXS data from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (a) and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (c) with vertical axis as Emission energy and horizontal axis as Excitation energy; Plot of corresponding integrated partial fluorescence yield (sPFY) data in the emission range of 522-525 eV vs excitation energy (b and d). Red circle in the mRIXS plot of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (c) shows enhanced intensity corresponding to the excitons of $\pi_u \rightarrow \sigma_u^*$ during the emission process⁹⁴.

Figures 5.8 show Resonant Inelastic X-ray Scattering (RIXS) energy maps of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$. In both $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$, two main features are observed, one within the excitation energy range of 530.5-532 eV, and the other at excitation energy range exceeding 534 eV. The former is linked to the excitation of oxygen 1s electron to the $\text{Fe}(3d)\text{-O}(2p)$ hybridized band⁹³, while the latter corresponds to the excitation of oxygen 1s electron to the $\text{Fe}(4s,4p)\text{-O}(2p)$ hybridized band⁹³.

From the mRIXS plot with the emission energy on the vertical axis and the excitation energy on the horizontal axis [Figures 5.8 (a, and c)], the intensities observed were integrated within the emission energy range of 522-525 eV. This integration resulted in the partial fluorescence yield (sPFY) data, illustrated in Figures 5.8 (b) and (d). A comparative analysis of the integrated fluorescence spectra between $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ reveals a clear distinction with an increased intensity for $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ at an excitation energy of 531.5 eV. The heightened intensity at the excitation energy of 531.5 eV is found to be linked with the emission energy of 523.75-524 eV, which is attributed to an intraband excitons of $\pi_u \rightarrow \sigma_u^*$ during the emission process⁹⁴ (Section 1.9).

This increased intensity at emission energies of 524 eV is also evident in the RIXS line at an excitation energy of 531.75 eV, depicted in Figure 5.9. These findings strongly suggest the involvement of oxygen redox processes during the chemical delithiation of the material.

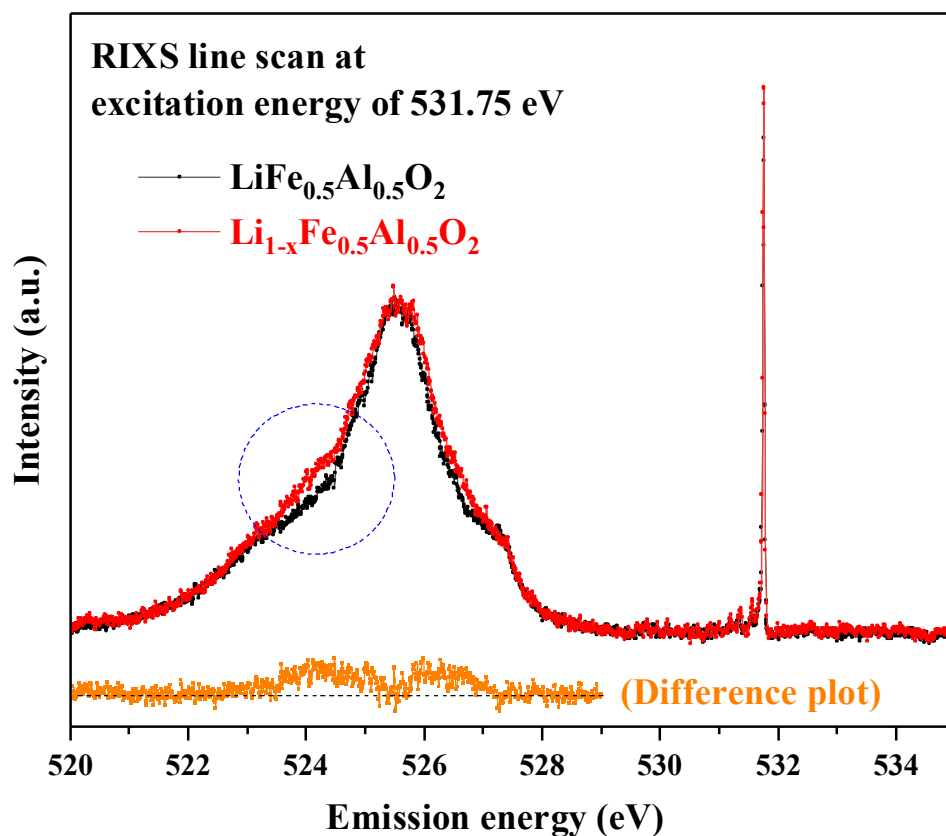


Figure 5. 9. RIXS line scan data from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (black line) and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (red line), Highlighted area indicates the enhanced intensities at emission energy ~ 524 eV which is a characteristic of oxygen oxidation

5.3.6. Electrochemical data

To investigate the electrochemical performance, cyclic voltammetry data from three charge-discharge cycles and galvanostatic capacity measurements up to 100 charge-discharge cycles were carried out. Following the approach described by Armstrong et al⁵⁵, who achieved a notable enhancement in capacity of T- LiFeO_2 by ball-milling $\beta\text{-NaFeO}_2$, we also have conducted electrochemical measurements on $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ prepared from ball-milled $\text{NaFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ to enable a similar outcome.

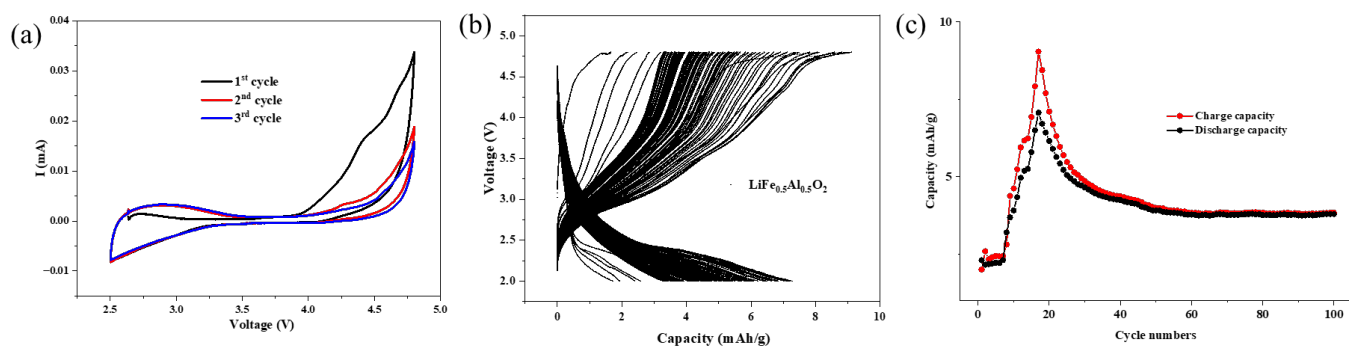


Figure 5.10. Plot of electrochemical cycling data of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$; CV in the voltage range of 2.5-4.8 V (a), Charge-discharge capacity plots in the voltage range of 2-4.8V (b,c)

As shown in Figure 5.10, the cyclic voltammogram (CV) from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ sample, exhibits similar feature to other reported metastable LiFeO_2 polymorphs^{160,56} showing a broad oxidation feature at voltage higher than 4 V and with corresponding reduction peak at low voltage being absent¹⁶¹(Section 1.7). The charge-discharge profile with $\sim \text{C}/15$ rate showed poor capacity ($< 10\text{mAh/g}$) and the number of lithium being cycled was found to be less than 0.1 Li^+ per formula unit in each cycle indicating kinetic limitations of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$.

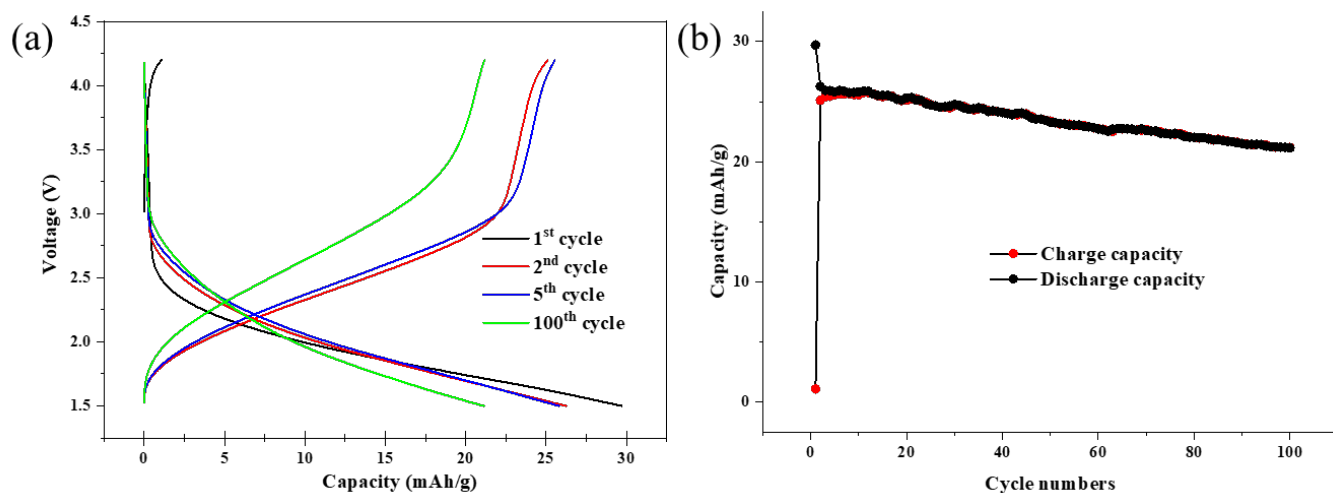


Figure 5.11. Electrochemical data of ball milled $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$; Charge-discharge capacity plots 1.5-4.25V (a,b)

To improve the electrochemical performance, direct ball milling was performed on $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ which led to the formation of 2-5 weight % of disorder rock salt type LiFeO_2 material as a secondary phase. The electrochemical measurements were conducted with $\sim\text{C}/15$ rate which shows a small reversible capacity ($\sim 30\text{mAh/g}$) that retains well up to 100 cycles as shown in Figure 5.11. However, the electrochemical feature observed in the voltage range of 1.5-3.0 V is likely to be originated from the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox which causes structural transformation from $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ to disorder rock salt type LiFeO_2 type phases as described in Section 4.3.3.

5.3.7. Discussion of the oxidised $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ samples

Based on SXRD analysis of the chemically oxidative lithium deintercalated $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ samples, it was found that samples with $0.75 \geq x \geq 0.25$, undergo no structural change and are only associated with slight change in the unit cell parameters. Unlike T- LiFeO_2 , for $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ samples the presence of 25% or more aluminium in the structure stops the iron migration inhibiting the LiFe_5O_8 spinel phase formation.

The bond-valence sum parameter extracted from the oxidised material after the structural refinements against the SXRD and NPD data shows enhancement in the Fe BVS value (Figure 5.6) and a decrease in $\langle\text{Fe-O}\rangle$ bond length which is consistent with the iron site getting slightly oxidised due to chemical delithiation. The treatment of oxidised $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ with LiI indicates partial re-insertion of lithium ($\sim 15\%$ lithium) as revealed by ICP-MS and titrations values (Appendix-I Tables 5a.8, 5a.9). Fe-K edge XANES and O-K edge XAS data reveal insignificant changes in both Fe-O edges suggesting the strong hybridisation present between Fe^{3+} and oxygen orbitals as reported for other LiFeO_2 polymorphs^{69,162}. This suggests a combination of Fe and oxygen redox participation, which is chemically reversible provided enough time.

Electrochemical data collected for $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ shows capacity of only ~ 12 mAh/g which would correspond to less than 0.1 Li^+ being cycled in the measured voltage window indicating that aluminium doping is accompanied with poor electrical conductivity.

Despite the presence of a minor charge process for $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ at high voltage during electrochemical cycling (Figure 5.11), the corresponding reverse discharge process is entirely absent. The absence of the reverse reduction can be attributed to the slow and non-complementary nature of the oxygen redox reaction, involving multiple-electron transfer processes $[\text{O}_2^{n-} + (4-n)e^- \leftrightarrow 2\text{O}^{2-}]$. Electrochemically reproducing this reverse process is challenging due to cycling rate limitations. Furthermore, the highest measured voltage window (4.8 V) during electrochemical cycling is lower than the redox potential of $\text{NO}_2^+/\text{NO}_2$ (5.1 V). This disparity could explain the varying degree of delithiation observed in electrochemical cycling compared to chemical oxidation, resulting in a smaller capacity in the galvanostatic measurement (Figure 5.11).

5.4. Results and discussion for Ga doped T-LiFeO₂ samples

5.4.1 Structural characterization (SXR D data)

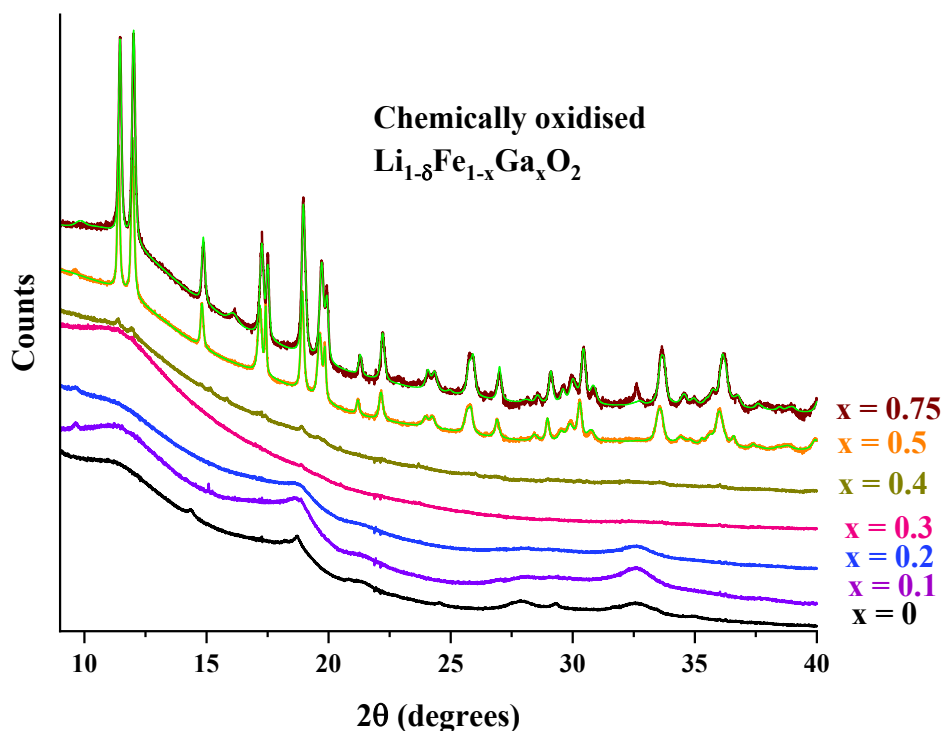


Figure 5. 12. Plot of observed and calculated intensities from $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ phases obtained during structural refinement against SXR D data

SXR D data were collected from delithiated $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ samples henceforth referred to as $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$. As shown in Figure 5.12, SXR D data for samples with $x \leq 0.4$ reveal absence of any sharp peak along with a complete loss of long-range ordering similar to delithiated T-LiFeO₂ (Section 5.3.1). SXR D patterns collected for samples with $x \geq 0.5$ show that the crystallinity is maintained after chemical delithiation and the data can be indexed on the basis of orthorhombic ($Pna2_1$) unit cells. Crystallographic models based on the disordered Fe/Ga structure ($Pna2_1$) was refined against the SXR D data collected from $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ which showed slight decrease in the unit cell parameters in comparison to corresponding

pristine $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ phases as shown in Figure 5.13. The structural refinement plot of $\text{Li}_{1-x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data is given in Appendix-I Figure and Table 5a.5.

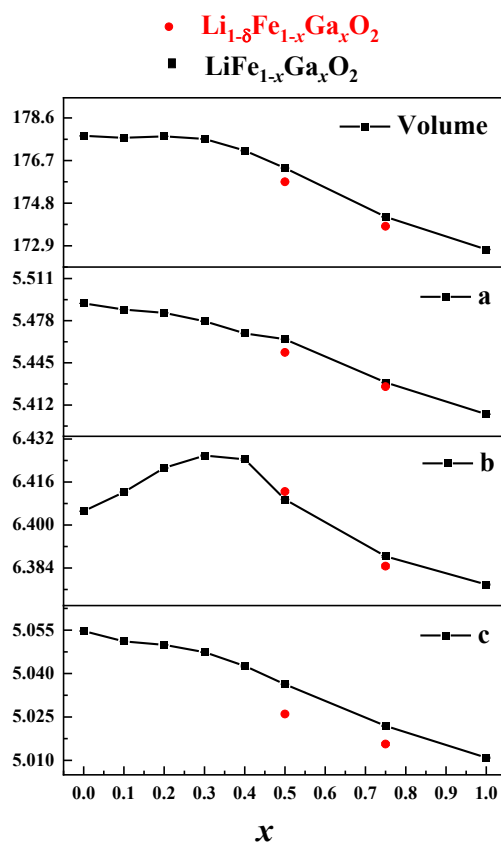


Figure 5. 13. Plot of lattice parameters of $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ (red circles) and $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ (black squares) as a function of composition determined from the structural refinement against SXRD data; error bars are smaller than the plotted points

5.4.2. Neutron diffraction data

To assist with structural refinement neutron powder diffraction data was collected from $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$. Crystallographic model based on the ordered Fe/Ga structure (space-group: Pn , $\text{Li}_2\text{ZnGeO}_4$ structure type¹⁵³) was refined against the data which yielded a rapid convergence as shown in Figure 5.14 with crystallographic parameter given in Table 5.12.

Due to the strong correlation present between the occupancy parameter (Fraction) and the isotropic thermal parameter (B_{eq}) of the lithium sites in $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, attempting to relax both parameters simultaneously resulted in physically implausible values. Therefore, the

structural refinement procedure involved fixing the occupancy parameters of lithium sites in accordance with the lithium content determined from ICP-MS characterization as $\text{Li}_{0.57}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ (Appendix-I, Table 5a.10). Subsequently, only the isotropic thermal parameters were refined, yielding credible and acceptable values, shown in Table 5.5.

Another outcome of this refinement was the observation of antsite mixing in both Fe and Ga-independent sites. Specifically, the two $2a$ sites showed occupancy parameters as Ga1/Fe1: 0.91(3)/0.09(3) and Fe2/Ga2: 0.95(4)/0.05(4). As shown in Figure 5.14, this antsite mixing led to a reduced intensity in the (010) reflection which was found to be associated with Fe/Ga ordering (Section 3.3.2.2.).

However, despite these structural changes, the calculated $\langle\text{Fe-O}\rangle$ and Fe-BVS values from the refined model exhibited almost no change compared to the pristine $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, as indicated in Table 5.13. This implies no significant oxidation of the iron site in $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ due to the chemical delithiation process.

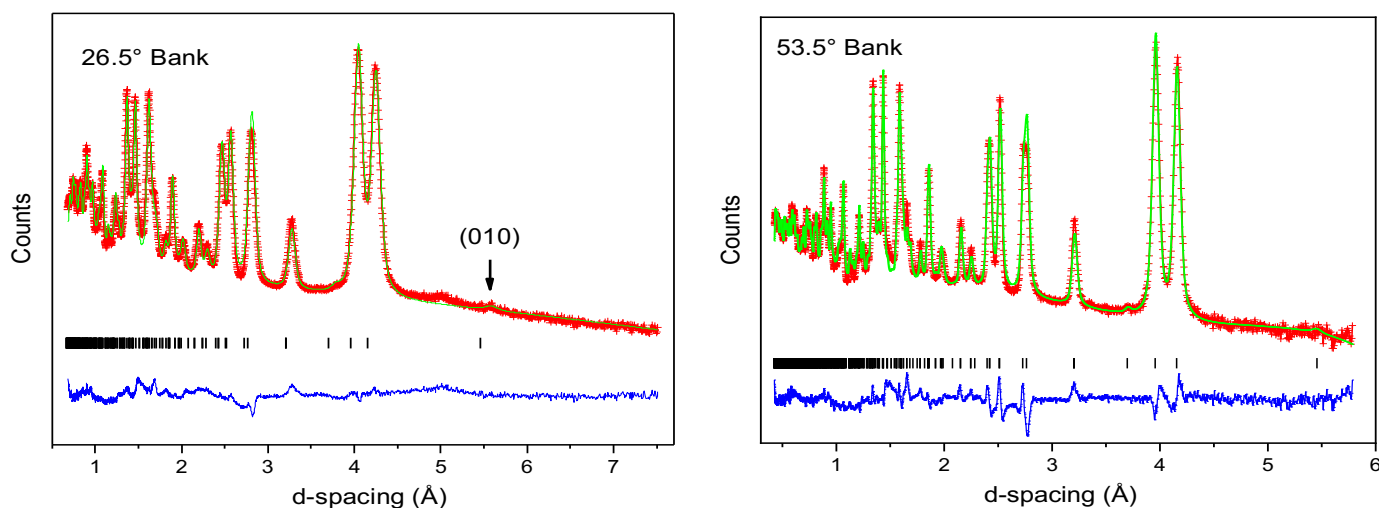


Figure 5. 14. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ against NPD data. bank 26.5°(left), bank 53.5° (right)

Table 5.5. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ ($\text{Li}_{1.2}\text{FeGaO}_4$) sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	$2a$	0.5135(61)	0.0891(43)	0.9427(57)	0.6	0.6(1)
Li2	$2a$	0.6905(43)	0.3971(53)	0.4724(75)	0.6	0.8(1)
Ga1/Fe1	$2a$	0.9964(6)	0.1702(9)	0.0089(11)	0.91(3)/0.09(3)	0.08(1)
Fe2/Ga2	$2a$	0.2483(5)	0.3226(7)	0.5040(9)	0.95(4)/0.05(4)	0.08(1)
O1	$2a$	0.5029(9)	0.1602(10)	0.4210(9)	1	0.15(2)
O2	$2a$	0.2808(8)	0.6819(10)	0.3881(8)	1	0.15(2)
O3	$2a$	0.0059(11)	0.1807(8)	0.3717(10)	1	0.15(2)
O4	$2a$	0.2112(7)	0.3412(11)	0.8833(11)	1	0.15(2)
$\text{Li}_{1.2}\text{FeGaO}_4$ – space group Pn (#7) $a = 6.4083(4) \text{ \AA}$, $b = 5.4555(3) \text{ \AA}$, $c = 5.0272(2) \text{ \AA}$, $\beta = 89.999^\circ(4)$ volume = 175.754 (17) $\text{\AA}^3$ Formula weight= 197.894 g mol $^{-1}$, $Z = 2$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 2.15 \%$, $wR_p = 2.96 \%$						

Table 5.6. Bond lengths and BVS parameter table for $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ ($\text{Li}_{1.2}\text{FeGaO}_4$)

$\langle \text{Fe2-O} \rangle (\text{\AA})$	Average $\langle \text{Fe-O} \rangle (\text{\AA})$	Fe2-BVS	$\langle \text{Ga1-O} \rangle (\text{\AA})$	Average $\langle \text{Ga-O} \rangle (\text{\AA})$	Ga2-BVS
1.859(8)	1.893(8)	2.800	1.778(8)	1.813(8)	3.1910
1.900(7)			1.794(7)		
1.902(8)			1.806(8)		
1.924(8)			1.856(8)		

Table 5.7. Bond lengths and BVS parameter table of pristine $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ and chemically oxidised $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ estimated against SXRD data

x	$\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$		$\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$	
	$\langle \text{Fe-O} \rangle (\text{\AA})$	Fe-BVS	$\langle \text{Fe-O} \rangle (\text{\AA})$	Fe-BVS
0.5	1.897(6)	2.761	1.893(7)	2.800
0.75	1.871(2)	3.069	1.871(3)	3.092

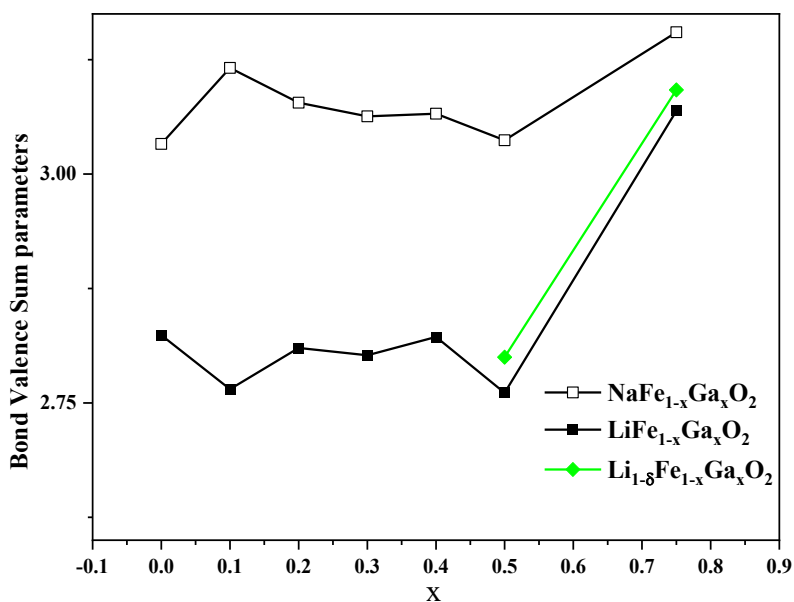


Figure 5. 15. Fe-BVS plot as function of composition for $\text{NaFe}_{1-x}\text{Ga}_x\text{O}_2$, $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$, and $\text{Li}_{1-\delta}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ determined from structural refinement against SXR and NPD data

5.4.3 X-ray absorption spectroscopy (XAS) data

X-ray absorption spectroscopy (XAS) data were collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, alongside Fe_2O_3 and SrFeO_3 . The collected XAS data was processed separately as X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data. XANES data was specifically examined to ascertain the iron oxidation state change in $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ following chemical delithiation.

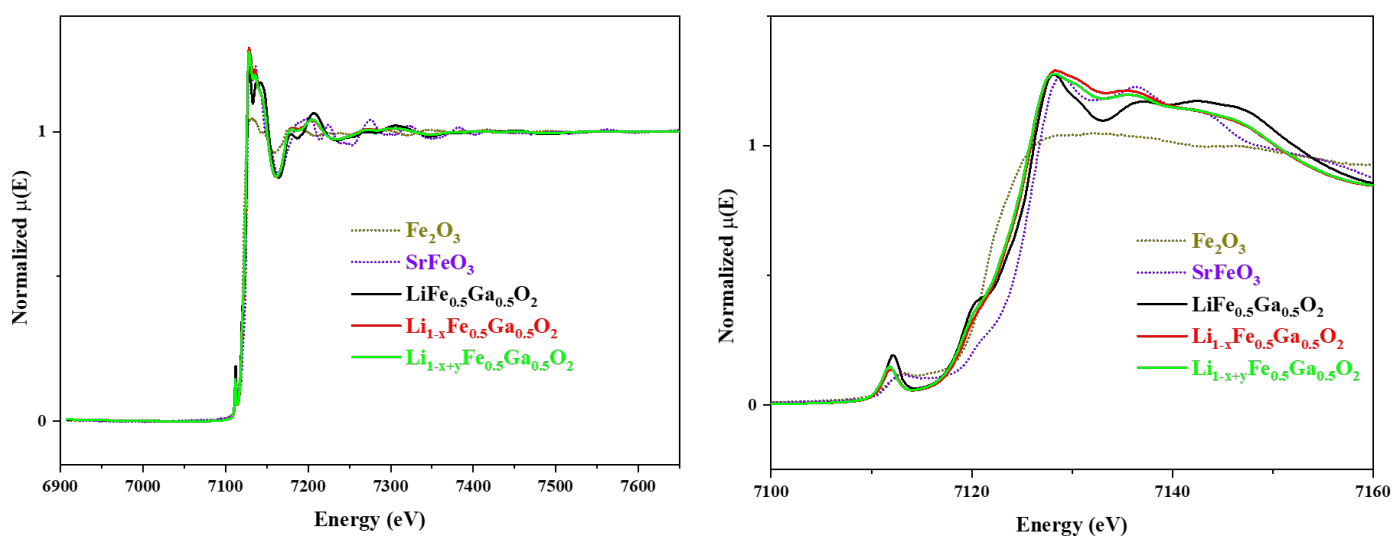


Figure 5. 16. XANES data of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ with references (dotted lines); normalization(left), Fe K-edge comparison(right).

As shown in Figure 5.16, Fe K-edge XANES data of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ exhibit a distinct pre-edge feature followed by a sharp K-edge feature. The pre-edge feature is attributed to the characteristic of the tetrahedral Fe-O coordination environment in $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ structure. No significant shift of the Fe-K-edge was observed for $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ indicating minimal oxidation of Fe^{3+} to Fe^{3+x+} due to chemical delithiation.

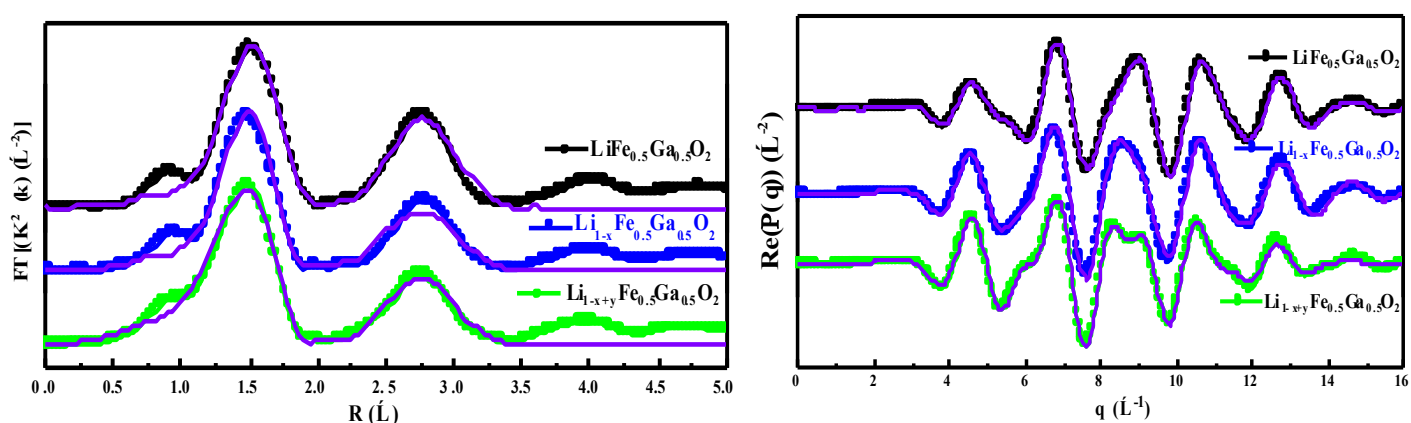


Figure 5. 17. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and oxidised sample system (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 5.8. Refined EXAFS parameter table for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ system

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD/SXRD (Å)
$\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	Fe-O	4	1.88(4)	3.7(4)	0.6	2.824	1.897(6)
	Fe-Fe	2	3.26(1)	6.9(3)			
	Fe-Ga	2	3.13(1)	5.2(1)			
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ ($x=0.43$)	Fe-O	4	1.87(3)	6.2(2)	1.4	2.823	1.893(7)
	Fe-Fe	2	2.99(5)	20.2(3)			
	Fe-Ga	2	3.11(2)	8.8(4)			
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ + LiI	Fe-O	4	1.87(4)	5.7(3)	1.16	2.841	1.908(4)
	Fe-Fe	2	3.01(4)	23.7			
	Fe-Ga	2	3.12(2)	8.6			

The XAS data collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, at energies higher than the absorption edge, were processed as EXAFS data. The crystallographic model obtained after the structural refinement against NPD data was refined to fit the data. During the fitting process, the observed oscillations in the first and second shells of the absorber atom were converged with the calculated oscillations to achieve a good fit as shown in Figure 5.17.

As shown in Figure 5.17, a good fit is achieved with $\langle\text{Fe-O}\rangle$ bond lengths values of $\sim 1.88 \text{ \AA}$ in all three samples ($\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, and $\text{Li}_{1-x+y}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$). The similarity of $\langle\text{Fe-O}\rangle$ bonds indicate minimal change in $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ due to chemical delithiation which is in good agreement with the NPD analysis. Although a close inspection of the data in q -space reveals that some distinct feature formed in $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ sample during the chemical oxidation are not reversible (Figure 5.17) after the NO_2BF_4 treatment.

5.4.4. O-K edge X-ray absorption spectroscopy (XAS)

Similar to the oxidised $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ sample (Section 5.3.7), oxygen K-edge X-ray absorption spectroscopy (XAS) data was collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$. The data obtained in fluorescence yield (FY) mode is presented below in Figure 5.18.

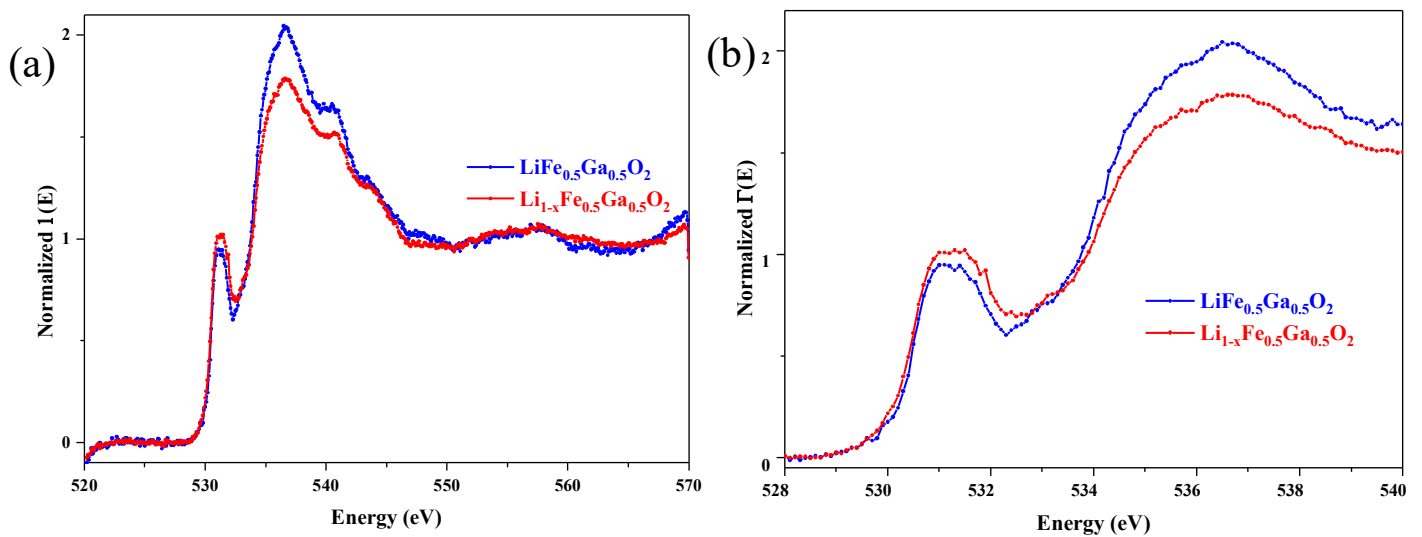


Figure 5. 18. Plot of O-K edge XAS from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ in Fluorescence mode data. Normalization (a), enlarged comparison (b)

As shown in Figure 5.18, both the pristine and oxidised material exhibit a sharp feature ~ 531 eV [due to $O\ 1s \rightarrow TM(3d)-O(2p)$]⁸³ followed by several broad features at energy higher than 534 eV [due to $O\ 1s \rightarrow TM(4s,4p)-O(2p)$]⁸³. A comparison of the data obtained between the pristine and oxidised material shows small increase in intensity at ~ 531 eV and movement of the broad feature to higher energy for the oxidised material. Both these observations are consistent with oxygen oxidation in $LiFe_{0.5}Ga_{0.5}O_2$ according to recent reports of charged cathode materials^{89,90,93,95,163,164}.

5.4.5. RIXS data

To further investigate the participation of oxygen redox, RIXS line scan data were collected from $LiFe_{0.5}Ga_{0.5}O_2$ and $Li_{1-x}Fe_{0.5}Ga_{0.5}O_2$ at an excitation energy of 531.75 eV, from 10 different points of the sample to avoid any beam damage. The final data was averaged from the 10 scans which are presented below.

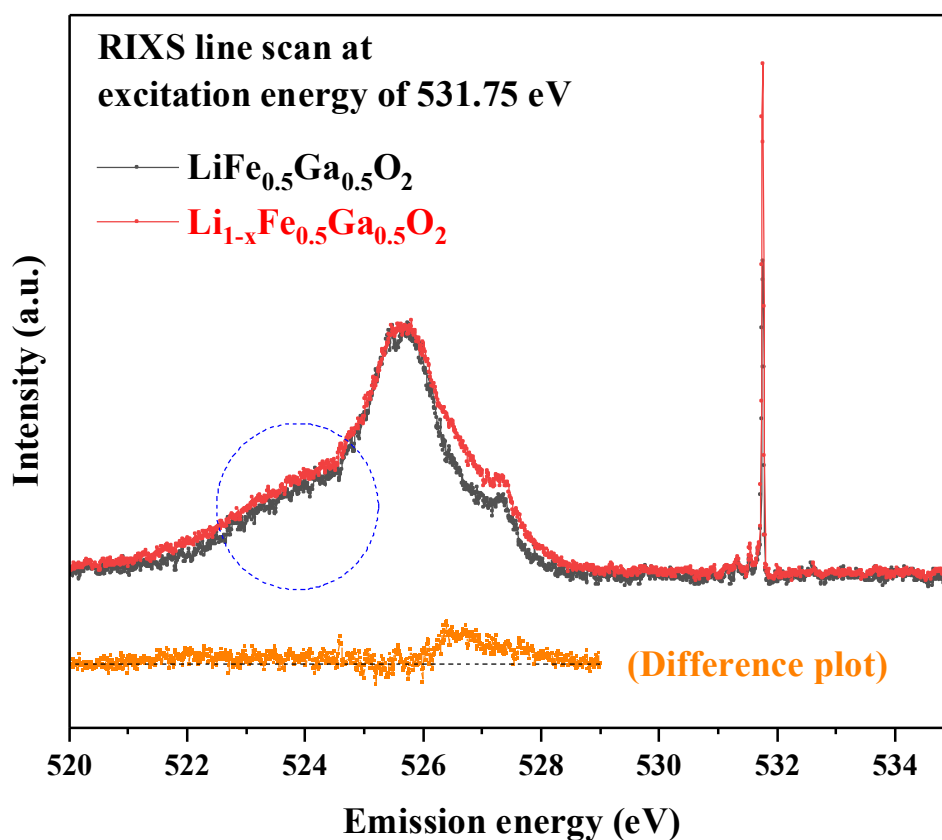


Figure 5. 19. RIXS line scan data from $LiFe_{0.5}Ga_{0.5}O_2$ (black line) and $Li_{1-x}Fe_{0.5}Ga_{0.5}O_2$ (red line)

Similar to the case of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (Section 5.3.8), RIXS line scan data from $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ show modest enhanced intensities at the emission energy range of 523-524 eV (Figure 5.19). The enhancement feature can be assigned to the intraband excitons of $\pi_u \rightarrow \sigma_u^*$ during the emission process⁹⁴ (Section 1.9) which is a hallmark for active oxygen redox. This observation is consistent with the participation of oxygen redox during the delithiation of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$.

5.4.6. Electrochemical data

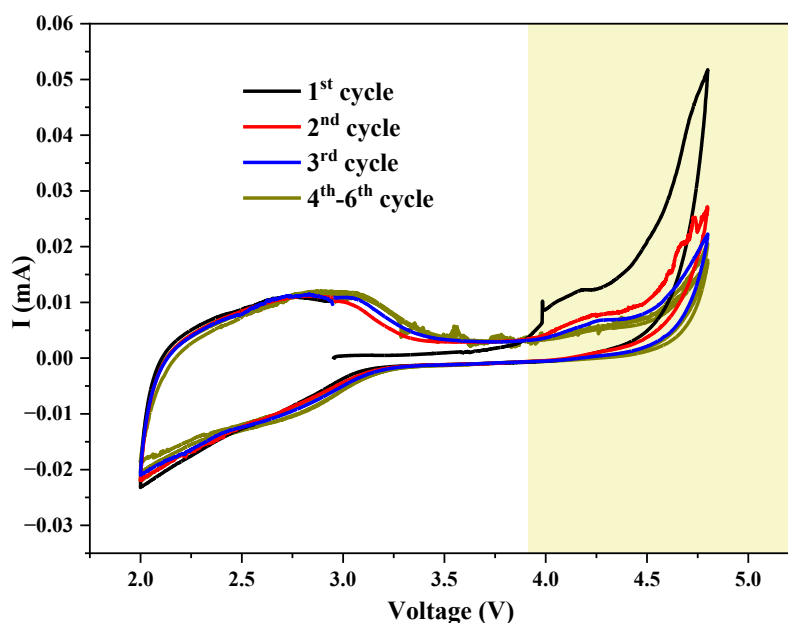


Figure 5. 20. Electrochemical data of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$; Cyclic voltammogram (left), Charge-discharge capacity plots (2.75- 4.8 V); Shaded region indicates irreversible oxidation

Cyclic voltammogram (CV) profile data was collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ in the voltage range of 2-4.8V up to six cycles, is shown in Figure 5.20. The electrochemical features observed for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ is found to be similar in nature to the metastable LiFeO_2 compound¹⁶⁰ (Section 1.7), and can be separated into two processes: (1) At lower voltage (2-3.5 V), a broad reversible feature is observed which can be assigned to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox. (2) At high voltage region ($> 4\text{V}$) an oxidation feature is observed that diminishes over the subsequent cycles. The corresponding reduction peak is found to be totally absent.

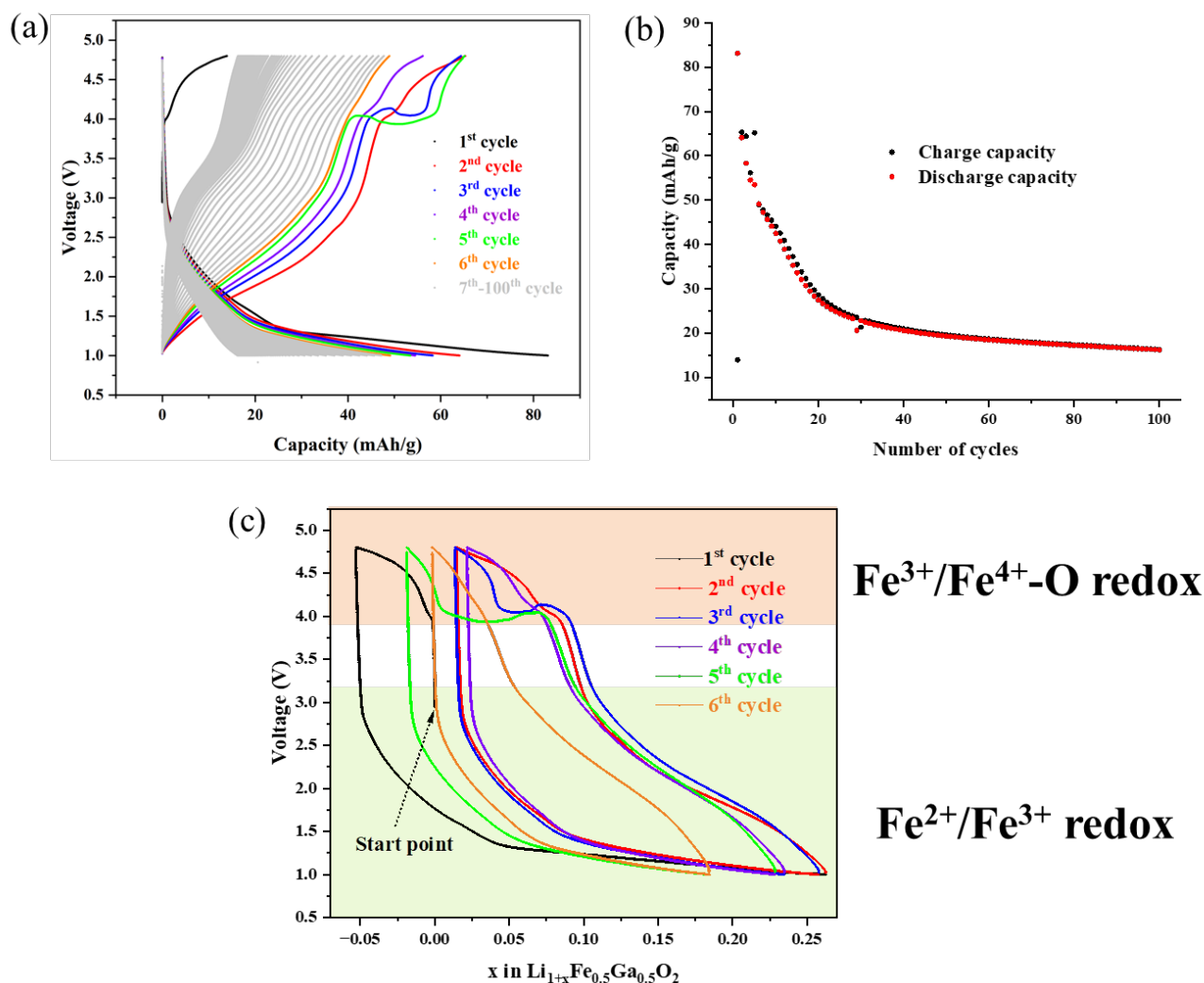


Figure 5. 21. Charge-discharge capacity profile of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ sample; (a) Voltage vs capacity plot, (b) Capacity vs number of cycles, (c) voltage vs number of lithium being inserted (x), green region indicates $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox in the voltage range of 1-3.25 V, orange region indicates combined $\text{Fe}^{3+}/\text{Fe}^{4+}/\text{O}$ redox in the voltage range above 4 V

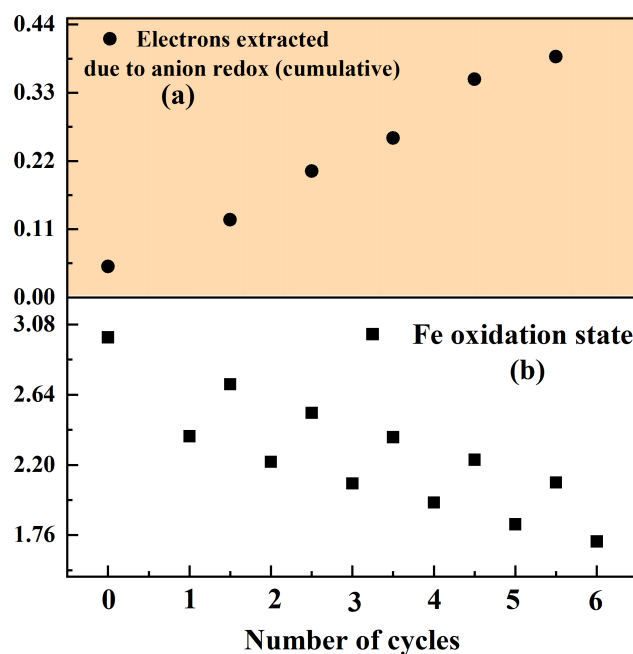


Figure 5. 22. Plot of (a) number of cumulative electrons extracted in the voltage range of 3.8-4.8 V due to anion redox (c) Change of iron oxidation state against the number of cycles.

Table 5.9. Table of lithium extracted, inserted with the corresponding $\text{Li}_x\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ composition and oxidation state of iron determined from the plot of voltage vs number of lithium being cycled (Figure 5.21, c)

Cycles	step	Lithium inserted	Lithium extracted	Composition	Oxidation state of iron	Oxygen redox
0				$\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	3	
1	charge-B		0.05	$\text{Li}_{0.95}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	3	Y
1	discharge	0.31		$\text{Li}_{1.26}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.38	
2	charge-A		0.163	$\text{Li}_{1.097}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.706	
2	charge-B		0.075	$\text{Li}_{1.022}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$		Y
2	discharge	0.243		$\text{Li}_{1.265}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.2	
3	charge-A		0.153	$\text{Li}_{1.112}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.526	
3	charge-B		0.0788	$\text{Li}_{1.033}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$		Y
3	discharge	0.221		$\text{Li}_{1.254}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.084	
4	charge-A		0.145	$\text{Li}_{1.109}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.374	
4	charge-B		0.053	$\text{Li}_{1.056}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$		Y
4	discharge	0.205		$\text{Li}_{1.261}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	1.964	
5	charge-A		0.134	$\text{Li}_{1.127}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.232	
5	charge-B		0.095	$\text{Li}_{1.032}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$		Y
5	discharge	0.202		$\text{Li}_{1.234}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	1.828	
6	charge-A		0.131	$\text{Li}_{1.103}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	2.09	
6	charge-B		0.036	$\text{Li}_{1.067}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$		Y
6	discharge	0.185		$\text{Li}_{1.252}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	1.72	

Charge-discharge capacity profile data collected from $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ in the voltage range of 1 V-4.8 V is shown in Figure 5.21. In the first discharge cycle a capacity of 83 mAh/g is observed which is equivalent to insertion of 0.31 lithium ions. However, this capacity sharply declined to 20 mAh/g after the initial cycles (Figure 5.21, b).

The distinct features observed within each cycle of the charge-discharge profile of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ (Figure 5.21) can be classified into three separate processes: (1) Discharge process [3.25-1 V], (2) Charge-A process [1-3.25 V], and (3) Charge-B process [3.25-4.8 V]. The amount of lithium being cycled, iron oxidation state change and the corresponding $\text{Li}_x\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ composition as a response of the electrochemical cycling for first six cycles is given in Table 5.9.

(1) Discharge Process: The discharge process in the voltage region of 1-3.25 V exhibits two steps. Initially, between 3.25-1.25 V, a minor amount of lithium insertion ($0.1 \text{ Li}^+/\text{f.u.}$) is witnessed. Subsequently, at voltages below 1.25 V, a sharp discharge process occurs, leading to a total lithium insertion of approximately $0.3 \text{ Li}^+/\text{f.u.}$ In the subsequent cycles, a reduction in the quantity of lithium inserted is observed.

(2) Charge-A Process: A single broad feature is observed in the voltage range of 1-3.25 V during the charge/oxidation. In each cycle, the quantity of lithium extracted during the charge process is found to be less than the lithium inserted during the discharge process. For instance, in Cycle-1-discharge step, 0.31 Li^+ is inserted but in Cycle 2-charge step, only 0.163 Li^+ ions are extracted (Table 5.17), which corresponds to approximately half of the lithium ions being not-recovered

(3) Charge-B Process: In the voltage range of 3.25-4.8 V [Figure 5.21 (c)] displays an oxidation feature (up to the first five cycles) associated with extractions of $0.05\text{-}0.09 \text{ Li}^+$ in each cycle, delivering 12-25 mAh/g of capacities. Notably, the corresponding reduction feature

is found entirely absent. Figure 5.22 (a) demonstrates the cumulative lithium/electrons extracted during the Charge-B process, revealing a gradual approach to a total of $\sim 0.5 \text{ Li}^+$ extraction which is consistent with the analysis of ICP-MS (Appendix-I Table 5a.10) and NPD data (Section 5.4.2) described earlier.

At the end of the charge-A process (1-3.25 V), the oxidation state of iron is consistently less than three (e.g., +2.7 in the first cycle, +2.5 in the second cycle, as extracted from Table 5.9). Subsequently, in the Charge-B process, an additional 0.07 Li^+ is extracted without oxidizing iron to the +3 state. Notably, this 0.07 Li^+ extraction results in the oxidation of the combined iron-oxygen band. The presence of such anion redox, even when the oxidation state of iron is less than +3, adds complexity to the electrochemical performance. At the end of the Charge-B process, the oxidation state of iron remains less than three (e.g., +2.7, +2.5, +2.3 in the first, second, and third cycles, respectively), mitigating the drive for further iron reduction. Consequently, fewer lithium ions are inserted in the subsequent cycles, leading to a decline in observed capacities.

In the 5th and 6th cycles (Table 5.9), an iron oxidation state of less than two is observed, which may appear unusual. This anomaly can be attributed to the assumption that only anion redox is operating at voltages higher than 3.25 V. However, it is plausible that a small degree of iron oxidation is occurring, providing a reasonable explanation for this anomaly.

The preservation of the iron site with an oxidation state less than three, even at a high potential range like 4.8 V, signifies the preferential stability of $\text{Fe}^{2.x+}$ in the structure, displaying reluctance to undergo oxidation easily. This suggests that once lithium insertion occurs, the structure of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ attains a robust stability plateau, resisting oxidation and maintaining its stability.

5.4.7. Discussion of the oxidised $\text{LiFe}_{1-x}\text{Ga}_x\text{O}_2$ samples

From the SXRD analysis, for $\text{Li}_{1-x}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ samples, it is clear that for $x \geq 0.5$, the structural integrity was maintained, and the Fe migration from the tetrahedral site to the octahedral site was stopped. The change of lattice parameter, and deficiency of lithium in the tetrahedral site are confirmed with ICP-MS and NPD characterization. ICP-MS data further confirms that, after chemical delithiation is partially reversible in nature.

The Fe-XANES and EXAFS data show no significant change in the iron oxidation state and the local environment of iron during the lithium extraction and re-insertion. O-XAS data and RIXS show a clear indication of oxidized oxygen when chemically delithiated. Although the exact nature of oxidised oxygen species generated was not identified.

The capacity loss observed in the electrochemical cycling of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ can be ascribed to the anion redox mechanism prevalent in the system. This mechanism exhibits a higher predisposition towards oxidation compared to $\text{Fe}^{2.x+}$. The stability of the $\text{Fe}^{2.x+}$ site and its resistance to oxidation can be linked to the size of the iron site in $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$.

During the synthesis of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ from $\text{NaFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ via cation exchange, it was noted that the iron-oxygen bond lengths in FeO_4 tetrahedra increased by $0.036 \text{ \AA}$, while the Fe-BVS value reduced from 3.037 to 2.761. This expansion of the iron site favours the presence of $\text{Fe}^{2.x+}$ and causes less susceptible to oxidation. This phenomenon contributes to the complex electrochemical cycling behaviour observed in $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$.

5.5. Results and discussion for both Al and Ga doped T-LiFeO₂

5.5.1. Structural characterization (SXRD data)

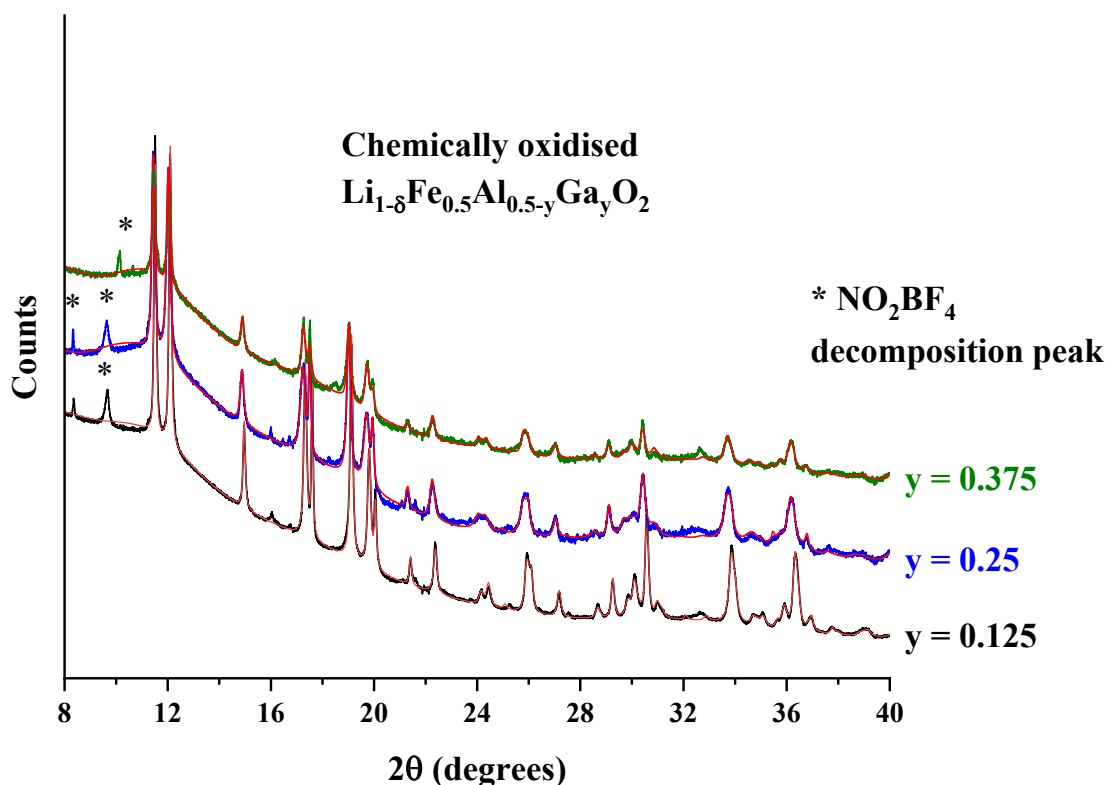


Figure 5. 23. Observed, calculated (red line) intensities from the structural refinement of $\text{Li}_{1-\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ against SXRD data

The SXRD data were collected from delithiated $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ phases with $y = 0.125, 0.25, 0.375$ are shown in Figure 5.23. Reflections associated with the NO_2BF_4 decomposition (indicated by * sign, in Figure 5.23) was observed for all three delithiated samples. Crystallographic models based on the disorder Fe/Al/Ga structure was refined against the data to yield a good fit as shown in Appendix-I Figures and Tables 5a.6-5a.7. From the crystallographic model obtained after the structural refinement, $\langle\text{Fe-O}\rangle$ bond distances and Fe-BVS were calculated. The Rietveld plot and the refinement parameters obtained from $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ are presented in Figure 5.24 and Table 5.10 respectively.

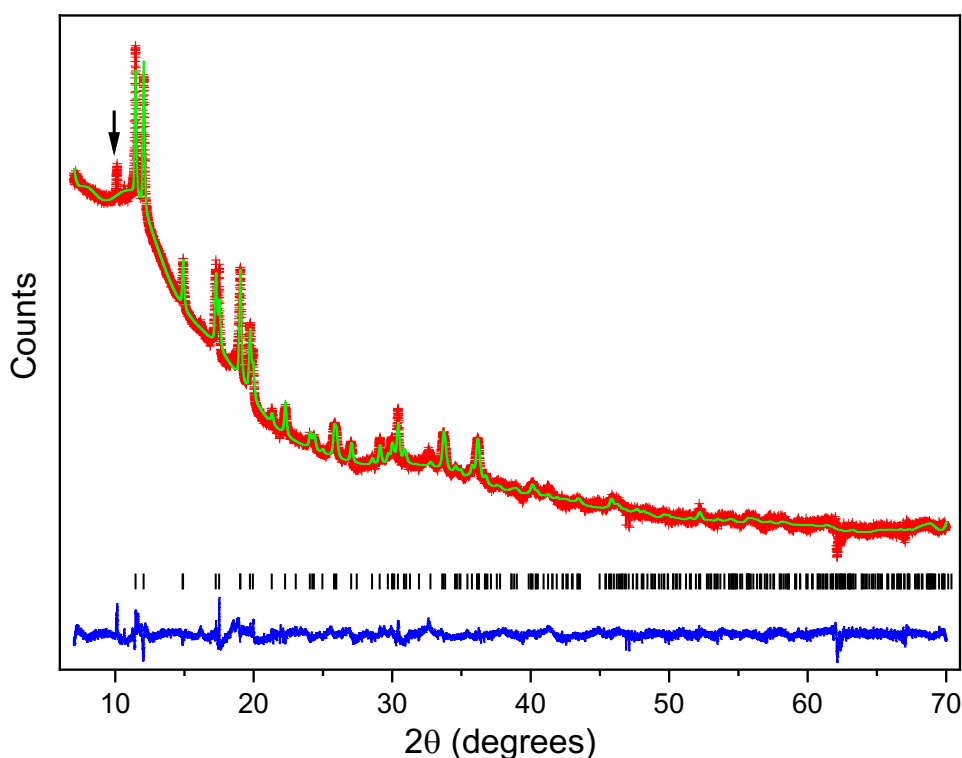


Figure 5. 24. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ against SXRD data collected at room temperature (Black arrow indicates NO_2BF_4 decomposition peak)

Table 5.10. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ sample against SXRD data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.451(2)	0.165(2)	0.502(16)	1	0.1
Fe/Al/Ga	$4a$	0.0831(5)	0.1302(4)	0	0.5/0.25/0.25	0.44(3)
O(1)	$4a$	0.0663(2)	0.0939(19)	0.3951(12)	1	0.1
O(2)	$4a$	0.4150(22)	0.0941(17)	0.8995(13)	1	0.1
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4342(3) \text{ \AA}$, $b = 6.3923(4) \text{ \AA}$, $c = 5.0028(2) \text{ \AA}$ volume = $173.802(18) \text{ \AA}^3$ Formula weight = $96.381 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.25\%$, $wR_p = 1.76\%$, $R_{\text{Bragg}} = 0.73$						

B_{eq} parameters of Li and O were fixed due to absorption issues

Table 5.11. Bond lengths and BVS parameter table of pristine $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ and chemically oxidised $\text{Li}_{1-\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ estimated against SXRD data

y	$\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$		$\text{Li}_{1-\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$	
	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS	$\langle\text{Fe-O}\rangle$ (Å)	Fe-BVS
0	1.823(6)	3.366	1.818(3)	3.414
0.125	1.848(2)	3.161	1.847(4)	3.181
0.25	1.893(3)	2.827	1.884(2)	2.926
0.375	1.884(4)	2.887	1.873(4)	2.979
0.5	1.897(3)	2.761	1.893(8)	2.800

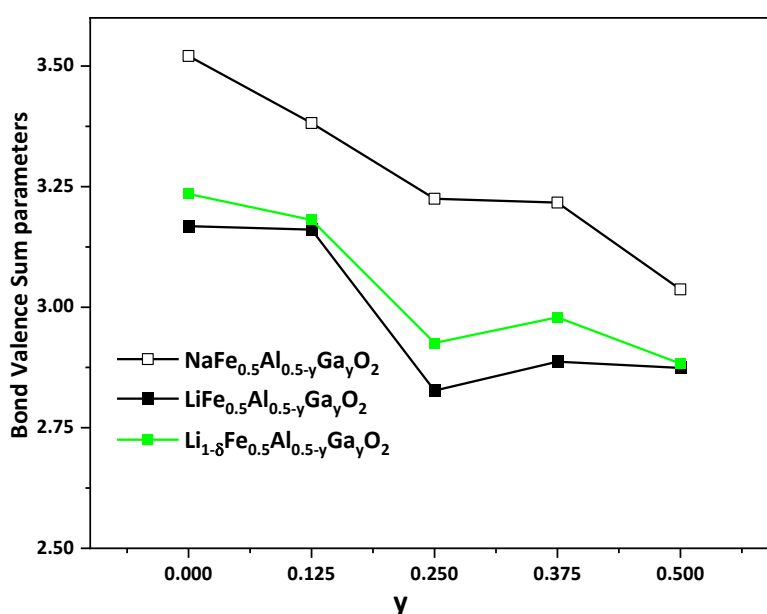


Figure 5. 25. Plot of Bond Valence Sum parameter extracted from SXRD data refinement

The $\langle\text{Fe-O}\rangle$ bond length calculated for delithiated $\text{Li}_{1-\delta}\text{Fe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ samples show a decrease in the bond length in comparison to the corresponding pristine materials (Table 5.11). The Fe-BVS parameter obtained from the crystallographic unit cell obtained after the refinement shows an increase in Fe-BVS parameter of the oxidised material in comparison to the corresponding pristine materials (Figure 5.25). Both these observations are in agreement with oxidative delithiation of iron in the structure.

5.5.2. X-ray absorption spectroscopy (XAS) data

X-ray absorption spectroscopy data were collected from $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ along with Fe_2O_3 and SrFeO_3 . The collected XAS data was processed separately as X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data. XANES data was specifically examined to ascertain the iron oxidation state change in $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ following chemical delithiation.

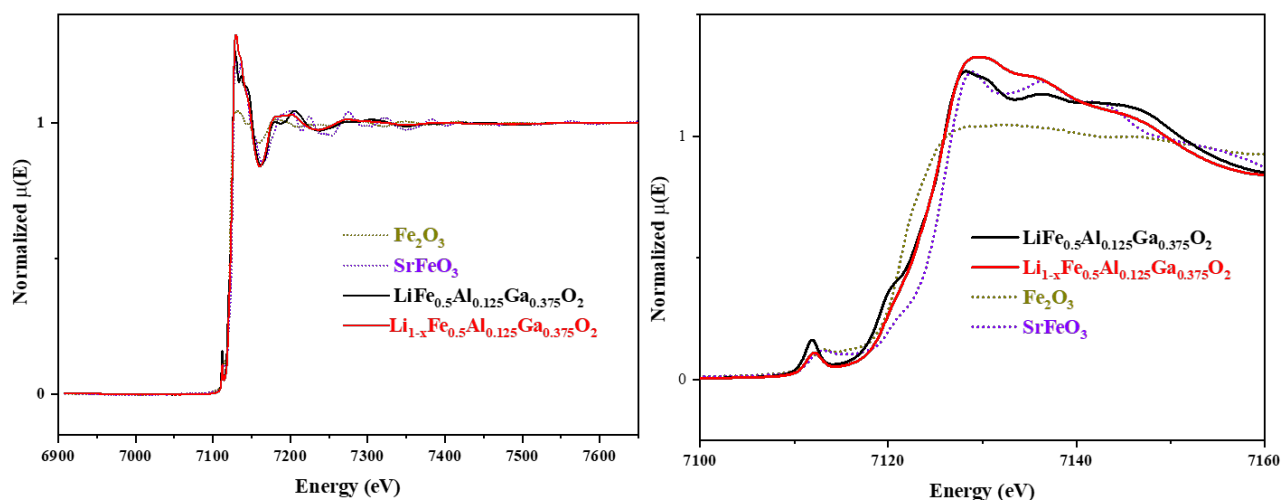


Figure 5. 26. XANES data of $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ with references (dotted lines); normalization(left), Fe K-edge comparison (right)

As shown in Figure 5.26, The XANES data of both the pristine and oxidised material exhibit a pre-edge feature at ~ 7112 eV and the K-edge matches with the Fe (III) standard K-edge spectra. Between the pristine and oxidised material, a difference of 1.5 eV energy is observed at the K-edge at energy < 7123 eV. This slight movement of the K-edge to higher energy is consistent with other samples from Al and Ga-doped T- LiFeO_2 materials indicating Fe centre being slightly oxidised to $\text{Fe}^{3.x+}$ when chemically delithiated.

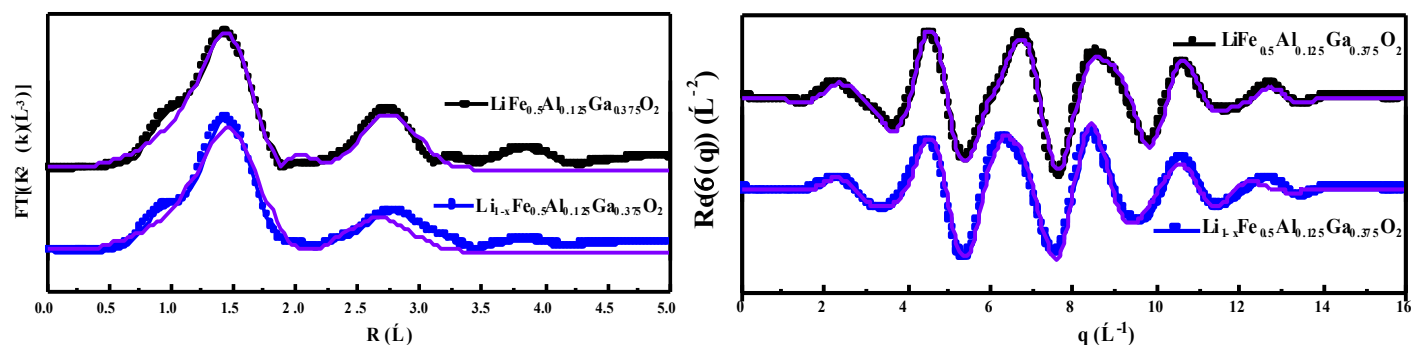


Figure 5. 27. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space

Table 5.12 Refined EXAFS parameters of $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from SXRD (Å)
$\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$	Fe-O	4	1.875(6)	4.29(1)	0.8	2.857	1.884(4)
	Fe-Fe	2	3.12(4)	8.48(3)			
	Fe-Ga	1	2.76(3)	8.48(3)			
	Fe-Al	1	3.14(7)	8.48(3)			
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$	Fe-O	4	1.88(3)	9.4(3)	6.8	2.837	1.873(3)
	Fe-Fe	2	2.95(3)	22.8(8)			
	Fe-Ga	1	2.89(1)	9.47(7)			
	Fe-Al	1	3.08(8)	22.8(8)			

The XAS data, post K-absorption edge were used for EXAFS analysis. The first and second shell was fitted with $\langle\text{Fe-O}\rangle$, $\langle\text{Fe-Ga}\rangle$ and, $\langle\text{Fe-Al}\rangle$ bond lengths (Figure 5.27). The $\langle\text{Fe-O}\rangle$ bond distances obtained from the EXAFS data fit at the Fe-tetrahedral environment for both pristine and oxidised material are found to be similar (1.875(6) Å for the pristine and 1.88(3) Å for the oxidised material). The Bond-Valence-Sum parameter calculated from the $\langle\text{Fe-O}\rangle$ obtained is in good agreement with the Bond-Valence-Sum calculated from the SXRD data analysis.

5.5.3. Discussion of the chemically oxidised $\text{LiFe}_{0.5}\text{Al}_{0.5-y}\text{Ga}_y\text{O}_2$ samples

A combination of Al and Ga doping on the T- LiFeO_2 shows a retention of the crystallinity and preservation of the Fe-Td site in the structure when chemically delithiated.

The XANES and EXAFS data obtained for $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ system (pristine and oxidised) is similar to the XANES and EXAFS data of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ system (pristine and oxidised). Thus, it would be safe to assume that, a combination of both iron and oxygen redox is in operation in $\text{LiFe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ when chemical delithiation is performed with NO_2BF_4 .

5.6. Conclusion

In this chapter, characterization results of the oxidative delithiation of aluminium and/or gallium doped T- LiFeO_2 samples are described. It is found that a minimum of 25% aluminium or 50% gallium substitution is required to stabilise the iron tetrahedral network in T- LiFeO_2 . This demonstrates the substitution of non-redox active element into the iron site is effective for stabilising iron-based cathode materials for lithium-ion batteries.

The delithiation process is found to be complicated involving both $\text{Fe}^{3+/4+}$ and oxygen redox, which is found to be only chemically reversible but electrochemically non-reversible.

Chapter 6 – Synthesis and characterization of aliovalent substituted $A\text{FeO}_2$ materials ($A = \text{Na}, \text{Li}$)

6.1. Introduction

Aliovalent substitution is a commonly employed technique in solid-state research to enhance the chemical and electrochemical properties of materials^{165–170}. In order to achieve aliovalent substitution in $A\text{FeO}_2$ materials ($A = \text{Na}^+, \text{Li}^+$), Si^{4+} was substituted for Fe^{3+} in the $A\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ materials (described in Chapter 3) to prepare a phase of composition $A_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$. Likewise, Ge^{4+} was substituted for Fe^{3+} in the $A\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ materials (described in Chapter 3) to prepare phases of composition $A_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, and $A_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. Phase diagrams representing these aliovalent substituted samples (pink dots) are shown in Figure 6.1.

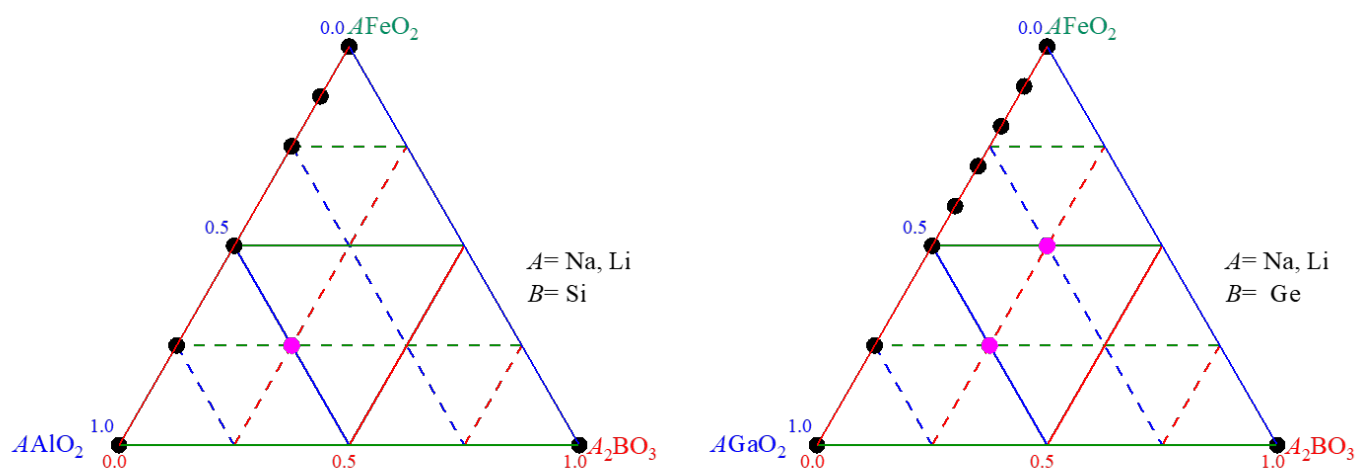


Figure 6. 1. Phase diagram of $A\text{FeO}_2$, $A\text{AlO}_2$, AGaO_2 , A_2BO_3 ($A=\text{Na}, \text{Li}$, and $B=\text{Si}, \text{Ge}$); Black dots: Al and Ga substituted $A\text{FeO}_2$ samples (discussed in chapter3-5), Pink dots: aliovalent substituted samples

The synthesis and characterization of these aliovalent substituted NaFeO_2 and LiFeO_2 samples ($A_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$) are described in this chapter.

6.2. Experimental work

6.2.1. Synthesis of aliovalent substituted NaFeO₂

Aliovalent substituted NaFeO₂ samples were synthesized by a high-temperature ceramic method (Section 2.1.1). Initially, the target compositions were selected as Na₂Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ where $M = \text{Al}^{3+}$, Ga^{3+} , $N = \text{Si}^{4+}$, Ge^{4+} and $x, y = 1$ or 0.5 . However, it was found during later analysis that the phases prepared were sodium deficient with the actual compositions being $\sim \text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ (indicating oxidation state of iron $\sim +3$). Hence, the target compositions were adjusted to $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$.

During the synthesis process, suitable ratios of Na₂CO₃ (>99%, BDH chemicals), FeC₂O₄·2H₂O (99.999%, Alfa Aesar), Fe₂O₃ (99.85%, Alfa Aesar), Al₂O₃ (99.9%, Alfa Aesar), SiO₂(Johnson Matthey), Ga₂O₃ (99.99% Alfa Aesar), and GeO₂ (99.9999%, Alfa Aesar), were weighed, ground and calcined in air at 750 °C for 12 hours. The powders were then reground and pressed into 13 mm pellets which were heated at 1000 °C for 12 hours. The grinding, pellet pressing and reheating cycles were continued until a pure Na_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ phase was obtained.

6.2.2. Synthesis of aliovalent substituted LiFeO₂

Following the synthesis of the Na_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ samples, low-temperature topochemical cation-exchange reactions were performed to prepare the corresponding Li_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ phases. Initially, a 10:1 molar ratio LiNO₃ (99.98 % Alfa Aesar) and Na_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ powders were ground together in a mortar and pestle, and the resulting mixture was then transferred into an open-ended Pyrex tube. This Pyrex tube was positioned in a vertical furnace and heated at 300°C for 48 hours. Subsequently, the mixture was washed with excess deionized water, and the lithium-exchanged phase was collected through vacuum filtration.

6.3. Results

6.3.1. Structural characterization of $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases

Synchrotron X-ray diffraction (SXRD) and Neutron powder diffraction (NPD) data

Room temperature synchrotron X-ray diffraction (SXRD) data were collected from the aliovalent doped NaFeO_2 samples, as shown in Figure 6.2. It was found that all three samples, namely ($\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$) exhibit similar features in the diffraction patterns with the highest intensity peak occurring at $2\theta \sim 11^\circ$ (Figure 6.2). The diffraction patterns from all three samples could be indexed using orthorhombic unit cells with reflection conditions consistent with both the $Pbca$ and $Pca2_1$ space groups. The unit cell parameters (a , b , and c) of $Pbca$ symmetry can be related to those (a' , b' , and c') of $Pca2_1$ symmetry through the transformation: $a' = b$, $b' = a$, and $c' = c$.

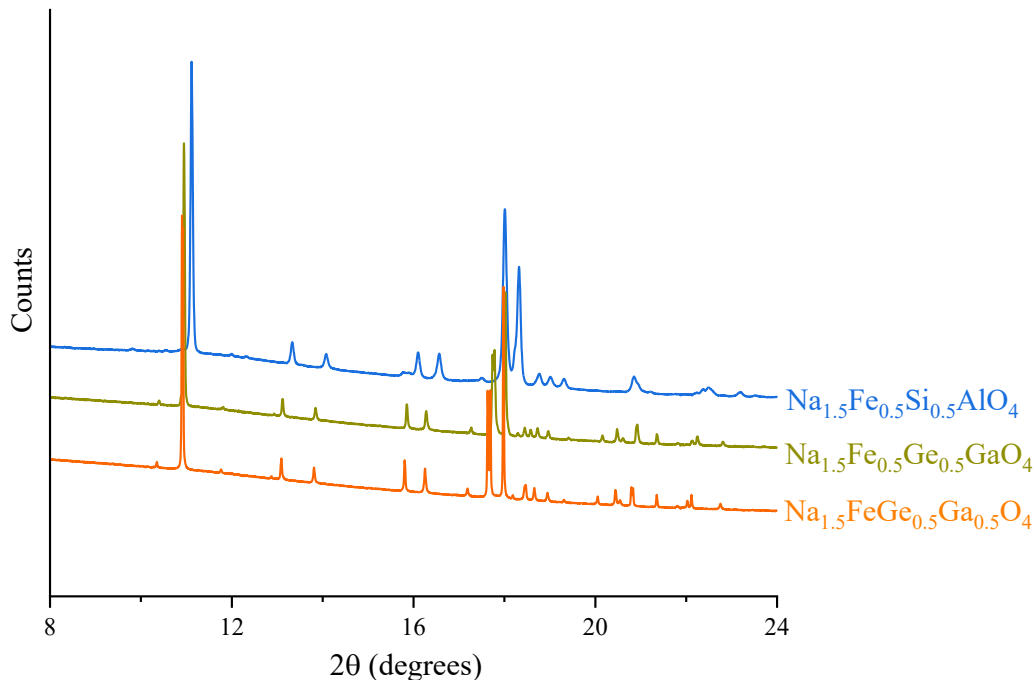


Figure 6. 2. Plot of the SXRD data collected from the aliovalent substituted NaFeO_2 samples

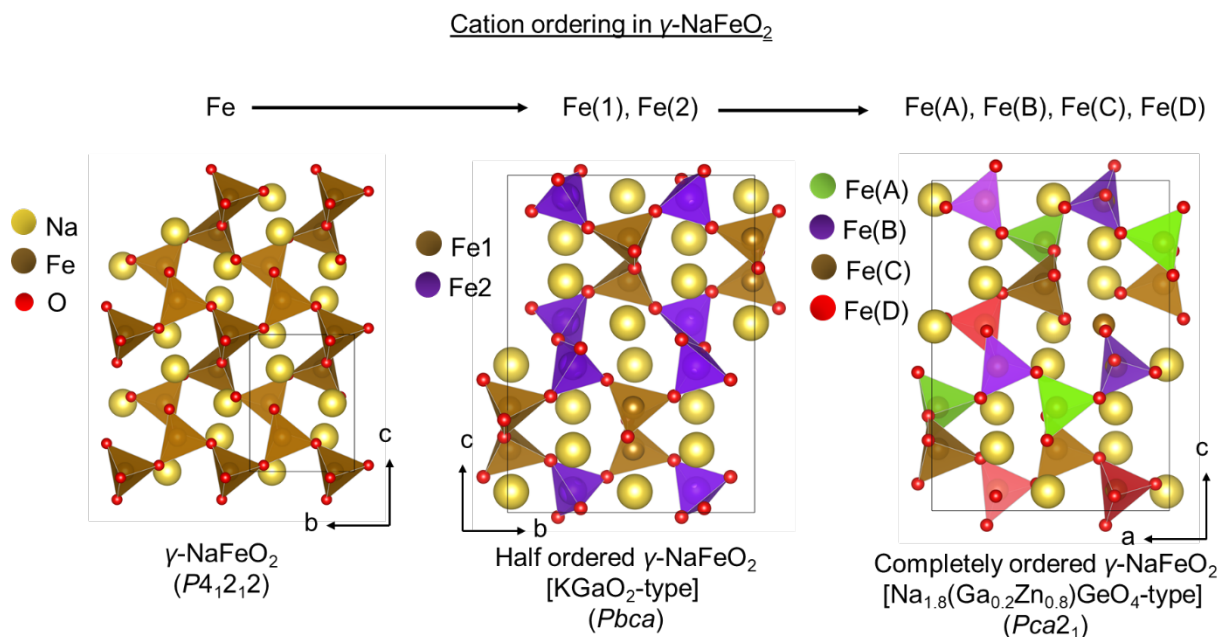


Figure 6. 3. Structures of γ -NaFeO₂ (left), structure of KGaO₂ shown as half ordered γ -NaFeO₂ (middle), structure of Na_{1.8}(Ga_{0.2}Zn_{0.8})GeO₄ shown as completely ordered γ -NaFeO₂ (right). The cation ordering is shown with the classification of Fe sites to Fe(1) ,Fe(2) and Fe(A), Fe(B), Fe(C), Fe(D) progressively.

Figure 6.3 shows the Fe/Na cation ordering in γ -NaFeO₂. The structures described in the $Pbca$ and $Pca2_1$ space groups respectively can be described as partially cation-ordered and completely cation-ordered γ -NaFeO₂-type structures. The structure described within the $Pbca$ space group (KGaO₂ structure type¹⁷¹) contain two separate 8c sites (brown and purple in Figure 6.3) for Fe/Al/Si/Ga/Ge cations, whereas the structure described within the $Pca2_1$ space group (Na_{1.8}(Ga_{0.2}Zn_{0.8})(GeO₄) structure type¹⁷²) comprises four separate 4a sites (brown, purple, green and red) for the cations (detailed discussion in Section 1.8).

Na_{1.5}Fe_{0.5}Si_{0.5}AlO₄, Na_{1.5}Fe_{0.5}Ge_{0.5}GaO₄, and Na_{1.5}FeGe_{0.5}Ga_{0.5}O₄ contain pairs of elements which are neighbours on the periodic table (e.g., Al/Si, Ga/Ge) which can not be distinguished between using X-ray diffraction. Thus, SXRD data cannot readily identify any cation order present in these phases so, NPD data were collected to accurately determine their structure.

Cation-ordered crystallographic models described in the $Pbca$ and $Pca2_1$ space groups were refined against NPD data collected from $Na_{1.5}Fe_{0.5}Si_{0.5}AlO_4$, $Na_{1.5}Fe_{0.5}Ge_{0.5}GaO_4$, and $Na_{1.5}FeGe_{0.5}Ga_{0.5}O_4$. Figure 6.4 presents a comparison of the fitted diffraction data for $Na_{1.5}Fe_{0.5}Ge_{0.5}GaO_4$ using models in both $Pbca$ and $Pca2_1$ space groups. A statistically better fit was achieved using the $Pca2_1$ crystallographic model compared to the $Pbca$ crystallographic model (Figure 6.4). Similar fitting statistics favouring the $Pca2_1$ models were observed for the other two samples— $Na_{1.5}Fe_{0.5}Si_{0.5}AlO_4$, and $Na_{1.5}FeGe_{0.5}Ga_{0.5}O_4$. Thus, crystallographic models described in $Pca2_1$ space group were continued to refine to achieve good fits to the data as shown in Figures 6.5-6.9 with crystallographic parameters given in Tables 6.1-6.6.

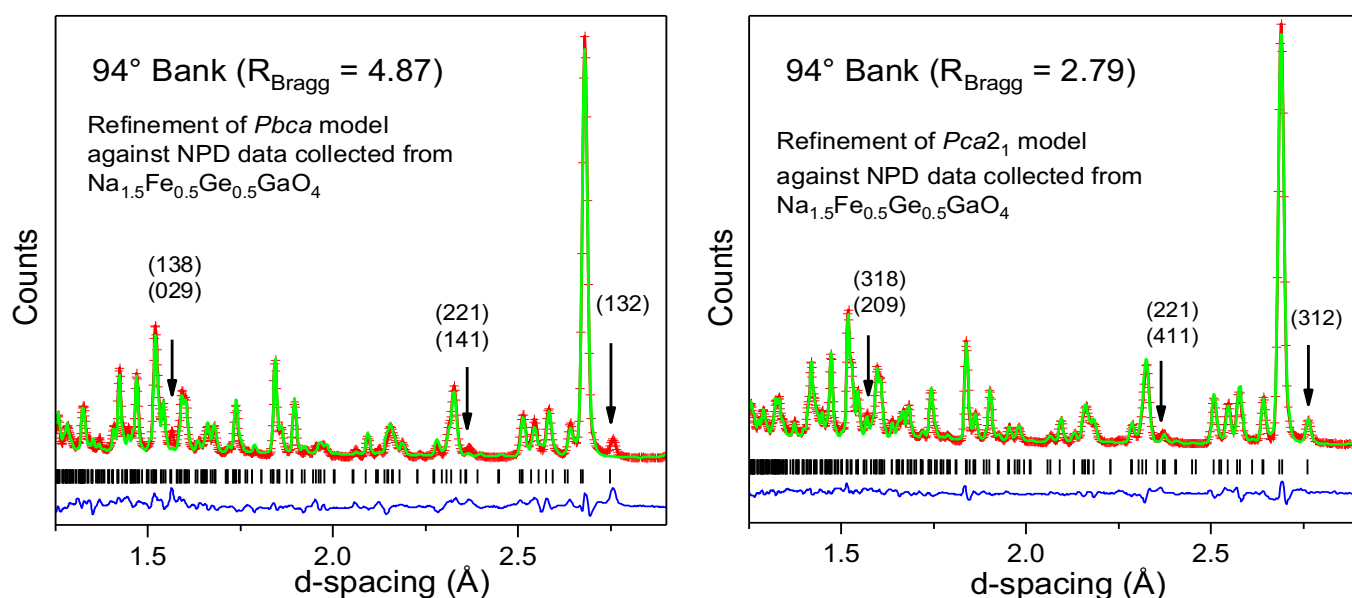


Figure 6. 4. Observed, calculated and difference plots from the structural refinement of $Na_{1.5}Fe_{0.5}Ge_{0.5}GaO_4$ against NPD data, bank 94°. Left: Refinement of $Pbca$ model against NPD data. Right: Refinement of $Pca2_1$ model against NPD data. A better fit is observed with the refinement of $Pca2_1$ model. Arrows indicate the reflections present in the data which are not well fitted using the $Pbca$ model but fitted using the $Pca2_1$ model

During the structural determination of $Na_{1.5}Fe_{0.5}Si_{0.5}AlO_4$ against NPD data, additional difficulties were encountered. The structure described in the $Pca2_1$ space group contains $4 \times 4a$ sites for the cations (Fe/Al/Si). The best fit to the data is obtained when one $4a$ site contained Si, while the remaining three sites were shared by Fe and Al in a 1:3 ratio. Examination of

scattering lengths (Section 2.2.1.3) for these $4a$ sites revealed comparable values as shown below.

Scattering length of Si = 4.149 fm

Scattering length of 25% Fe and 75 % Al = $(9.45 \times 0.25 + 3.449 \times 0.75)$ fm = 4.949 fm

Thus, in order to determine the precise cation ordering in $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, a combined SXRD and NPD refinement was conducted. The refined crystallographic parameters and the fitted pattern are presented in Figure 6.5 and Table 6.1. This analysis confirmed that the cation ordering derived from NPD data refinement aligns with the results obtained from SXRD refinement.

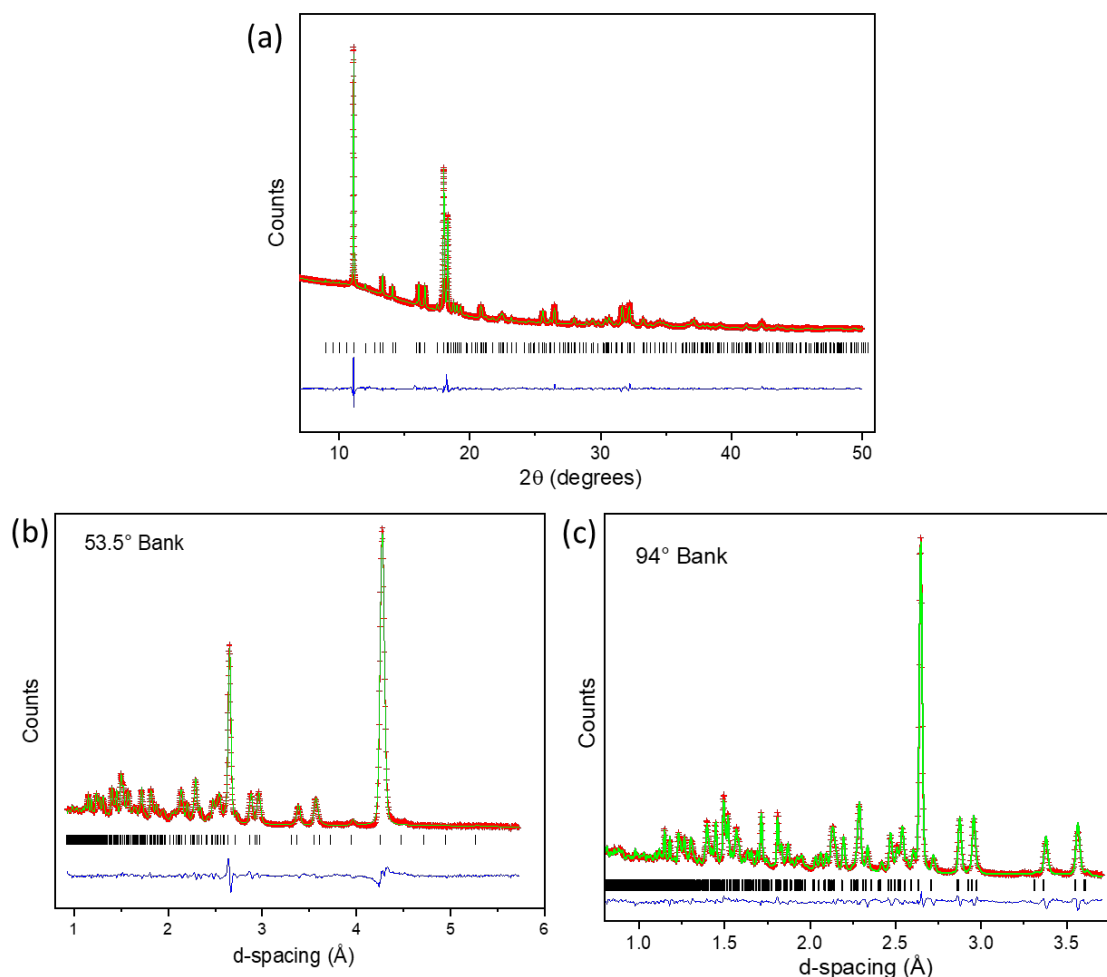


Figure 6. 5. Observed, calculated and difference plots from the structural refinement of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ against combined SXRD data (a) and NPD data bank 53.5° (b), bank 94° (c)

Table 6.1. Parameters from the structural refinement of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ sample against combined SXRD and NPD data

Atom	site	<i>x</i>	<i>y</i>	<i>z</i>	Fraction	<i>B</i> _{eq} (Å ²)
Na1	4 <i>a</i>	0.0066(15)	0.5151(17)	0.4287(23)	0.5	1.5(1)
Na2	4 <i>a</i>	0.0015(8)	0.0318(24)	0.0681(11)	1	1.5(1)
Na3	4 <i>a</i>	0.2198(10)	0.5374(26)	0.3062(9)	0.75	1.5(1)
Na4	4 <i>a</i>	0.2348(9)	0.0457(26)	0.1919(10)	0.75	1.5(1)
Fe1/Al1	4 <i>a</i>	0.2413(5)	0.0474(12)	0.4391(5)	0.25/0.75	0.72(5)
Fe2/Al2	4 <i>a</i>	0.0324(5)	0.4527(13)	0.6825(5)	0.25/0.75	0.72(5)
Fe3/Al3	4 <i>a</i>	0.2217(6)	0.5513(12)	0.0565(4)	0.25/0.75	0.72(5)
Si1	4 <i>a</i>	0.9933(6)	0.9513(20)	0.8041(5)	1	0.91(1)
O1	4 <i>a</i>	0.1288(10)	0.9785(20)	0.8231(7)	1	0.12(4)
O2	4 <i>a</i>	0.1854(10)	0.4748(17)	0.6492(8)	1	0.12(4)
O3	4 <i>a</i>	0.2289(10)	0.3617(20)	0.4619(9)	1	0.12(4)
O4	4 <i>a</i>	0.2169(10)	0.9007(19)	0.0577(7)	1	0.12(4)
O5	4 <i>a</i>	0.0945(9)	0.9776(20)	0.4090(5)	1	0.12(4)
O6	4 <i>a</i>	0.0443(11)	0.4568(21)	0.0822(9)	1	0.12(4)
O7	4 <i>a</i>	0.0068(9)	0.8651(22)	0.2091(8)	1	0.12(4)
O8	4 <i>a</i>	0.0184(12)	0.4001(31)	0.2736(6)	1	0.12(4)

$\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ – space group *Pca*2₁ (#29)
 $a = 10.5679(2)$ Å, $b = 5.2779(1)$ Å, $c = 14.4472(3)$ Å, volume = 805.821 (23) Å³
 Formula weight = 163.23375 g mol⁻¹, Z = 8
 Radiation source: neutron, Time of flight
 Temperature: 298 K
 $R_p = 1.68$ %, $wR_p = 2.71$ %

Table 6.2. Table of bond lengths and BVS parameters for $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ estimated from structural refinement against NPD data

Bonds	Average < <i>M</i> -O> (Å)	Fe-BVS	Al-BVS	Si-BVS
Fe1/Al1-O	1.8763(14)	2.916	2.175	
Fe2/Al2-O	1.7823(13)	3.458	2.805	
Fe3/Al3-O	1.8281(15)	3.285	2.478	
Si1-O	1.6949(13)			3.302

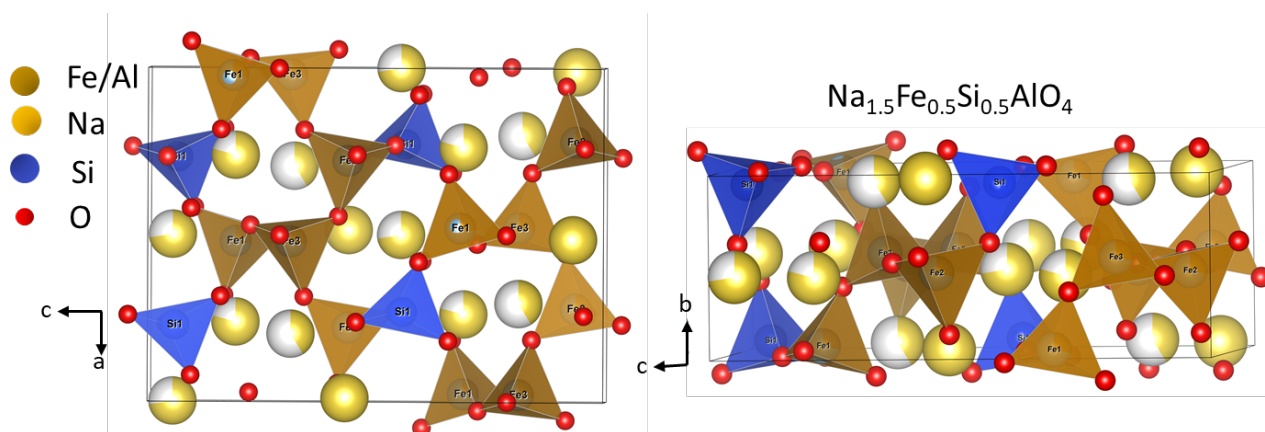


Figure 6. 6. Refined structure of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$

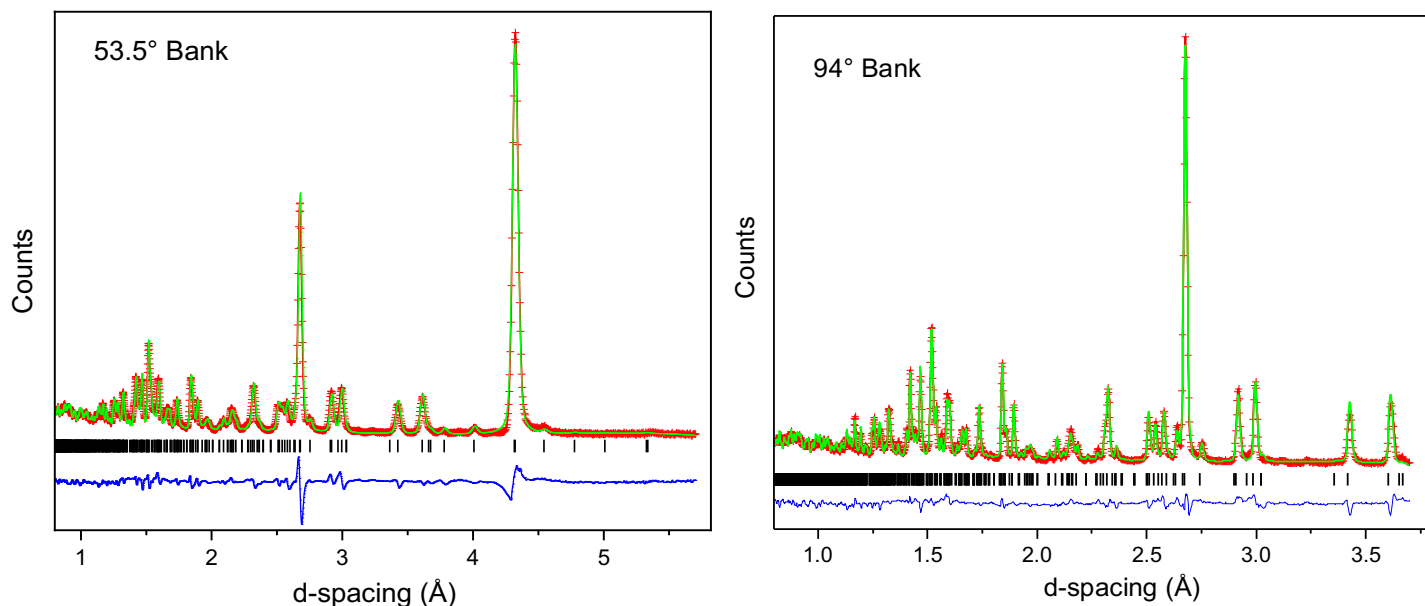


Figure 6. 7. Observed, calculated and difference plots from the structural refinement of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ against NPD data, bank 53.5° (left), bank 94° (right)

Table 6.3. Parameters from the structural refinement of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na1	4a	0.0041(11)	0.0413(14)	0.0595(10)	1	0.70(11)
Na2	4a	0.0039(14)	0.5415(18)	0.4405(11)	0.5	0.70(11)
Na3	4a	0.2252(11)	0.0548(24)	0.1839(12)	0.5	0.70(11)
Na4	4a	0.2251(67)	0.5576(13)	0.3156(75)	1	0.70(11)
Fe1/Ge1	4a	0.2246(41)	0.5532(61)	0.0614(35)	0.5/0.5	0.64(4)
Fe2/Ge2	4a	0.0262(28)	0.9443(71)	0.8138(46)	0.5/0.5	0.64(4)
Ga1	4a	0.0267(31)	0.4436(18)	0.6856(51)	1	0.42(2)
Ga2	4a	0.2250(41)	0.0520(18)	0.4386(41)	1	0.42(2)
O1	4a	0.1951(35)	0.4791(60)	0.6684(24)	1	0.13(2)
O2	4a	0.1951(34)	0.9786(61)	0.8314(23)	1	0.13(2)
O3	4a	0.2275(45)	0.3946(64)	0.4561(21)	1	0.13(2)
O4	4a	0.2275(44)	0.8948(64)	0.0439(22)	1	0.13(2)
O5	4a	0.0585(38)	0.4626(83)	0.0834(22)	1	0.13(2)
O6	4a	0.0585(36)	0.9628(82)	0.4168(22)	1	0.13(2)
O7	4a	0.01769(44)	0.3724(63)	0.2865(19)	1	0.13(2)
O8	4a	0.0173(43)	0.8731(62)	0.2133(19)	1	0.13(2)
$\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ – space group $Pca2_1$ (#29) $a = 10.6758(2) \text{ \AA}$, $b = 5.3489(1) \text{ \AA}$, $c = 14.6972(3) \text{ \AA}$, volume = $839.287 (33) \text{ \AA}^3$ Formula weight = $234.86375 \text{ g mol}^{-1}$, $Z = 8$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 5.20 \%$, $wR_p = 6.477 \%$						

Table 6.4. Table of bond lengths and BVS parameters for $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ estimated from structural refinement against NPD data

Bonds	Average <M-O> (Å)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1/Ge1-O	1.84(6)	3.1729	3.0800	
Fe2/Ge2-O	1.82(6)	3.3492	3.2512	
Ga1-O	1.82(6)			3.121
Ga2-O	1.84(6)			2.932

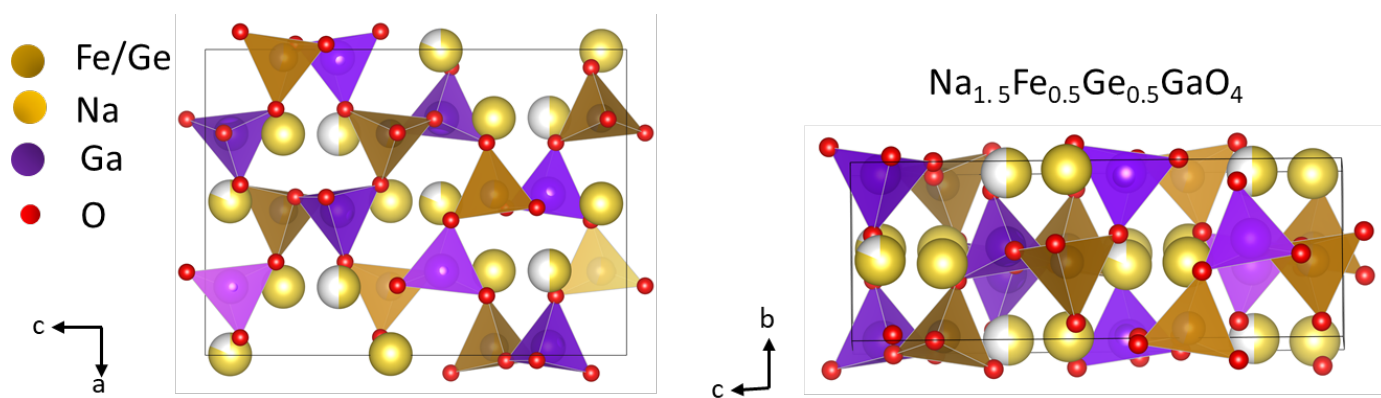


Figure 6. 8. Refined structure of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$

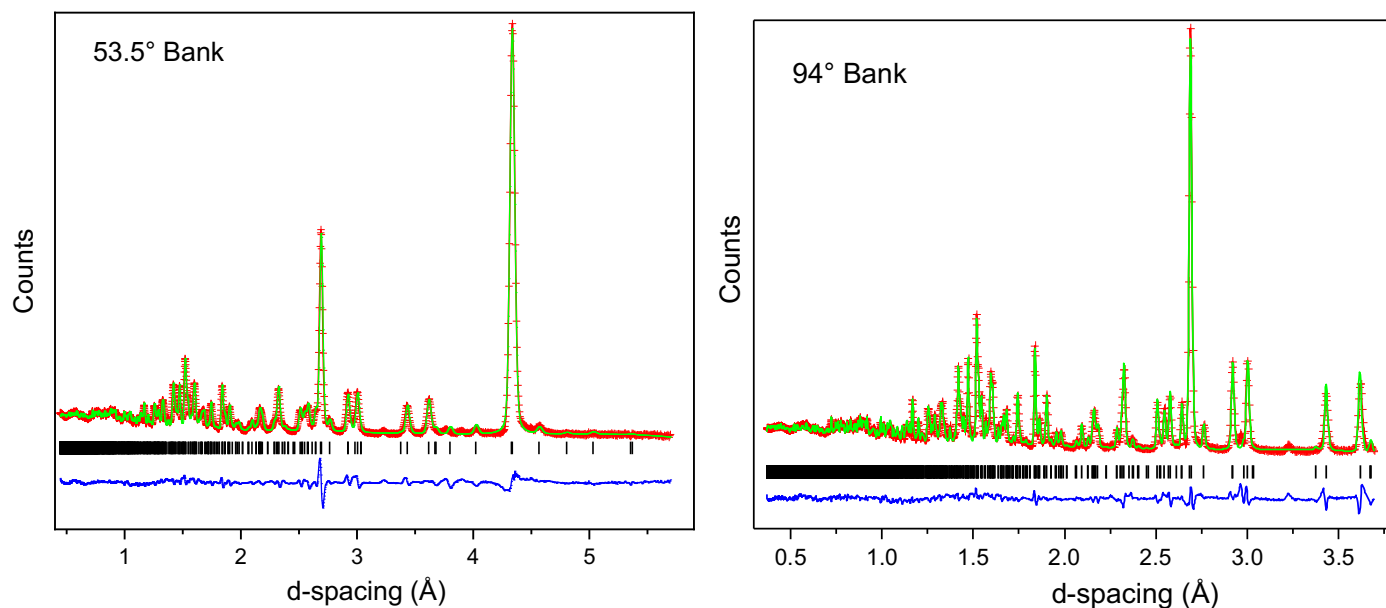


Figure 6. 9. Observed, calculated and difference plots from the structural refinement of $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ against NPD data, bank 53.5° (left), bank 94° (right)

Table 6.5. Parameters from the structural refinement of $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na1	4a	0.0093(10)	0.0249(25)	0.0683(14)	1	1.03(13)
Na2	4a	0.9878(20)	0.5895(46)	0.4489(15)	0.5	1.03(13)
Na3	4a	0.2563(36)	0.9972(58)	0.1928(52)	0.5	1.03(13)
Na4	4a	0.2093(10)	0.5667(26)	0.3187(9)	1	1.03(13)
Fe1/Ge1	4a	0.2256(5)	0.5557(12)	0.0644(5)	0.5/0.5	0.74(9)
Fe2/Ge2	4a	0.0249(5)	0.9366(10)	0.8152(5)	0.5/0.5	0.74(3)
Fe3	4a	0.2235(5)	0.056(10)	0.4395(4)	1	0.14(3)
Ga1	4a	0.0297(6)	0.4459(12)	0.6881(7)	1	0.26(11)
O1	4a	0.1960(9)	0.4961(14)	0.6697(7)	1	0.13(1)
O2	4a	0.1945(9)	0.9586(16)	0.8348(6)	1	0.13(1)
O3	4a	0.2190(7)	0.3988(16)	0.4880(6)	1	0.13(1)
O4	4a	0.2435(7)	0.8855(17)	0.0432(7)	1	0.13(1)
O5	4a	0.0549(8)	0.4381(15)	0.0853(5)	1	0.13(1)
O6	4a	0.0634(8)	0.9868(14)	0.4146(6)	1	0.13(1)
O7	4a	0.0310(8)	0.3683(16)	0.2806(5)	1	0.13(1)
O8	4a	0.0052(8)	0.8873(16)	0.2073(6)	1	0.13(1)
$\text{Na}_{1.435}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ – space group $Pca2_1$ (#29) $a = 10.7338(2) \text{ \AA}$, $b = 5.3818(1) \text{ \AA}$, $c = 14.6844(3) \text{ \AA}$, volume = $848.296 (26) \text{ \AA}^3$ Formula weight = $223.33 \text{ g mol}^{-1}$, $Z = 8$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 3.87 \%$, $wR_p = 5.07 \%$						

Table 6.6. Table of bond lengths and BVS parameters for $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ estimated from structural refinement against NPD data

Bonds	Average <M-O> (Å)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1-O	1.858(12)	3.103		
Fe2/Ge1-O	1.832(12)	3.2933	3.1968	
Fe3/Ge2-O	1.830(12)	3.3109	3.2139	
Ga1-O	1.839(12)			2.980

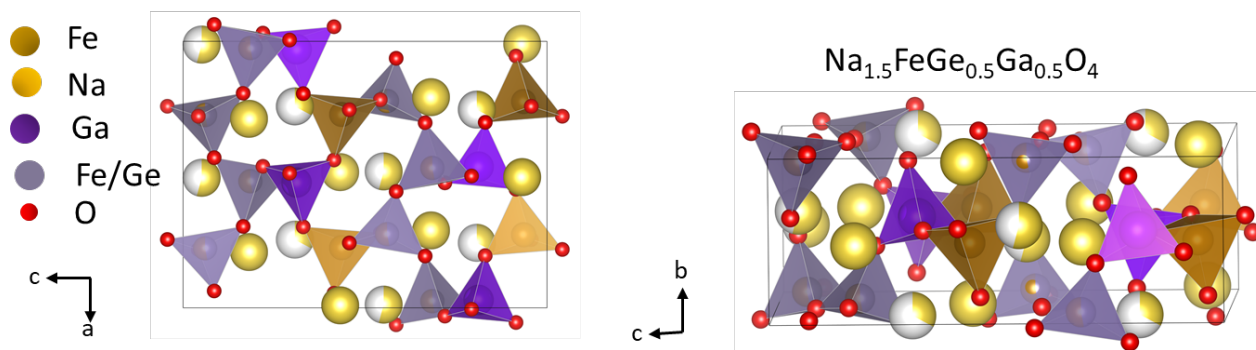


Figure 6. 10. Refined structure of $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$

Tables 6.2, 6.4, and 6.6 present the <Fe/M/N-O> bond lengths and bond valence sum (BVS) parameters determined from the crystallographic model obtained after the structural refinement of aliovalent substituted NaFeO_2 phases against neutron powder diffraction (NPD) data. <Si-O> bond lengths (1.6949(13) Å) determined from the structure of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ are slightly larger than the expected <Si-O> bond lengths, based on the previous reports of materials¹⁷³ containing Si^{4+} . This divergence can be attributed to the presence of atomic disorder in the structure.

Likewise, in the cases of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ (Tables 6.4 and 6.6), larger <Ge-O> bond lengths than expected were determined, which can be attributed to the presence of Fe/Ge disorder in these phases. Moreover, for other <Fe/M/N-O> bond lengths and BVS parameters determined from $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases are found to be consistent with the presence of Fe^{3+} , Al^{3+} , and Ga^{3+} in the structure.

The structure described in space group $Pca2_1$, can be regarded as a distorted, ordered variant of γ -NaFeO₂ structure (Figure 6.2), featuring four independent tetrahedral sites for Fe, M ($=\text{Al}^{3+}$, Ga^{3+}), or N ($=\text{Si}^{4+}$, Ge^{4+}) cations in the structures of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. These cations are located at the centre of tetrahedra, forming corner-shared zig-zag chains that run along the a axis of the unit cell (Figure 6.11). Within the zig-zag chains, half of the tetrahedra point up, and the other half point down, perpendicular to the ac plane. The four independent tetrahedral sites for the Fe- M - N cations in the structure of $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases are designated as A, B, C, and D (see Figure 6.11). The structural determination based on NPD data reveals specific distributions of cations for the three samples as follows:

1. In the structure of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, the Si^{4+} cations occupy an independent tetrahedral site (B, Table 6.7), while the Fe^{3+} and the Al^{3+} cations share the remaining three tetrahedral sites (A, B, and C, Table 6.7). This non mixing of Si with the Fe/Al cations allows Si^{4+} to be well separated from other Si^{4+} cations in the structure, which minimizes the inter cation repulsion. This disorder between Fe/Al cations was also observed for $A\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ phases (Chapter 3) which is consistent with the cation ordering observed in $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$.
2. In the structure of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, the Ga^{3+} cations occupy two of the tetrahedral sites (B, and C, Table 6.7), while the Fe^{3+} and the Ge^{4+} cations share the remaining two tetrahedral sites (A, and D, Table 6.7). Atomic ordering between Fe/Ga was also observed for $A\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ phases (Chapter 3) which is consistent with the ordering observed in $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$.

3. In the structure of $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, the order of metallic cations resembles that of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, with the only difference being the replacement of half the Ga cations (B, Table 6.7) with Fe cations.

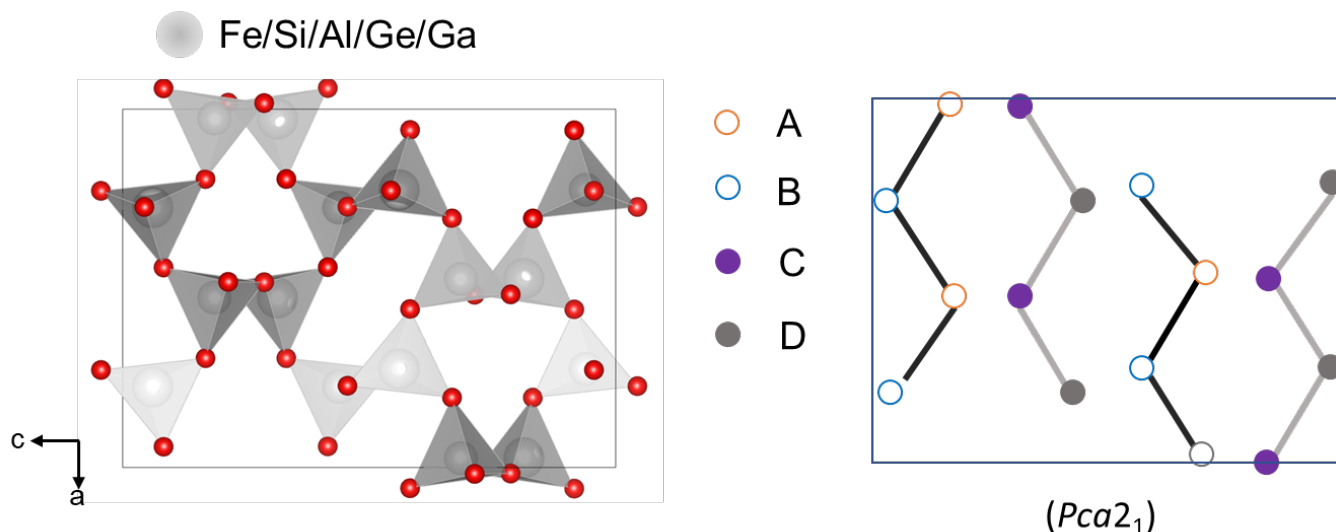


Figure 6. 11. Structure of $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phase, showing only the Fe/M/NO_4 tetrahedral site (left). Zig-zag lines running along the a axis of the unit cell (right). The independent tetrahedral sites are designated as A, B, C, and D

Table 6.7. Cationic-distribution of the $4a$ Td sites in $Pca2_1$ structure determined from structural refinements against NPD data

Composition	Structure ($Pca2_1$)			
	Site A ($4a$)	Site B ($4a$)	Site C ($4a$)	Site D ($4a$)
$\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	Fe/Al (1:3)	Si	Fe/Al (1:3)	Fe/Al (1:3)
$\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	Fe/Ge (1:1)	Ga	Ga	Fe/Ge (1:1)
$\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$	Fe/Ge (1:1)	Fe	Ga	Fe/Ge (1:1)

The cation order observed in $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases, allows the formulation of some general rules. For example, Fe^{3+} cations are observed to share sites with Al^{3+} or Ge^{4+} , but not with Ga^{3+} or Si^{4+} . Considering the ionic radii of Al^{3+} (0.39 Å)¹⁵⁴, Fe^{3+} (0.49 Å)¹⁵⁴, Si^{4+} (0.26 Å)¹⁵⁴, Ga^{3+} (0.47 Å)¹⁵⁴, and Ge^{4+} (0.39 Å)¹⁵⁴ it is hard to explain the ordering patterns observed on size alone. For example, Al^{3+} is more dissimilar in size to Fe^{3+} than Ga^{3+} but mixing of Fe/Al and non mixing of Fe/Ga is observed. This suggests that additional factors, such as ionic charge and local geometric requirements, play crucial role in determining the cationic arrangements within these structures.

6.3.2. Structural characterization of $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$

Synchrotron X-ray diffraction (SXRd) and Neutron powder diffraction (NPD) data

The Synchrotron X-ray diffraction (SXRd) data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ phases are shown in Figure 6.12. The diffraction peak of the Na-precursor phases at $2\theta \sim 11^\circ$ (Section 6.3.1) is found to be split into two peaks (at $2\theta = 11.37^\circ$ and 11.88°) in the SXRd data from the corresponding $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases. These data could not be indexed using the unit cells of corresponding $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases based on orthorhombic unit cells. This implies, upon lithiation either a non-topochemical structural change occurs or a breaking of symmetry but conservation of the parent topology occurs.

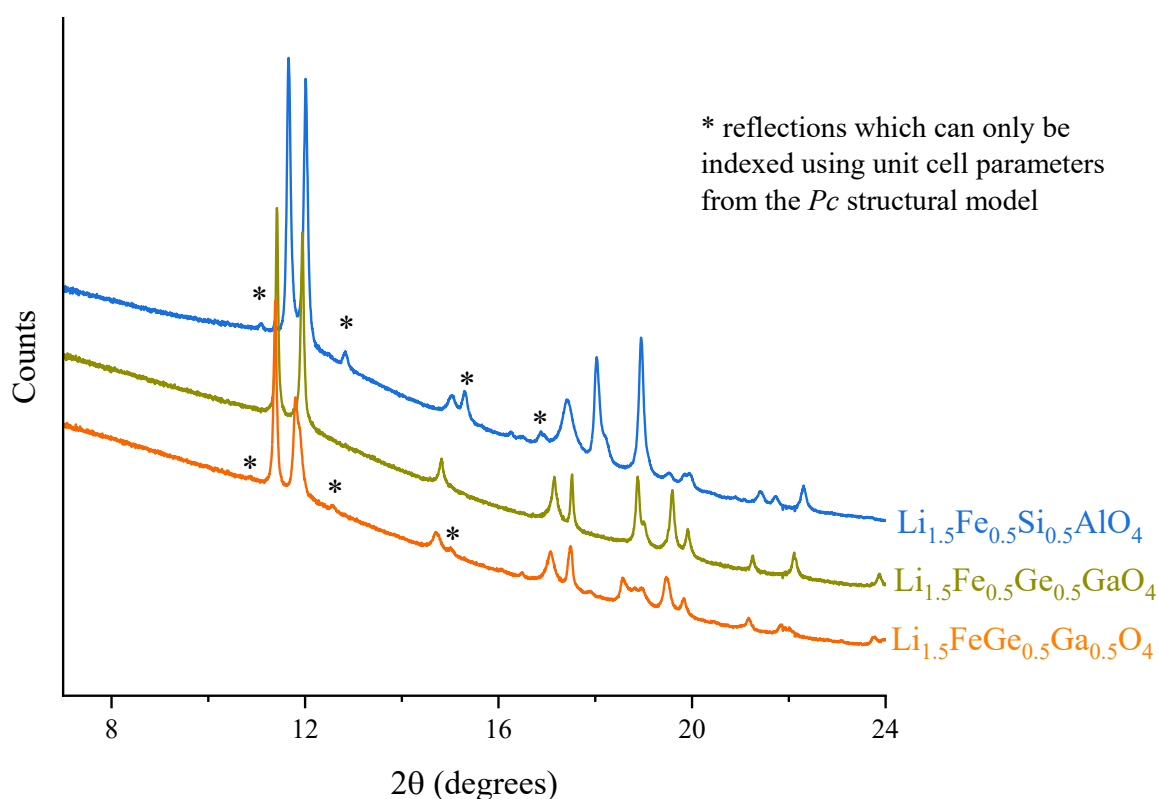


Figure 6. 12. Plot of SXRd data collected from aliovalent doped LiFeO_2 samples, * indicates reflections which can not be indexed using the unit cell parameters from the ordered $T\text{-LiFeO}_2$ structural model, but can be indexed using the unit cell parameters of the Pc structural model

SXRD data from $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases were indexed as follows:

Data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ were indexed using slightly smaller unit cell parameters than the corresponding $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ phases, coupled with a reduction in symmetry from the $Pca2_1$ space group to the lower symmetry Pc space group. This suggests both $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, upon lithium exchange not only results in shorter unit cell parameters but also undergoes a structural distortion leading to the description of the Li-exchanged phases in monoclinic crystal system with the Pc space group.

On the other hand, data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ were indexed using a monoclinic unit cell with reflections conditions consistent with the space group Pn (ordered T-LiFeO₂ structure type)¹⁵³. The unit cell parameters of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ are related with the unit cell parameters of the corresponding $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ by a transformation of $a' = a \times 1/2$, $b' = b \times 1/2$, and $c' = c \times 1$. This indexing of the data suggests $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, originally described in space group $Pca2_1$, upon lithium exchange undergoes a structural rearrangement resulting in the description of the lithium exchanged phase in the space group Pn .

6.3.2.1. Structural determination of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$

To assist with structural determination, neutron powder diffraction (NPD) data were collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. The indexing of the SXRD data indicated the need for a crystallographic model with unit cell parameters shorter than the corresponding $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ phases as well as being described in space group Pc . However, no reported structural models consistent with such conditions were found. Thus, prior to the structural refinement process, structural models of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ were uploaded to ISODISTORT program¹⁷⁴ and the symmetry of these crystallographic models were reduced from space group $Pca2_1$ to space group Pc . The resultant crystallographic model described in Pc space group was refined against

the data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ to achieve good fits as shown in Figures 6.13-6.15 with refined parameters given in Tables 6.8-6.10. In addition, in the case of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, to determine the distribution of cations accurately, the crystallographic model described in the Pc space group was refined against the SXRD and the NPD data simultaneously (similar to the case of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, Section 6.3.1).

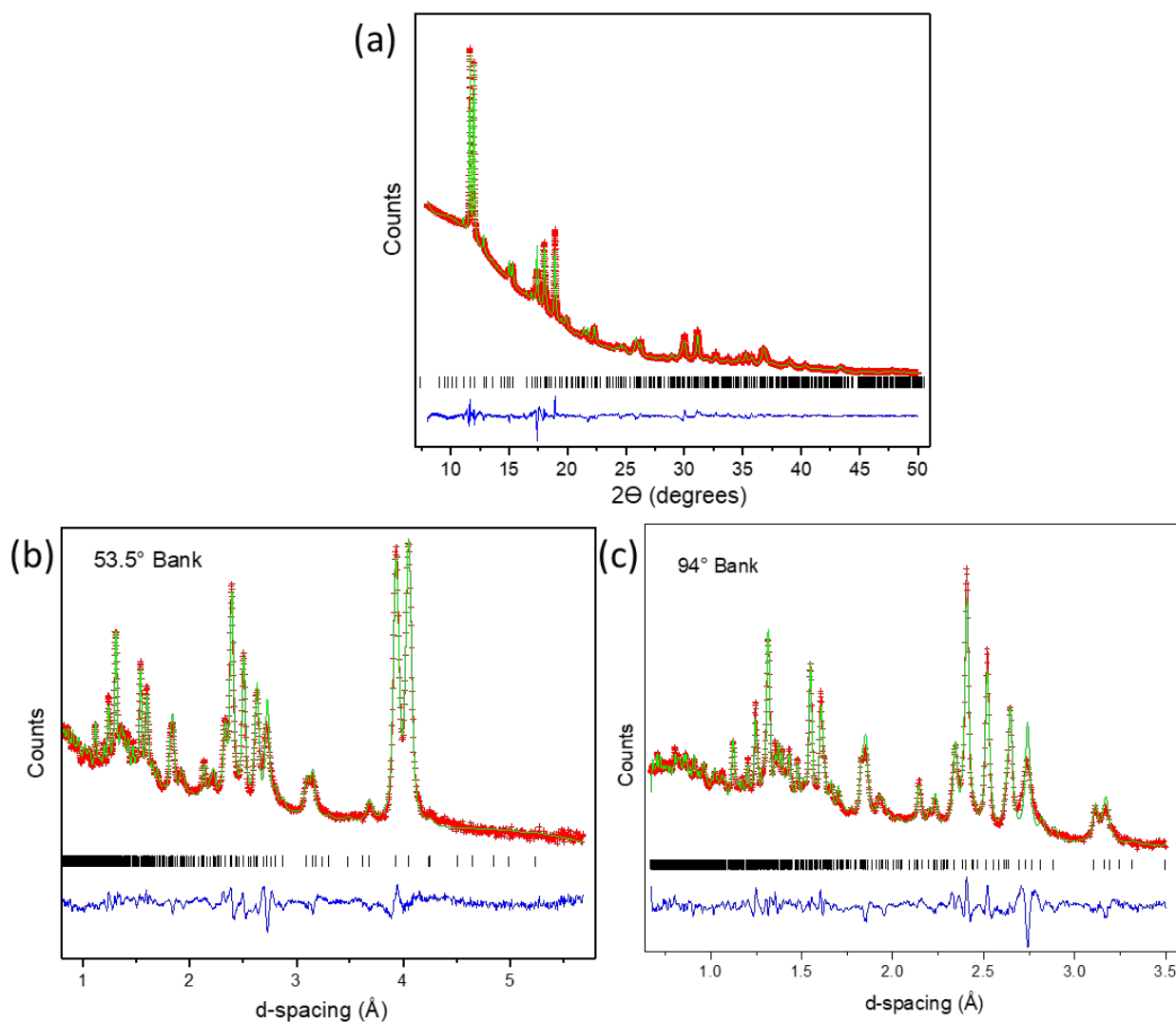


Figure 6. 13. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ against combined SXRD data (a) and NPD data, bank 53.5° (b), bank 94° (c)

Table 6.8. Parameters from the structural refinement of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ sample against SXRD and NPD data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	$2a$	0.8999(27)	0.5839(69)	0.7656(28)	0.75	0.78(1)
Li2	$2a$	0.3999(27)	0.4145(69)	0.7656(28)	0.75	0.78(1)
Li3	$2a$	0.8089(23)	0.0312(88)	0.6604(31)	0.75	0.78(1)
Li4	$2a$	0.3089(23)	0.9727(88)	0.6604(31)	0.75	0.78(1)
Li5	$2a$	0.5596(30)	0.4509(67)	0.0245(31)	0.75	0.78(1)
Li6	$2a$	0.0596(3)	0.5501(67)	0.0245(31)	0.75	0.78(1)
Li7	$2a$	0.6775(31)	0.8888(59)	0.9698(32)	0.75	0.78(1)
Li8	$2a$	0.1775(31)	0.1112(59)	0.9698(32)	0.75	0.78(1)
Fe1/Al1	$2a$	0.0666(20)	0.0525(50)	0.1889(23)	0.25/0.75	0.35(7)
Fe2/Al2	$2a$	0.5642(21)	0.9144(50)	0.1990(24)	0.25/0.75	0.35(7)
Fe3/Al3	$2a$	0.9206(18)	0.0861(50)	0.9628(20)	0.25/0.75	0.35(7)
Fe4/Al4	$2a$	0.4343(20)	0.0575(43)	0.9430(20)	0.25/0.75	0.35(7)
Fe5/Al5	$2a$	0.6920(17)	0.6025(42)	0.7639(21)	0.25/0.75	0.35(7)
Fe6/Al6	$2a$	0.1859(18)	0.4945(32)	0.7616(24)	0.25/0.75	0.35(7)
Si1	$2a$	0.8012(7)	0.4599(47)	0.5253(17)	1	0.2(1)
Si2	$2a$	0.3012(7)	0.4639(28)	0.4976(17)	1	0.2(1)
O1	$2a$	0.9155(15)	0.4540(35)	0.9800(18)	1	0.15(1)
O2	$2a$	0.4155(16)	0.4390(37)	0.9688(20)	1	0.15(1)
O3	$2a$	0.0440(19)	0.9988(38)	0.0288(21)	1	0.15(1)
O4	$2a$	0.5496(18)	0.9855(36)	0.0278(21)	1	0.15(1)
O5	$2a$	0.8077(18)	0.4766(42)	0.6952(16)	1	0.15(1)
O6	$2a$	0.2944(18)	0.5388(38)	0.6777(19)	1	0.15(1)
O7	$2a$	0.6715(16)	0.8248(32)	0.7620(15)	1	0.15(1)
O8	$2a$	0.1801(17)	0.1045(35)	0.7488(17)	1	0.15(1)
O9	$2a$	0.9544(17)	0.0432(46)	0.7805(18)	1	0.15(1)
O10	$2a$	0.4568(15)	0.9421(41)	0.7864(22)	1	0.15(1)
O11	$2a$	0.0720(19)	0.4011(33)	0.2250(18)	1	0.15(1)
O12	$2a$	0.5810(19)	0.5420(35)	0.2177(17)	1	0.15(1)
O13	$2a$	0.8208(17)	0.0745(42)	0.4421(22)	1	0.15(1)
O14	$2a$	0.3299(13)	0.0885(36)	0.5345(22)	1	0.15(1)
O15	$2a$	0.7122(15)	0.4399(34)	0.9333(17)	1	0.15(1)
O16	$2a$	0.1963(16)	0.5222(43)	0.9333(17)	1	0.15(1)
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ – space group Pc (#7) $a = 12.7599(7) \text{ \AA}$, $b = 5.0212(3) \text{ \AA}$, $c = 10.5455(6) \text{ \AA}$, $\beta = 89.999^\circ(2)$ volume = $675.652 (29) \text{ \AA}^3$ Formula weight = $139.38625 \text{ g mol}^{-1}$, $Z = 8$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 1.37 \%$, $wR_p = 2.13 \%$						

Table 6.9. Table of bond lengths and BVS parameters for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ estimated from structural refinement against NPD data

Bonds	Average <M-O> (Å)	Fe-BVS	Al-BVS	Si-BVS
Fe1/Al1-O	1.800(8)	3.580	2.682	
Fe2/Al2-O	1.820(8)	3.424	2.557	
Fe3/Al3-O	1.812(10)	3.559	2.658	
Fe4/Al4-O	1.810(10)	3.471	2.592	
Fe5/Al5-O	1.763(9)	4.238	3.165	
Fe6/Al6-O	1.763(9)	4.353	3.251	
Si1-O	1.731(14)			3.209
Si2-O	1.733(13)			3.214

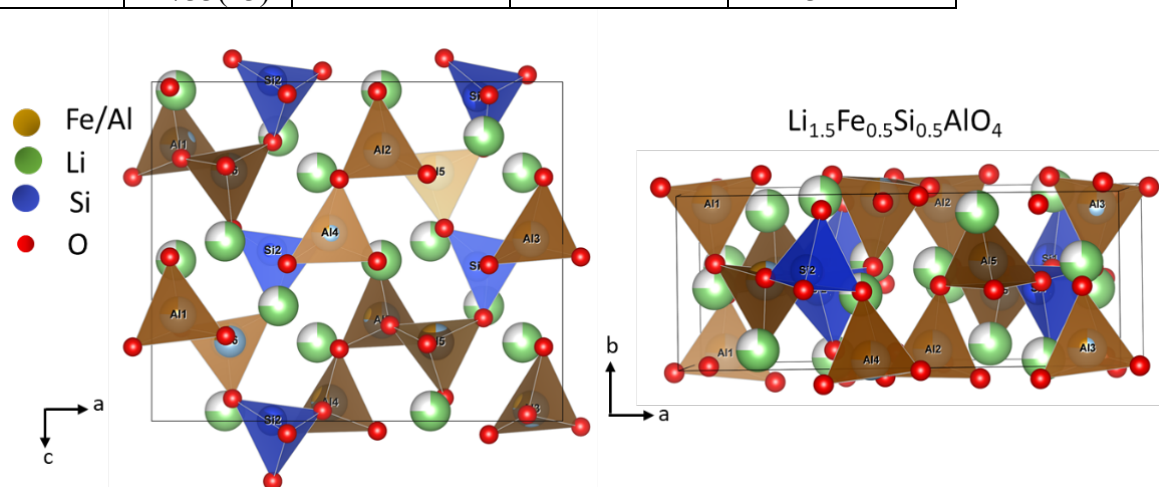


Figure 6. 14. Refined structure of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$

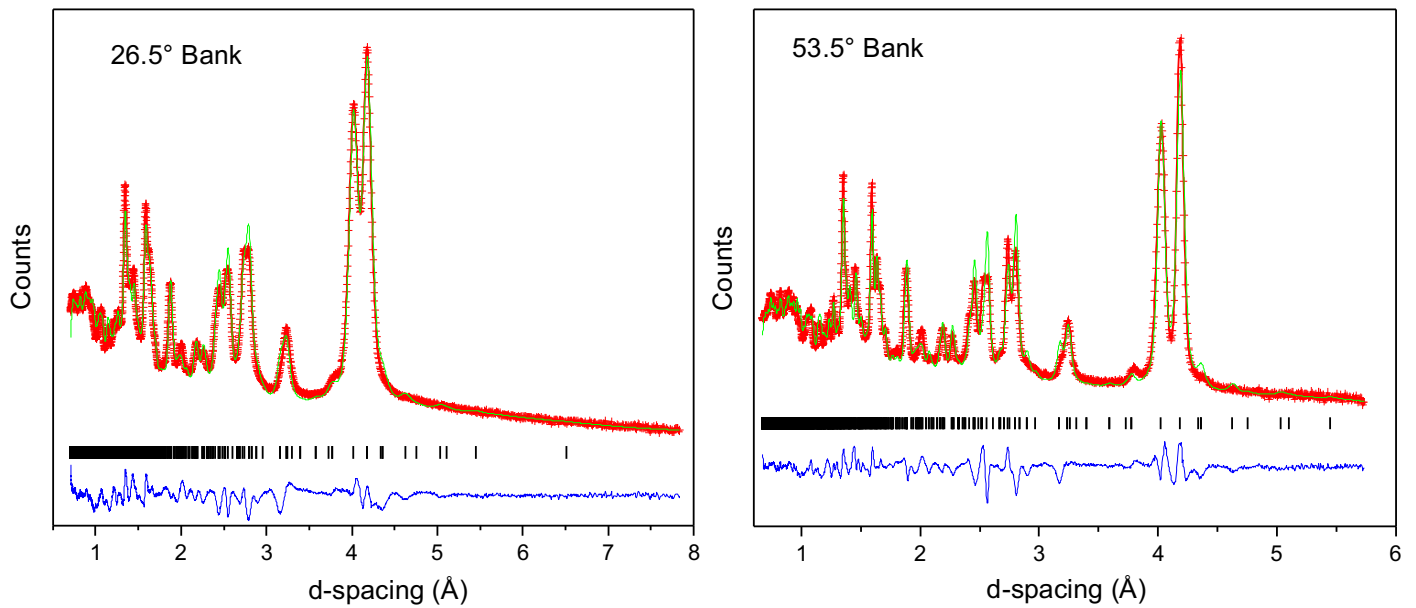


Figure 6.15. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ against NPD data bank 26.5° (left), bank 53.5° (right)

Table 6.10. Parameters from the structural refinement of $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	$2a$	0.893(5)	0.475(1)	0.782(5)	0.75	1.9(2)
Li2	$2a$	0.393(5)	0.525(1)	0.782(5)	0.75	1.9(2)
Li3	$2a$	0.804(5)	0.125(1)	0.697(5)	0.75	1.9(2)
Li4	$2a$	0.304(5)	0.987(1)	0.697(5)	0.75	1.9(2)
Li5	$2a$	0.563(5)	0.477(2)	0.255(5)	0.75	1.9(2)
Li6	$2a$	0.063(5)	0.522(2)	0.255(5)	0.75	1.9(2)
Li7	$2a$	0.676(6)	0.966(1)	0.954(5)	0.75	1.9(2)
Li8	$2a$	0.177(6)	0.034(1)	0.954(5)	0.75	1.9(2)
Ga1	$2a$	0.0339(4)	0.093(3)	0.201(4)	1	0.65(20)
Ga2	$2a$	0.548(3)	0.907(3)	0.201(4)	1	0.65(20)
Fe1	$2a$	0.9254(3)	0.107(4)	0.963(4)	1	0.97(11)
Fe2	$2a$	0.410(4)	0.909(2)	0.963(4)	1	0.97(11)
Ge1/Fe3	$2a$	0.677(3)	0.627(2)	0.768(4)	0.5/0.5	0.41(15)
Ge2/Fe4	$2a$	0.156(3)	0.372(2)	0.795(4)	0.5/0.5	0.41(15)
Ge3/Fe5	$2a$	0.781(3)	0.424(2)	0.522(5)	0.5/0.5	0.41(15)
Ge4/Fe6	$2a$	0.296(3)	0.575(2)	0.529(4)	0.5/0.5	0.41(15)
O1	$2a$	0.906(3)	0.615(5)	0.944(5)	1	0.30(1)
O2	$2a$	0.406(3)	0.561(6)	0.947(6)	1	0.30(1)
O3	$2a$	0.034(3)	0.201(8)	0.027(5)	1	0.30(1)
O4	$2a$	0.534(3)	0.047(7)	0.036(4)	1	0.30(1)
O5	$2a$	0.781(2)	0.503(6)	0.694(5)	1	0.30(1)
O6	$2a$	0.281(2)	0.503(6)	0.694(5)	1	0.30(1)
O7	$2a$	0.653(3)	0.015(3)	0.779(5)	1	0.30(1)
O8	$2a$	0.153(3)	0.015(3)	0.768(5)	1	0.30(1)

O9	2a	0.929(2)	0.011(7)	0.787(5)	1	0.30(1)
O10	2a	0.429(3)	0.964(5)	0.789(5)	1	0.30(1)
O11	2a	0.049(3)	0.474(3)	0.235(4)	1	0.30(1)
O12	2a	0.549(3)	0.525(3)	0.218(5)	1	0.30(1)
O13	2a	0.8085(4)	0.964(6)	0.546(5)	1	0.30(1)
O14	2a	0.2968(3)	0.9771(6)	0.544(5)	1	0.30(1)
O15	2a	0.660(3)	0.515(5)	0.946(4)	1	0.30(1)
O16	2a	0.184(3)	0.567(5)	0.943(4)	1	0.30(1)
$\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ – space group <i>Pc</i> (#7) $a = 12.9269(15) \text{ \AA}$, $b = 5.0725(6) \text{ \AA}$, $c = 10.8421(11) \text{ \AA}$, $\beta = 89.975^\circ (4)$, volume = $710.948 (144) \text{ \AA}^3$ Formula weight = $200.91625 \text{ g mol}^{-1}$, $Z = 8$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 4.77 \%$, $wR_p = 6.55 \%$						

Table 6.11. Table of bond lengths and BVS parameters for $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ estimated from structural refinement against NPD data

Bonds	Average <Fe/Ge-O> /<Ga-O> ($\text{\AA}$)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1-O	1.999(15)	2.268		
Fe2-O	1.850(16)	3.170		
Ga1-O	1.852(15)			2.982
Ga2-O	1.865(15)			2.961
Fe3/Ge1-O	1.915(15)	2.732	2.652	
Fe4/Ge2-O	1.881(15)	3.040	2.959	
Fe5/Ge3-O	1.936(18)	2.771	2.690	
Fe6/Ge4-O	1.892(16)	2.864	2.780	

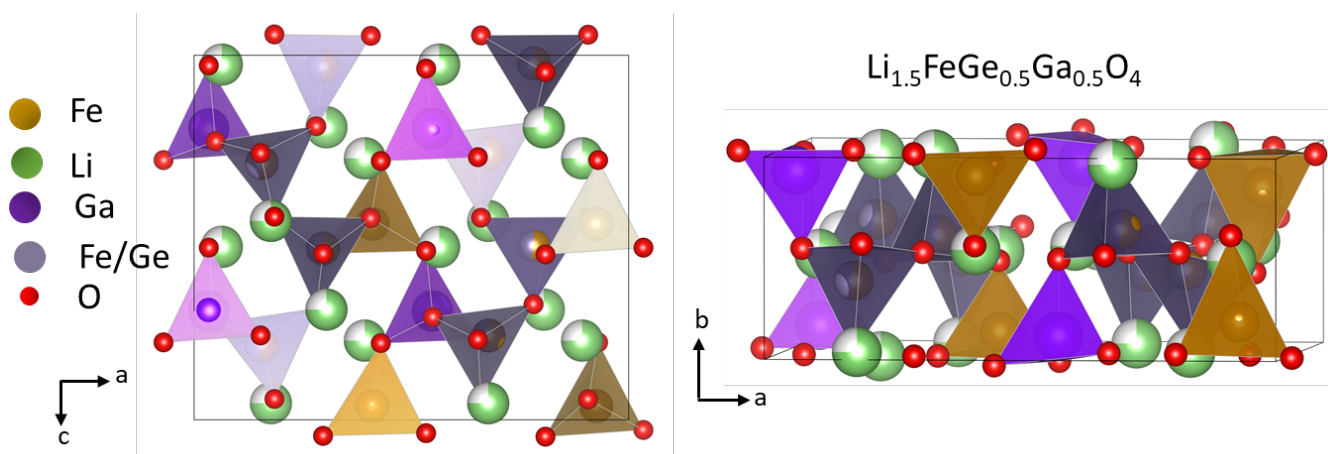


Figure 6. 16. Refined structure of $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ sample

Figures 6.14 and 6.16 present the refined structure of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$. Comparison of these structures with the corresponding Na-precursor phases reveals structural distortion taking place during the lithium exchange process. This distortion results in the lowering of symmetry of the Na-precursor phases, initially described in the $Pca2_1$ space group to the Li-exchanged products, now described in the Pc space group. A close inspection of both the structures of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$ reveal that within the structure, half of the tetrahedra point in one direction, and the other half points in the opposite direction perpendicular to the ac plane (Figures 6.14-6.16). This indicates the retention of the $\gamma\text{-NaFeO}_2$ structure type in both $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$ after lithium exchange. Tables 6.7 and 6.15 show that cation ordering in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$ being same with the corresponding Na-precursor phases, indicating no change in the cationic ordering during the lithium exchange process. This implies despite the structural distortion, and lowering of the symmetry, the parent topology being retained. in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$ upon lithium exchange.

A comparison of the $\langle\text{Fe-O}\rangle$ bond lengths and Fe-BVS values between $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ reveal the elongation of $\langle\text{Fe-O}\rangle$ bond lengths and decrease in Fe-BVS parameters upon lithium exchange. A similar trend of increase in $\langle\text{Fe-O}\rangle$ bond lengths and decrease in Fe-BVS is observed for $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$ in comparison to $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$.

6.3.2.2. Structural determination of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$

To assist with structural determination, neutron powder diffraction (NPD) data were collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$. A crystallographic model described in space group Pn (ordered T- LiFeO_2 structure type) was refined against the data to achieve good fits as shown in Figure 6.19, with refined parameters given in Table 6.12.

Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄ (NPD data)

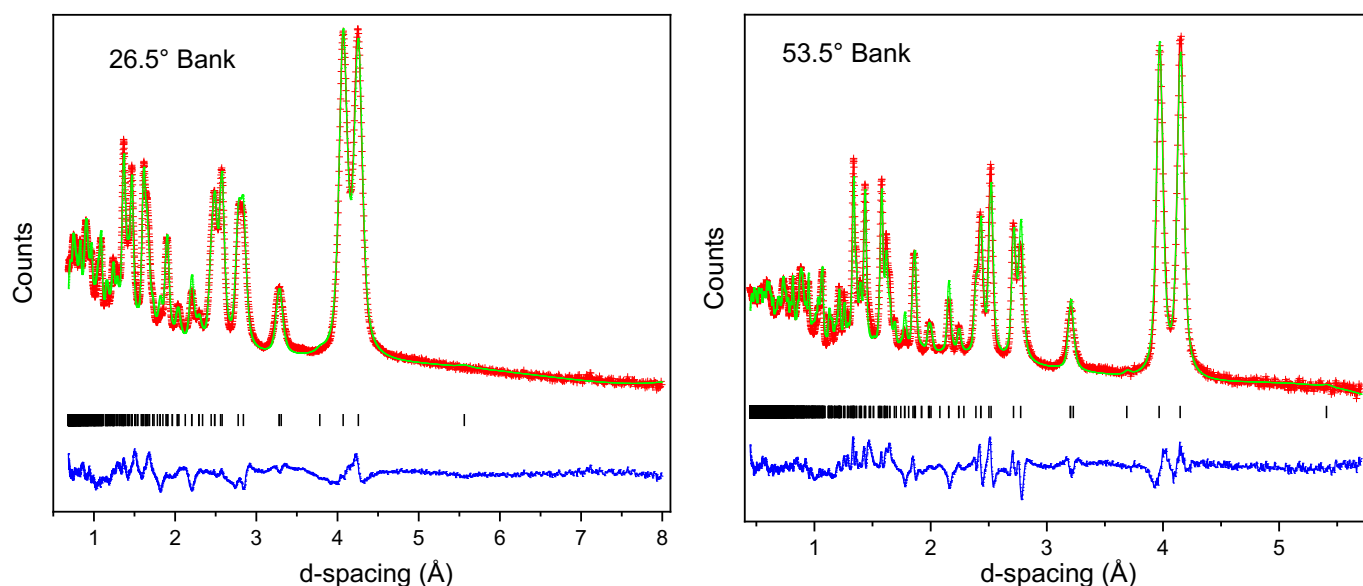


Figure 6. 17. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ against NPD data, bank 26.5° (left), bank 53.5° (right)

Table 6.12. Parameters from the structural refinement of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	$2a$	0.5	0.1287(18)	0	0.75	1.0(2)
Li2	$2a$	0.75	0.3712(18)	0.5	0.75	1.0(2)
Fe1/Ge1	$2a$	0.0063(11)	0.1848(17)	0.0010(12)	0.5/0.5	0.47(9)
Ga1	$2a$	0.2586(10)	0.3238(11)	0.4821(9)	1	0.20(6)
O1	$2a$	0.4830(7)	0.1572(5)	0.3605(10)	1	0.15(3)
O2	$2a$	0.2670(7)	0.6572(5)	0.3895(10)	1	0.15(3)
O3	$2a$	0.0134(7)	0.1817(5)	0.3969(8)	1	0.15(3)
O4	$2a$	0.2365(7)	0.3182(5)	0.8530(8)	1	0.15(3)
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ – space group Pn (#7) $a = 6.4450(4) \text{ \AA}$, $b = 5.4131(2) \text{ \AA}$, $c = 5.0264(3) \text{ \AA}$, $\beta = 89.754^\circ$ (6), volume = $175.364 (20) \text{ \AA}^3$ Formula weight = $208.3575 \text{ g mol}^{-1}$, $Z = 2$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 3.61 \%$, $wR_p = 4.81 \%$						

Table 6.13. Table of bond lengths and BVS parameters for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ estimated from structural refinement against NPD data

Bonds	Average <M-O> (Å)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1/Ge1-O	1.859(7)	3.218	3.123	
Ga1-O	1.840(8)			2.990

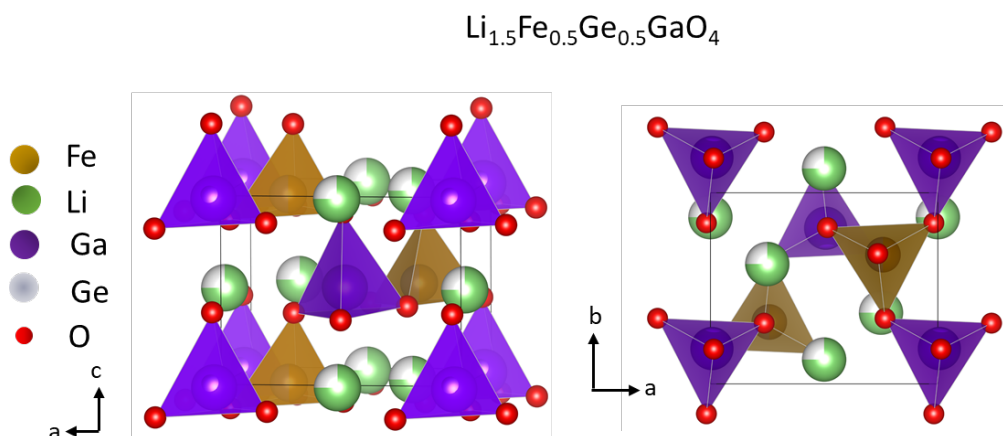


Figure 6. 18. Refined structure of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$

Comparison of the structure of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (described in the $Pca2_1$ space group) and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (described in the Pn space group) reveals a structural rearrangement taking place upon lithium exchange. As detailed in Section 6.3.1, the structure of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ contains half of the tetrahedra pointing in one direction and the other half pointing in the opposite direction, which is indicative of the $\gamma\text{-NaFeO}_2$ structure type. Conversely, in the structure described in space group Pn (Figure 6.18), all the tetrahedra are found to point in the same direction, reflecting the trait of the $\beta\text{-NaFeO}_2$ structure type. Thus, a structural transition from $\gamma\text{-NaFeO}_2$ structure type in $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ to the $\beta\text{-NaFeO}_2$ structure type in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ is observed as a result of lithium exchange.

Upon closer examination of the refined structure, it is evident that although a structural change occurs during lithium exchange reaction, the cationic distribution in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ remains unchanged in comparison to $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (Tables 6.7 and 6.15). This implies that, despite the structural rearrangement in $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ upon

lithium exchange which changes the γ -NaFeO₂ structure type to β -NaFeO₂ structure type, the parent topology of Na_{1.5}Fe_{0.5}Ge_{0.5}GaO₄ is largely retained in Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄.

<Fe-O> bond lengths determined from the structure of Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄ are found to slightly elongated than the corresponding Na_{1.5}Fe_{0.5}Ge_{0.5}GaO₄ phase. A similar increase in <Fe-O> bond lengths was observed for Li_{1.5}Fe_{0.5}Si_{0.5}AlO₄ and Li_{1.5}FeGe_{0.5}GaO₄ phases (section 6.3.2.1) in comparison to the corresponding Na-precursor phases. This elongation of tetrahedral <Fe-O> bond lengths after lithium exchange is found to be a common feature in the aliovalent doped AFeO₂ materials.

Based on the analysis of the NPD data from $A_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O_4$ phases, it is observed that during the lithium exchange process, each aliovalent-doped NaFeO₂ sample (Na_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄) undergoes a structural rearrangement from the structure described in *Pca*2₁ space group to either a structure described in the *Pc* space group (new γ -NaFeO₂ structure variant) or in the *Pn* space group (ordered T-LiFeO₂ structure type).

Figure 6.19 shows the structure of Li_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ phases with Fe/M/NO₄ tetrahedra forming zig-zag chain which run along the *c* axis of the structure described in *Pc* space-group and along *a* axis of the structure described in *Pc* space-group. Notably the patterns of the zig-zag chains observed for Li_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ are distinct from the corresponding Na_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ phases (Figure 6.11). Introducing the A, B, C, and D type classification (similar to Na_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ phases) to the tetrahedral sites present in the lithium-exchanged sample (Li_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄) reveals that, in the structure described in space group *Pc*, A, B, C, and D sites split into eight sites (A1, A2, B1, B2, C1, C2, D1, and D2). Conversely, for the structure described in the *Pn* space group, the four independent sites merge into two independent sites with the conditions A=D and B=C. The distribution of cations in the lithium-exchanged phase with A, B, C, and D classification is presented in Table 6.15.

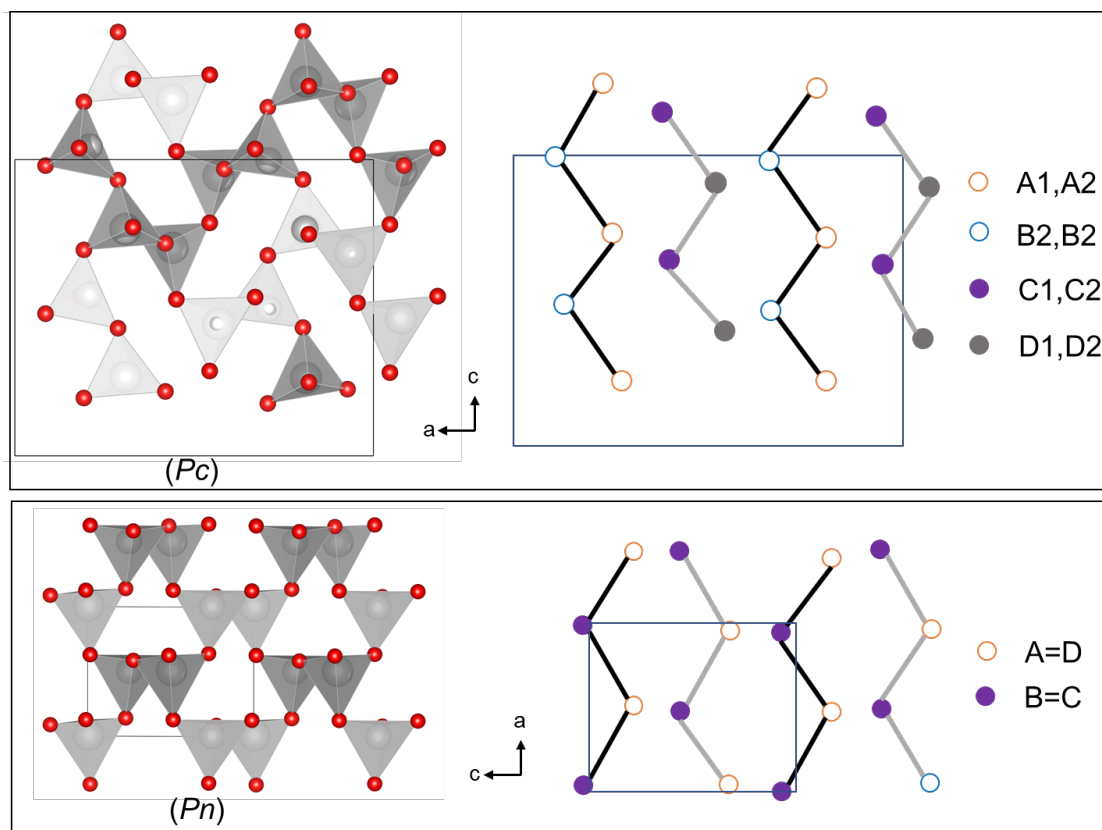


Figure 6. 19. Structure of $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phase, showing only the Fe/M/ NO_4 tetrahedral site (left). The tetrahedral sites in the structure are designated as A, B, C and D. Top: structure described in space group Pn . Bottom: Structure described in space group Pc .

Table 6.15. Distribution of cations in the aliovalent doped LiFeO_2 samples

Composition	Structure (Pn)	
	B = C (2a)	A = D (2a)
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	Ga	Fe/Ge (1:1)

Composition	Structure (Pc)			
	Site A (2a) (A1, A2)	Site B (2a) (B1, B2)	Site C (2a) (C1, C2)	Site D (2a) (D1, D2)
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	Fe/Al (1:3)	Si	Fe/Al (1:3)	Fe/Al (1:3)
$\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$	Fe/Ge (1:1)	Fe	Ga	Fe/Ge (1:1)

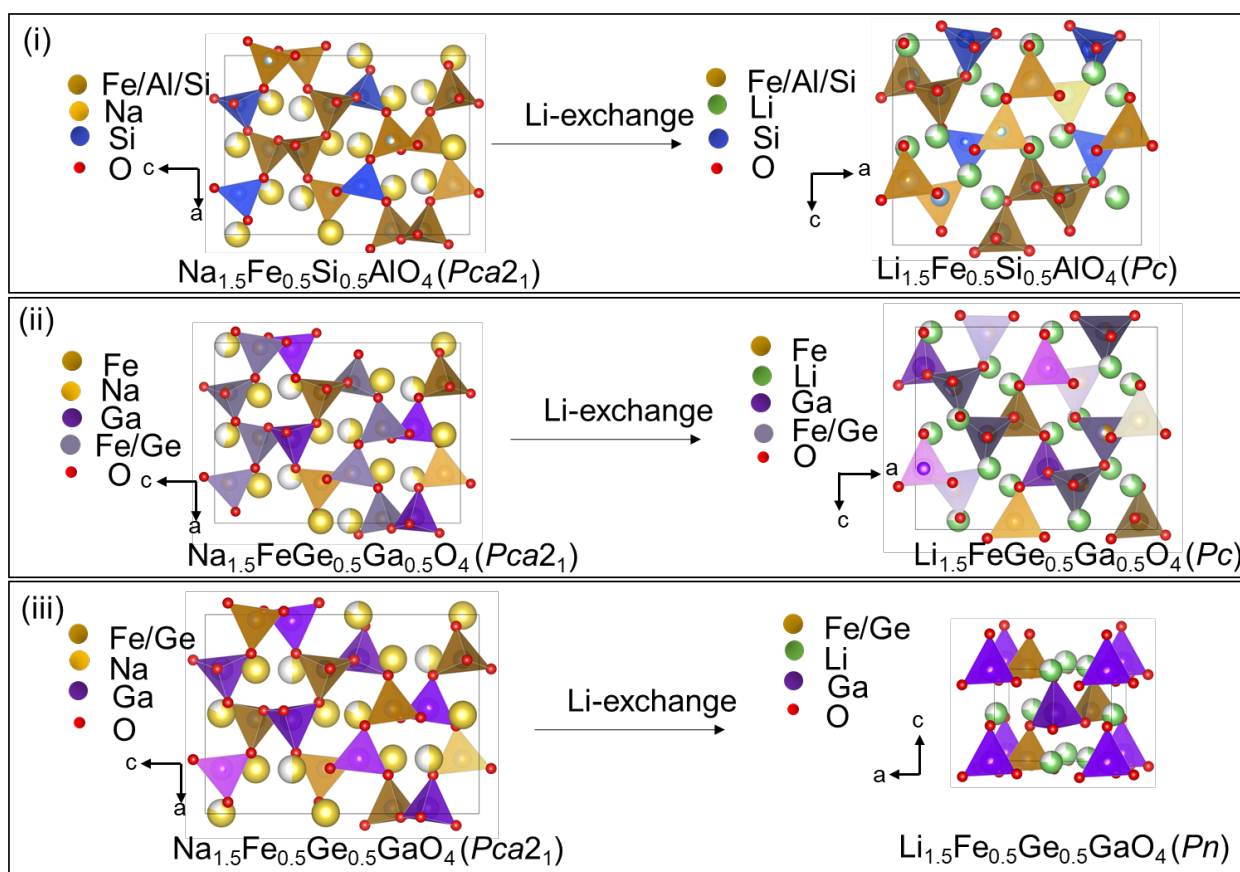


Figure 6. 20. Schematics of structural change during lithium exchange. (i) Structural change from $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ to $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (ii) structural change from $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ to $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, (iii) structural change from $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ to $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$.

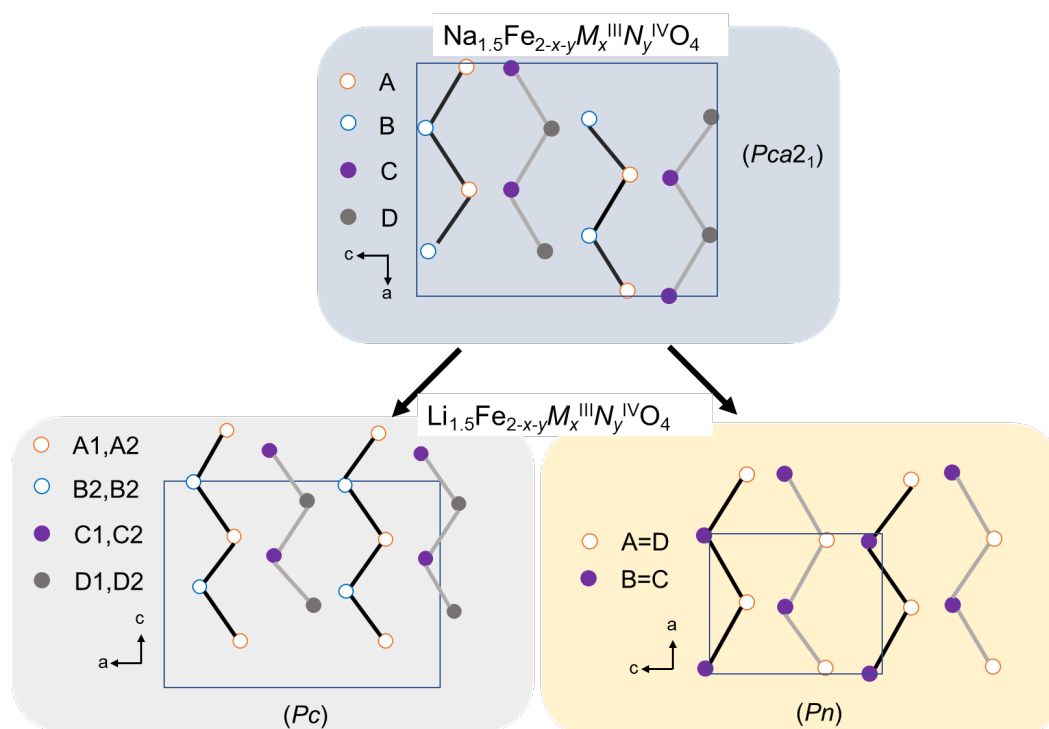


Figure 6. 21. Comparison of the zig-zag chains in $Pca2_1$, Pc and Pn structure types, as observed in $\text{A}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases

6.4. Discussion

Through the structural characterization of $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases, it is evident that aliovalent substitution in NaFeO_2 , induces the formation of a distorted $\gamma\text{-NaFeO}_2$ -type structure ($Pca2_1$ space-group), characterized by the complete ordering of zig-zag chains running along the a axis of the unit cell. A preference of $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases to adopt the structure described in the $Pca2_1$ space group over the structure described in the $Pbca$ space group was observed which can be explained on the basis of minimum charge repulsion.

The structure described in the $Pbca$ space group contain the $8c$ sites adjacent to each other (e.g., Fe1-Fe1 and Fe2-Fe2, Figure 6.2), whereas the structure described in $Pca2_1$ space group contain the $4a$ sites well separated (Figure 6.2) which minimises the intra cation repulsion between Fe-Fe, M - M or N - N cations. Hence, the structure described in $Pca2_1$ space group is preferred for $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases.

In Section 6.3.2, the structural rearrangement from $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases to corresponding $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases during the lithium exchange are detailed. Upon exchanging the sodium cations by lithium, $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, undergo a structural transformation from $Pca2_1$ to Pc , accompanied by the translation of the zig-zag chain. However, both the phases after lithium exchange retain the trait of the $\gamma\text{-NaFeO}_2$ structure, with half of the tetrahedra pointing in one direction and the other half pointing in the opposite direction. On the other hand, $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, also undergoes a structural transformation from $Pca2_1$ to Pn symmetry, accompanied by the translation of the zig-zag chain. Furthermore, it additionally acquires the trait of the $\beta\text{-NaFeO}_2$ structure rather than the $\gamma\text{-NaFeO}_2$ where all the tetrahedra point in one direction.

Figures 6.20 and 6.21 illustrates the structural changes and the relaxation of the zig-zag chains as observed from $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ to $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ due to lithium

exchange. It is evident that the content of the A, B, C, D sites of $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ is preserved in $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ after the exchange reaction and the cation exchange process is associated with the translation of the zig-zag lines in the a/c axis of the unit cell. This movement results in a partial rearrangement of the structure, leading to the description of the resulting structure in either the Pn or Pc space group.

The retention of $\gamma\text{-NaFeO}_2$ structure type during the lithium exchange from $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ to $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, and transformation of $\gamma\text{-NaFeO}_2$ structure to $\beta\text{-NaFeO}_2$ structure type during the lithium exchange from $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ to $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ can be rationalized on the basis of structures of LiAlO_2 ($P4_12_12$ space group, $\gamma\text{-NaFeO}_2$ type)¹⁷⁵, LiGaO_2 ($Pna2_1$ space group, $\beta\text{-NaFeO}_2$ type)¹⁷⁶.

The structure of LiAlO_2 , exhibits features consistent with the structure of $\gamma\text{-NaFeO}_2$. Therefore, it is reasonable to infer that aluminium rich sample, i.e., $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, retain the $\gamma\text{-NaFeO}_2$ framework after lithium exchange.

Conversely, the structure of LiGaO_2 exhibits features consistent with the structure of $\beta\text{-NaFeO}_2$. Hence, it is reasonable to conclude that the gallium-rich sample, i.e., $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, adopt the ordered $\beta\text{-NaFeO}_2$ structural framework after lithium exchange.

However, this argument does not explain the retention of $\gamma\text{-NaFeO}_2$ structure type during the lithium exchange from $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ to $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ indicating that there are additional factors responsible for the structural transition in aliovalent doped NaFeO_2 materials during lithium exchange reactions.

Chapter 7 – Reduction of $A_{1.5}Fe_{2-x-y}M_x^{III}N_y^{IV}O_4$ phases ($A = Na, Li$)

7.1. Introduction

Sodium naphthalenide has an electrode potential of -0.39 V vs the Na^+/Na redox couple¹⁷⁷ and *n*-butyl lithium (BuLi) has an electrode potential of 1.04 V vs the Li^+/Li redox couple¹⁵⁵. Hence, reductive Na^+ and Li^+ insertion reactions with sodium naphthalenide and *n*-BuLi respectively, can be considered as chemical equivalents of the electrochemical discharge processes of cathode materials in Na/Li-ion batteries¹⁰⁷.

Sodium intercalation into $Na_{1.5}FeGe_{0.5}Ga_{0.5}O_4$ was achieved through treatment with sodium naphthalenide in THF, while lithium insertion into $Li_{1.5}Fe_{0.5}Si_{0.5}AlO_4$, $Li_{1.5}FeGe_{0.5}Ga_{0.5}O_4$, and $Li_{1.5}Fe_{0.5}Ge_{0.5}GaO_4$ was achieved through treatment with *n*-BuLi in hexane. The resulting products were characterized using SXRD, NPD, XAS, and iodometric titrations techniques. The outcomes derived from these analyses are detailed within this chapter. Furthermore, the electrochemical behaviour of $Li_{1.5}FeGe_{0.5}Ga_{0.5}O_4$ is also described and discussed.

7.2. Experimental section

7.2.1. Sodium intercalation in $Na_{1.5}FeGe_{0.5}Ga_{0.5}O_4$

Initially, a 1.0 M sodium naphthalenide solution was prepared by mixing 1.1 : 1 molar ratios of metallic sodium and naphthalene powder (99%, Sigma Aldrich) within a Schlenk tube inside a glovebox. The Schlenk tube was sealed with a glass cap and transferred to a Schlenk line under a nitrogen atmosphere. 10 mL of dry tetrahydrofuran (THF) was introduced into the Schlenk tube, and the tube was sealed with a glass cap. The mixture within the Schlenk tube were stirred for 12 hours.

Approximately 200 mg of a $Na_{1.5}FeGe_{0.5}Ga_{0.5}O_4$ sample was introduced into the Schlenk tube, maintaining a 1:5 molar ratio of $Na_{1.5}FeGe_{0.5}Ga_{0.5}O_4$: Na-naphthalenide. The

tube was then sealed, and the contents inside were stirred for 48 hours. The contents inside were washed and filtered with excess THF under nitrogen. The sodiated powders were dried using a vacuum line and subsequently transferred into the glovebox for storage.

To evaluate the reversibility of sodium intercalation, the sodiated sample was treated with a known concentration of iodine in acetonitrile. Following the reaction, the remaining iodine was titrated against a standardized thiosulphate solution.

7.2.2. Lithium intercalation in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$

Approximately 200 mg of each aliovalent doped LiFeO_2 sample was placed in a small Schlenk tube under a nitrogen atmosphere. Then, 6-8 mL of a 1.6 M solution of *n*-BuLi in *n*-hexanes (Merck Life Sciences) was added to achieve a 1:5 molar ratio of $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$: *n*-BuLi. The tube was sealed with a glass cap, and the contents inside were stirred at room temperature for 48 hours. A colour change of the powder from orange/dark brown to black was observed. The black suspension was filtered and washed with excess toluene under nitrogen. Finally, the black powder was dried using a vacuum line and transferred into an argon-filled glove-box.

To evaluate the reversibility of lithium intercalation, the lithiated samples were treated with a known concentration of iodine in acetonitrile. Following the reaction, the remaining iodine was titrated against a standardized thiosulphate solution.

7.2.3. Galvanostatic measurements

A mixture with a 80:10:10 mass ratio of $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$: carbon black : polyvinylidene fluoride (PVDF) was weighed and ground into a fine powder. 0.3 mL of 1-methyl-2-pyrrolidone (NMP) was then added and the mixture was mechanically shaken until a homogeneous viscous slurry was obtained. The slurry was poured onto a carbon-coated

aluminium foil and first dried in air and then heated for 12 hours at 80°C in a vacuum oven. The dry slurry cast was cut into 12 mm disc cathodes and transferred into the glovebox. A coin cell was assembled using Cambridge Energy Solutions SS316 CR2032 coin cell cases, a lithium chip (15.6 mm diameter, 0.25 mm thick), a Whatman glass fiber membrane separator (16mm diameter), and the cast cathode. The separator was soaked with 10 μ L of electrolyte and the coin cell was sealed. Cyclic voltammograms and charge-discharge capacity profile measurements were conducted after assembling the coin cell.

7.3. Results and discussion for sodiated $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$

7.3.1. Structural characterization

Synchrotron X-ray diffraction (SXR) and Neutron powder diffraction (NPD) data

Room temperature SXR data were collected from sodiated $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. A comparison of the SXR data from $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ and $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ (Figure 7.1) reveals that the diffraction peak of $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ at $2\theta \sim 11^\circ$ is split into two peaks in the SXR pattern collected from $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. The SXR data from $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ could not be indexed using the unit cell parameters of pristine $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ phase indicating either a non-topochemical structural change or conservation of the parent topology but the breaking of symmetry occurs upon sodiation.

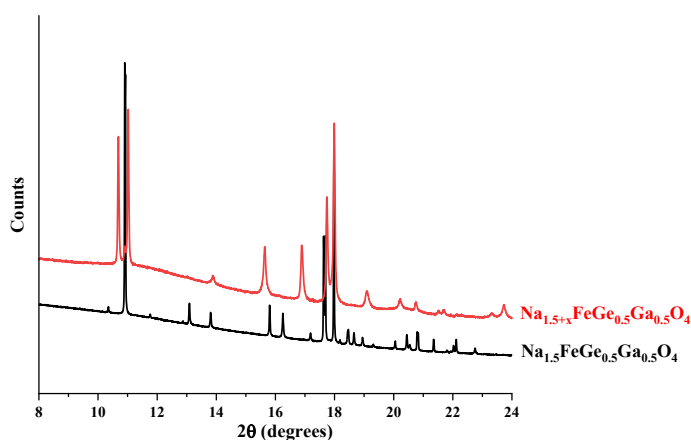


Figure 7. 1. Plot of SXR data collected from $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ and $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$

For detailed structural characterization, NPD data were collected from sodiated $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. These data were indexed using a triclinic unit cell with reflection conditions consistent with the $P1$ space group. The triclinic unit cell can be related to the ordered T-LiFeO_2 structural model (described in Pn space group)¹⁵³ by lowering the symmetry from Pn to $P1$ space group. Thus, prior to the structural refinement, a structural model based on the ordered T-LiFeO_2 structure described in space group Pn , were constructed where the Li sites were replaced with Na sites, and the Fe sites were replaced with Fe/Ga/Ge sites according to the composition of the phase. The symmetry of this structural model was reduced to $P1$ using the ISODISTORT program¹⁷⁴. The resultant structural model was refined against the data to achieve good fits as shown in Figure 7.2, with crystallographic parameters given in Table 7.1.

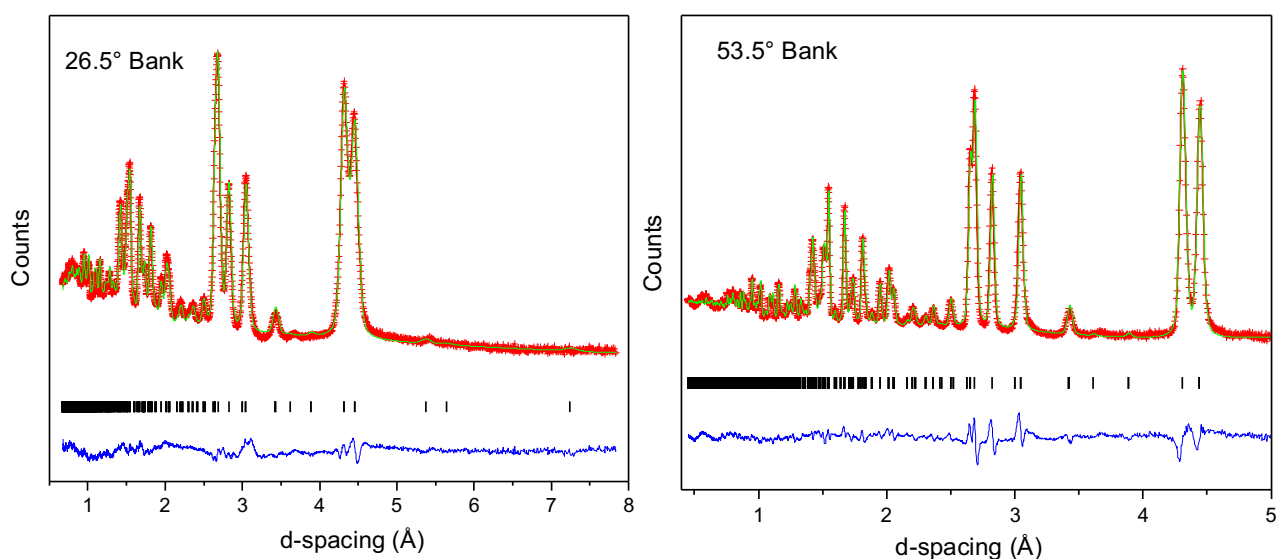


Figure 7. 2. Observed, calculated and difference plots from the structural refinement of $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ against NPD data, bank 26.5° (left), bank 53.5° (right)

Table 7.1. Parameters from the structural refinement of Na_{2.32}FeGe_{0.5}Ga_{0.5}O₄ against neutron powder diffraction data

Atom	site	<i>x</i>	<i>y</i>	<i>z</i>	Fraction	B _{iso}
Na1	1 <i>a</i>	0.4328(5)	0.1224(6)	0.4810(6)	1	0.88(6)
Na2	1 <i>a</i>	0.5672(5)	0.8776(6)	0.9810(6)	1	0.88(6)
Na3	1 <i>a</i>	0.9328(5)	0.3776(6)	0.4810(6)	1	0.88(6)
Na4	1 <i>a</i>	0.0672(5)	0.6224(6)	0.9810(6)	1	0.88(6)
Na5	1 <i>a</i>	0.2935(33)	0.8405(26)	0.3862(32)	0.32(6)	0.88(6)
Na6	1 <i>a</i>	0.7065(33)	0.1596(26)	0.8862(32)	0.33(6)	0.88(6)
Fe1/Ge1	1 <i>a</i>	0.0629(2)	0.1254(2)	0.9929(44)	1	0.68(3)
Fe2/Ge2	1 <i>a</i>	0.5629(2)	0.3746(2)	0.0072(63)	0.5/0.5	0.68(1)
Fe3	1 <i>a</i>	0.4370(2)	0.6254(2)	0.5031(60)	0.5/0.5	0.37(1)
Ga1	1 <i>a</i>	0.9370(2)	0.8746(28)	0.5030(65)	1	0.45(1)
O1	1 <i>a</i>	0.0337(4)	0.0912(3)	0.3471(2)	1	0.9(1)
O2	1 <i>a</i>	0.9662(4)	0.9087(3)	0.8472(2)	1	0.9(1)
O3	1 <i>a</i>	0.5337(4)	0.4087(3)	0.3472(2)	1	0.9(1)
O4	1 <i>a</i>	0.4662(3)	0.5912(3)	0.8471(2)	1	0.9(1)
O5	1 <i>a</i>	0.3844(3)	0.1678(3)	0.9189(3)	1	0.9(1)
O6	1 <i>a</i>	0.6155(3)	0.8322(3)	0.4189(3)	1	0.9(1)
O7	1 <i>a</i>	0.8845(3)	0.3322(3)	0.9189(3)	1	0.9(1)
O8	1 <i>a</i>	0.1155(3)	0.6678(3)	0.4189(3)	1	0.9(1)
Na _{2.32} FeGe _{0.5} Ga _{0.5} O ₄ – space group <i>P</i> 1 (#1) <i>a</i> = 5.6161(1) Å, <i>b</i> = 7.1990(1) Å, <i>c</i> = 5.3476(1) Å, <i>α</i> = 89.999(4)°, <i>β</i> = 90.0002(4)°, <i>γ</i> = 89.999(4)°, volume = 216.237 (9) Å ³ Formula weight= 244.231 g mol ⁻¹ , <i>Z</i> = 2 Radiation source: neutron, Time of flight Temperature: 298 K <i>R</i> _p = 2.55 %, <i>wR</i> _p =3.73 %						

Table 7.2. Bond lengths and BVS parameter table for Na_{2.32}FeGe_{0.5}Ga_{0.5}O₄

Bonds	Average <Fe-O> /<Al-O> (Å)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1-O	1.865(9)	3.002		
Fe2/Ge1-O	1.862(9)	3.000	2.947	
Fe3/Ge2-O	1.865(8)	3.002	2.945	
Ga1-O	1.862(8)			2.798

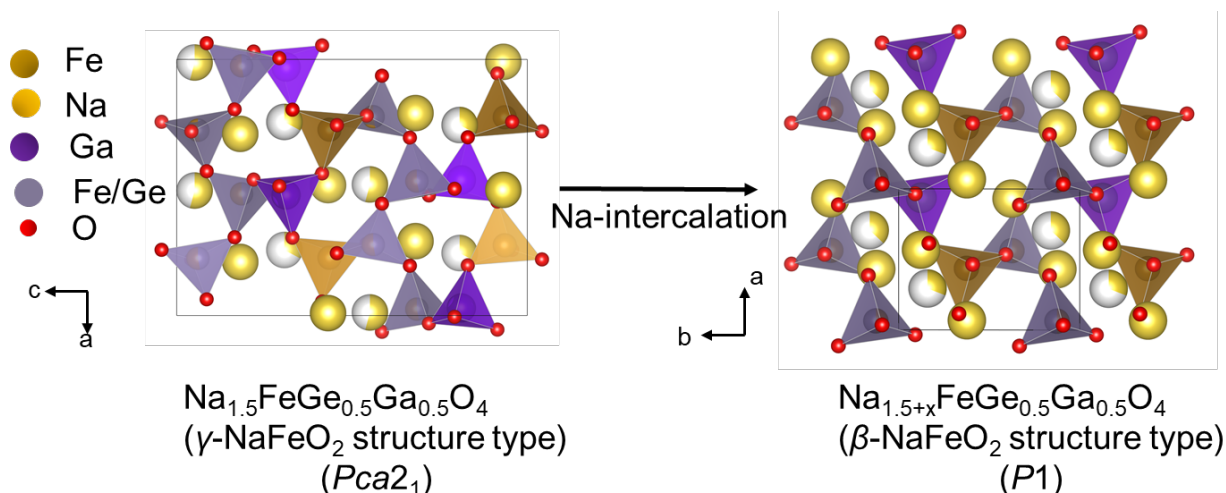


Figure 7. 3. Schematics of the structural transformation from $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ to $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$

A close inspection of the structural model obtained for reduced $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ reveals a structural rearrangement has occurred on sodium insertion into pristine $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$. In Section 6.4, it was observed that pristine $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ exhibits a structure analogous to $\gamma\text{-NaFeO}_2$, where half of the MO_4 ($M = \text{Fe/Ge/Ga}$) tetrahedra point in one direction (i.e., up), and the other half point in the opposite direction (i.e., down) along the c -axis. Conversely, in the structure of reduced $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, all the MO_4 ($M = \text{Fe/Ge/Ga}$) tetrahedra uniformly point in one direction (i.e., up) along the c axis, exhibiting a structure analogous to that of $\beta\text{-NaFeO}_2$ (Figure 7.2). This structural transformation from the $\gamma\text{-NaFeO}_2$ -type $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ to the $\beta\text{-NaFeO}_2$ -type $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ is shown in Figure 7.3. In addition, a detailed examination of the refined structural models for $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ and $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ reveals that the cation distributions and ordering are unchanged upon sodiation.

Within the structure of pristine $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, vacant Na-sites are present (Section 6.4). During the structural refinement, the occupancy of these existing Na-sites was refined. In addition, additional Na-cations were placed in the vacant octahedral sites within the framework, sharing faces with the MO_4 ($M = \text{Fe/Ge/Ga}$) tetrahedra. The positions and occupancies of these additional Na-cations were also refined. This refinement indicated that

Na cations were inserted into both the existing Na-vacancies within the structure and also into the additional octahedral sites, resulting in the occupancy parameters of the additional Na⁺ in the octahedral sites having a value of 0.32(6) (Table 7.1). The final composition, determined from the refined structural model was Na_{2.32}FeGe_{0.5}Ga_{0.5}O₄ and was found to be in good agreement with the sodium content determined from the iodometric titrations and ICP-MS analysis (Appendix-I, Tables 7a.1-7a.2).

The <Fe-O> bond lengths and Fe-BVS parameters calculated from the refined structural model of Na_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄ are given in Table 7.2. An increase in <Fe-O> bond lengths and decrease in Fe-BVS parameters in comparison to Na_{1.5}FeGe_{0.5}Ga_{0.5}O₄ is observed, which is consistent with reductive Na-intercalation in Na_{1.5}FeGe_{0.5}Ga_{0.5}O₄.

7.3.2. X-ray absorption spectroscopy (XAS) data

X-ray absorption near edge structure (XANES) data were collected from Na_{1.5}FeGe_{0.5}Ga_{0.5}O₄ and Na_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄ along with FeO and Fe₂O₃. The Fe K-edge XANES data from Fe₂O₃ and FeO were used as references for Fe (III) and Fe (II), respectively. Figure 7.4 presents the normalized XANES data with a specific focus on changes in the iron K-edge energies induced by chemical sodium intercalation.

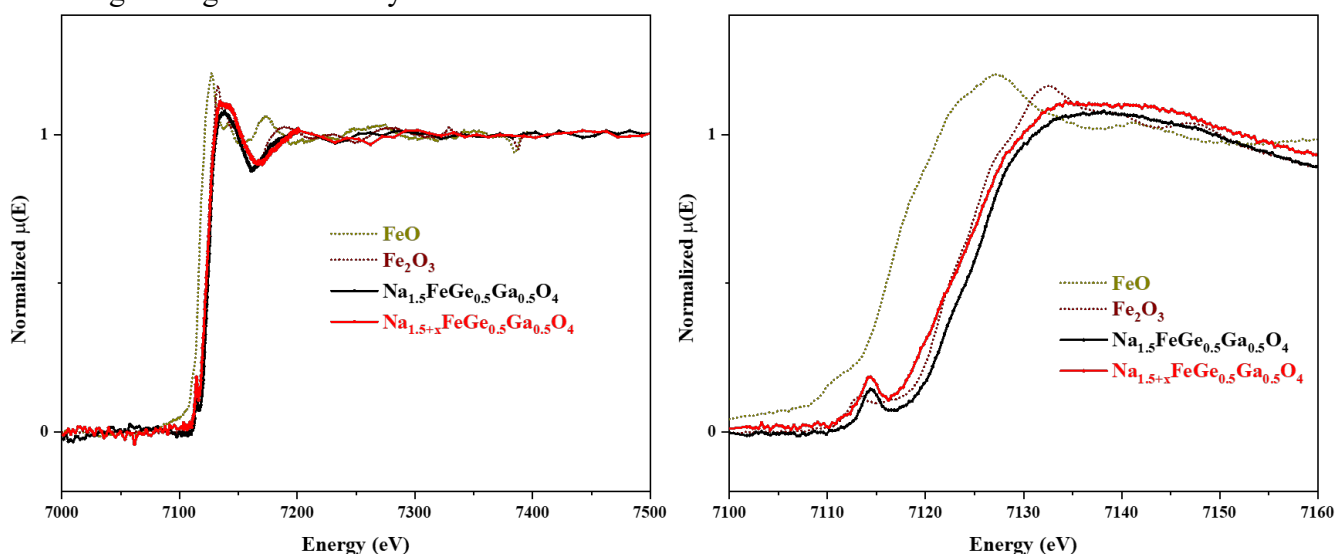


Figure 7. 4. XANES data from Na_{1.5}FeGe_{0.5}Ga_{0.5}O₄ and Na_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄ with references (dotted lines); normalization(left), Fe K-edge comparison(right).

As shown in Figure 7.4, Fe K-edge XANES data from both pristine and sodiated $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ phases, show a characteristic pre-edge feature at energies around ~ 7112 eV, indicative of the presence of FeO_4 tetrahedra in the structure. A comparison of the Fe K-edge between the pristine and sodiated phase reveals a shift towards lower energy for the sodiated material in comparison to pristine material. This shift in the Fe K-edge XANES data is consistent with the reduction of the Fe-cations on sodium intercalation.

7.3.4. Discussion for reduced $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$

Structural characterization of reduced $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ reveals a structural change from a γ - NaFeO_2 to a β - NaFeO_2 structure type on sodium intercalation. However, the cation distribution in $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ before and after sodiation is found to be unchanged. The additional sodium cations inserted on reaction with sodium naphthalenide fill both the sodium vacancies in the tetrahedral sites and the empty octahedral sites in the structure. The Fe-BVS parameters and Fe-XANES data are consistent with reduction of Fe-sites on sodium intercalation.

X-ray diffraction data from the sodiated $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ material after the treatment with I_2 (Appendix-I, Figure 7a.1) show the retention of β - NaFeO_2 structure type indicating the change from γ - NaFeO_2 to β - NaFeO_2 upon sodium intercalation being irreversible in nature, under the oxidising conditions used.

7.4. Results and discussion for lithiated $\text{Li}_{1.5+\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases

7.4.1. Synchrotron X-ray diffraction (SXRD) data

Room temperature synchrotron X-ray diffraction data collected from three chemically reduced aliovalent doped LiFeO_2 samples, henceforth referred to as $\text{Li}_{1.5+\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases, are presented in Figure 7.5. It is found that the crystallinity of the lithiated phases: $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, and $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ is maintained, indicating this level of substitution is sufficient to inhibit the structural decomposition of LiFeO_2 materials under reductive conditions (Section 4.3.3).

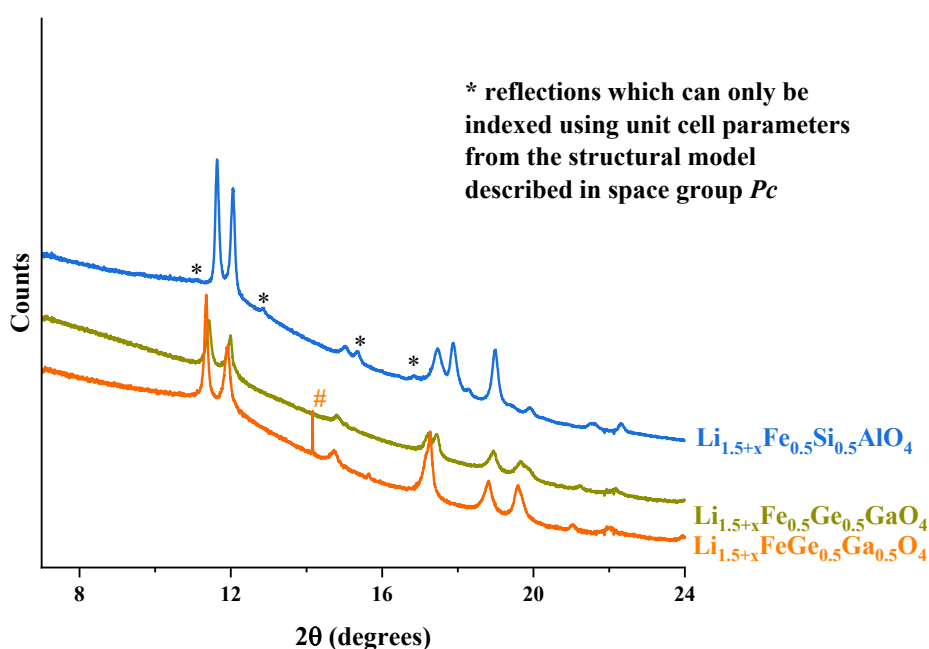


Figure 7. 5. Plot of the collected SXRD data of reduced, aliovalent doped LiFeO_2 samples; * indicate reflections which can only be indexed using the unit cell parameters from the structure described in space group Pc , # indicates peaks from unknown phase

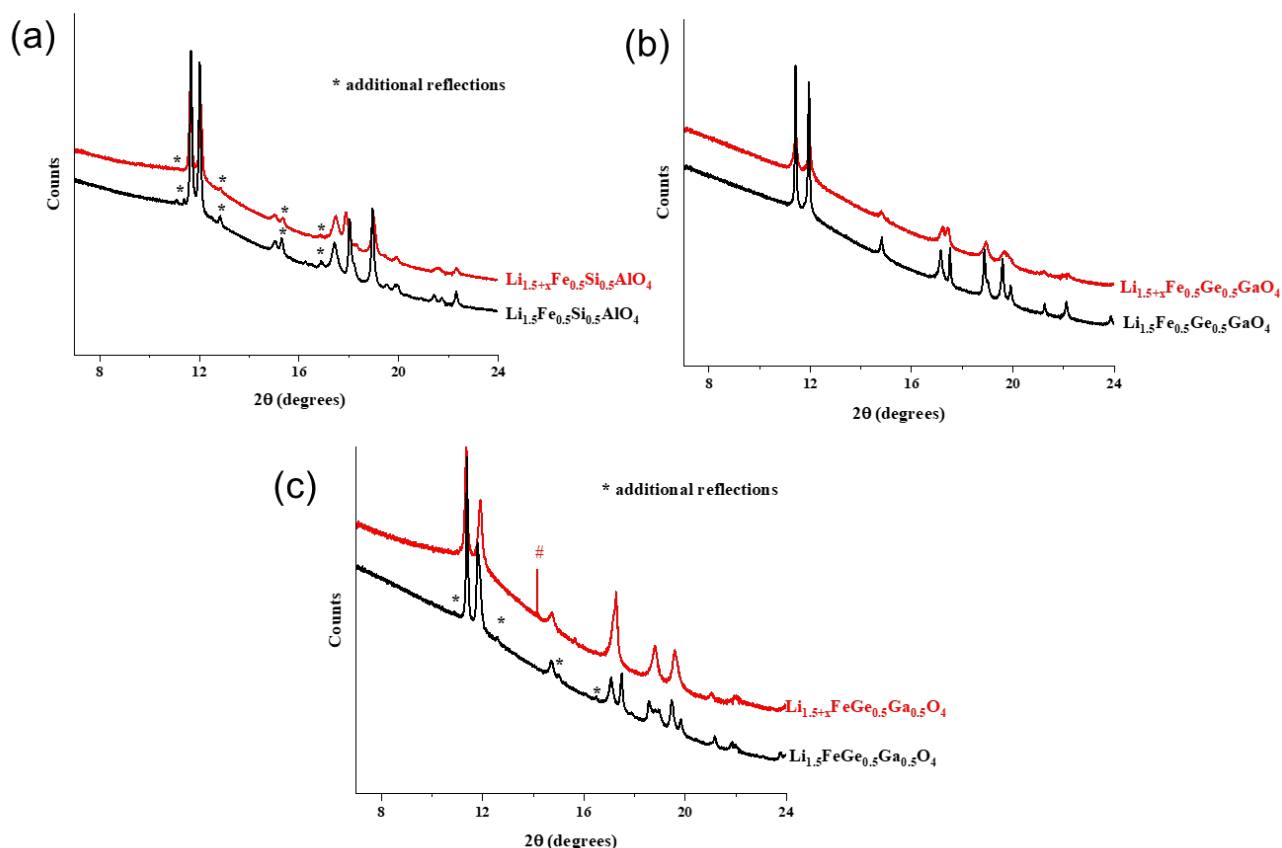


Figure 7. 6. (a) Plot of SXR D data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (b) Plot of SXR D data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, (c) Plot of SXR D data collected from $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$; * indicate reflections which can only be indexed using the unit cell parameters from the structure described in space group Pc , # indicates peaks from unknown phase

In Sections 6.3 and 6.4, it was discussed that both $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ adopt structures described in Pc space group, while $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ adopts a structure described in the Pn space group. The structure of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ are considered as ordered variants of the $\gamma\text{-NaFeO}_2$ structure, whereas the structure of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ is considered as an ordered variant of the $\beta\text{-NaFeO}_2$ structure. SXR D data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ showed reflections at $2\theta = 10.95, 12.84, \text{ and } 15.317^\circ$, indicative of Pc symmetry adoption.

A comparison of the SXR D data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ phases before and after lithiation is shown in Figure 7.6. In the data collected from lithiated $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ (Figure 7.6, a), reflections (at $2\theta = 10.95, 12.84,$

and 15.317°) associated with space group Pc , persist after chemical lithiation. SXRD data collected from $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ exhibits similar diffraction patterns when compared to the SXRD data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (Figure 7.6, b). However, SXRD collected from lithiated $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ shows the absence of reflections (at $2\theta = 10.95$, 12.84 , and 15.317°) associated with Pc symmetry which were evident in the SXRD data from pristine $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ (Figure 7.6, c). This comparison of SXRD data, indicates that $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ undergo no structural rearrangement upon lithium insertion. However, $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ experiences a structural rearrangement during lithium insertion.

7.4.2. Neutron diffraction data (NPD)

To assist with structural determination, neutron powder diffraction (NPD) data were collected at room temperature from the chemically lithiated $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ phases. During the structural refinement of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, a crystallographic model described in the Pc space-group (similar to the pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, Section 6.3.3) was refined against the data to achieve a good fit as shown in Figure 7.8, with crystallographic parameter detailed in Table 7.3.

During the analysis of NPD data collected from the lithiated $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, it was observed that a structural model with “Pristine” composition (i.e., $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ with no additional lithium) fit the data well, making it hard to unambiguously determine the positions of the inserted lithium cations. To address this problem, Fourier difference maps were calculated from the fits of the “Pristine” model to the NPD data. Given the negative neutron scattering length of lithium (-1.90 fm)¹⁷⁸, the additional lithium cations were found by detecting regions in the Fourier difference plots which have the largest negative values. Figure 7.7 displays a plot of the Fourier difference map from $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$. It was observed that the locations of the largest negative scattering density coincided with the locations of the

partially occupied (75% occupation) lithium sites within the “Pristine” structure, suggesting the inserted lithium cations are localised on these sites rather than occupying new sites within the framework. Thus, the structural refinement involved refining the lithium site occupancies rather than adding additional lithium sites, resulting in a final composition of $\text{Li}_2\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, consistent with lithium content determined from iodometric analysis of the lithiated $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ sample (Appendix-I Table 7a.3).

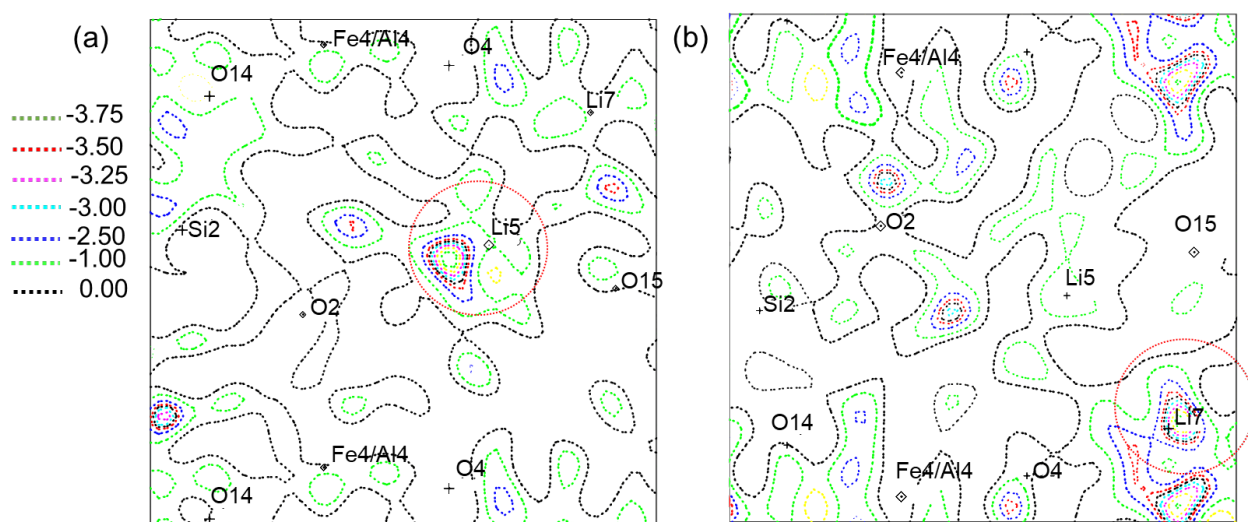


Figure 7. 7. Plot of Fourier difference map calculated during the structural refinement of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ against NPD data. Plots were conducted with centre of reference (0.5, 0.5, 0) with height from the centre 0 Å (a) and 4.75 Å (b). Red dotted circles represent the highest negative scattering density coinciding with the positions of existing lithium atoms in the structure

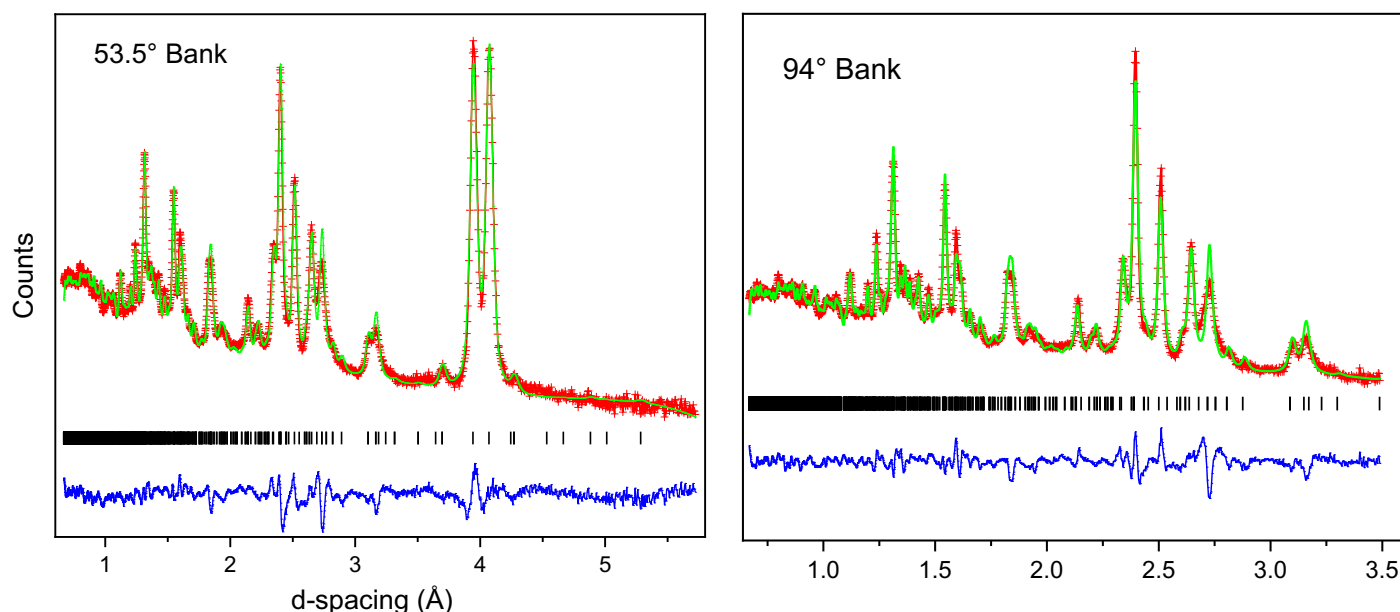


Figure 7. 8. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ against NPD data, bank 53.5° (left), bank 94° (right)

Table 7.3. Parameters from the structural refinement of $\text{Li}_2\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	2a	0.898(1)	0.529(4)	0.756(1)	1	0.51(15)
Li2	2a	0.398(1)	0.470(4)	0.756(1)	1	0.51(15)
Li3	2a	0.817(2)	0.050(4)	0.648(1)	1	0.51(15)
Li4	2a	0.317(2)	0.949(4)	0.648(1)	1	0.51(15)
Li5	2a	0.560(2)	0.455(4)	0.027(1)	1	0.51(15)
Li6	2a	0.060(2)	0.544(4)	0.027(1)	1	0.51(15)
Li7	2a	0.694(1)	0.861(4)	0.968(1)	1	0.51(15)
Li8	2a	0.194(1)	0.139(4)	0.968(1)	1	0.51(15)
Fe1/Al1	2a	0.068(1)	0.057(3)	0.184(1)	0.25/0.75	1.25(7)
Fe2/Al2	2a	0.555(2)	0.905(3)	0.208(1)	0.25/0.75	1.25(7)
Fe3/Al3	2a	0.921(1)	0.967(4)	0.961(2)	0.25/0.75	1.25(7)
Fe4/Al4	2a	0.432(2)	0.040(3)	0.951(2)	0.25/0.75	1.25(7)
Fe5/Al5	2a	0.692(1)	0.599(4)	0.771(2)	0.25/0.75	1.25(7)
Fe6/Al6	2a	0.191(2)	0.405(3)	0.768(2)	0.25/0.75	1.25(7)
Si1	2a	0.791(1)	0.439(7)	0.540(3)	1	0.85(19)
Si2	2a	0.291(1)	0.430(7)	0.540(3)	1	0.85(19)
O1	2a	0.91(1)	0.451(3)	0.830(1)	1	0.60(3)
O2	2a	0.414(2)	0.442(3)	0.968(1)	1	0.60(3)
O3	2a	0.042(2)	0.992(3)	0.111(1)	1	0.60(3)
O4	2a	0.547(1)	0.988(4)	0.029(2)	1	0.60(3)
O5	2a	0.806(2)	0.472(4)	0.695(1)	1	0.60(3)
O6	2a	0.295(2)	0.538(4)	0.676(2)	1	0.60(3)
O7	2a	0.671(1)	0.938(3)	0.775(1)	1	0.60(3)
O8	2a	0.179(2)	0.097(3)	0.749(1)	1	0.60(3)
O9	2a	0.950(2)	0.036(4)	0.778(2)	1	0.60(3)
O10	2a	0.455(2)	0.935(4)	0.788(2)	1	0.60(3)
O11	2a	0.072(2)	0.395(3)	0.225(1)	1	0.60(3)
O12	2a	0.581(2)	0.528(3)	0.215(1)	1	0.60(3)
O13	2a	0.821(1)	0.056(4)	0.536(2)	1	0.60(3)
O14	2a	0.328(1)	0.089(3)	0.534(2)	1	0.60(3)
O15	2a	0.710(2)	0.439(3)	0.929(1)	1	0.60(3)
O16	2a	0.195(1)	0.521(4)	0.933(2)	1	0.60(3)
$\text{Li}_2\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ – space group Pc (#7) $a = 12.6896(8) \text{ \AA}$, $b = 5.0001(3) \text{ \AA}$, $c = 10.5475(6) \text{ \AA}$, $\beta = 90.0804 (14)^\circ$ volume = $669.354 (78) \text{ \AA}^3$ Formula weight = $142.75 \text{ g mol}^{-1}$, $Z = 8$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 2.51 \%$, $wR_p = 3.28 \%$						

Table 7.4. Table of bond lengths and BVS parameters for $\text{Li}_2\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ estimated from structural refinement against NPD data

Bonds	Average <M-O> (Å)	Fe-BVS	Al-BVS	Si-BVS
Fe1/Al1-O	1.809(10)	3.534	2.639	
Fe2/Al2-O	1.846(13)	3.256	2.432	
Fe3/Al3-O	1.791(13)	3.824	2.856	
Fe4/Al4-O	1.816(11)	3.609	2.695	
Fe5/Al5-O	1.751(11)	4.158	3.105	
Fe6/Al6-O	1.757(10)	4.257	3.179	
Si1-O	1.763(11)			3.171
Si2-O	1.710(14)			3.344

NPD data collected from lithiated $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ exhibits similar features to those of pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$. Therefore, similar to the parent $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, a crystallographic model based on a monoclinic cell with Pn symmetry (Section 6.3.3) was refined against the data, resulting a good-fit to the data as shown in Figure 7.10, with crystallographic parameters given in Table 7.5.

The location of additional lithium ions was determined from the largest negative scattering density in the Fourier difference map calculated from the data (Figure 7.9), revealing that the additional lithium ions are situated in the additional octahedral sites ($2a$) sharing faces with nearby MO_4 ($M=\text{Fe/Ge, Ga}$) tetrahedra. Hence, during the structural refinement, the additional lithium ions were initially placed in the $2a$ octahedral sites, and their positions and occupancy parameters refined. This resulted in the composition of the final model refining to $\text{Li}_2\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, matching well with the additional lithium content determined from iodometric titrations (Appendix-I Table 7a.4).

During the structural refinement, the occupancy parameters of the existing Li-sites were also refined which revealed the occupancy parameter of these sites as 0.77(2), indicating the

additional lithium ions do not fill the available vacancy of these existing lithium sites, rather they occupy the empty octahedral sites (2a) in the structure.

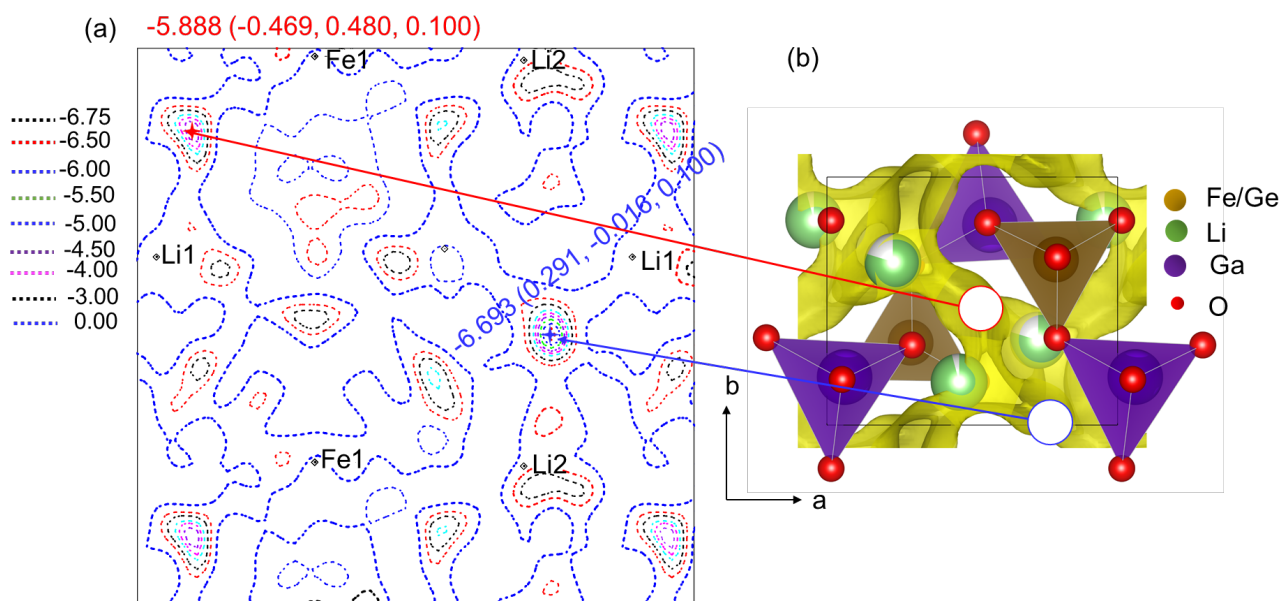


Figure 7.9. Plot of Fourier difference map with centre of reference (0,0,0) and height from the centre 0.5 Å, calculated from the structural refinement of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ against NPD data (a); '+' signs indicate the highest negative scattering density observed in the Fourier difference map. (b) Bond Valence Energy Landscape (BVEL) map for lithium ions within $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ structure. Yellow isosurfaces represent a constant Bond Valence Sum (BVS) value for lithium ions, calculated with a percolation energy of 3 eV. The empty octahedral sites, shown by dotted circles, exhibit the highest density of lithium percolation channels.

The correlations between the highest negative scattering density and highest density of lithium percolations are indicated by red and purple arrows.

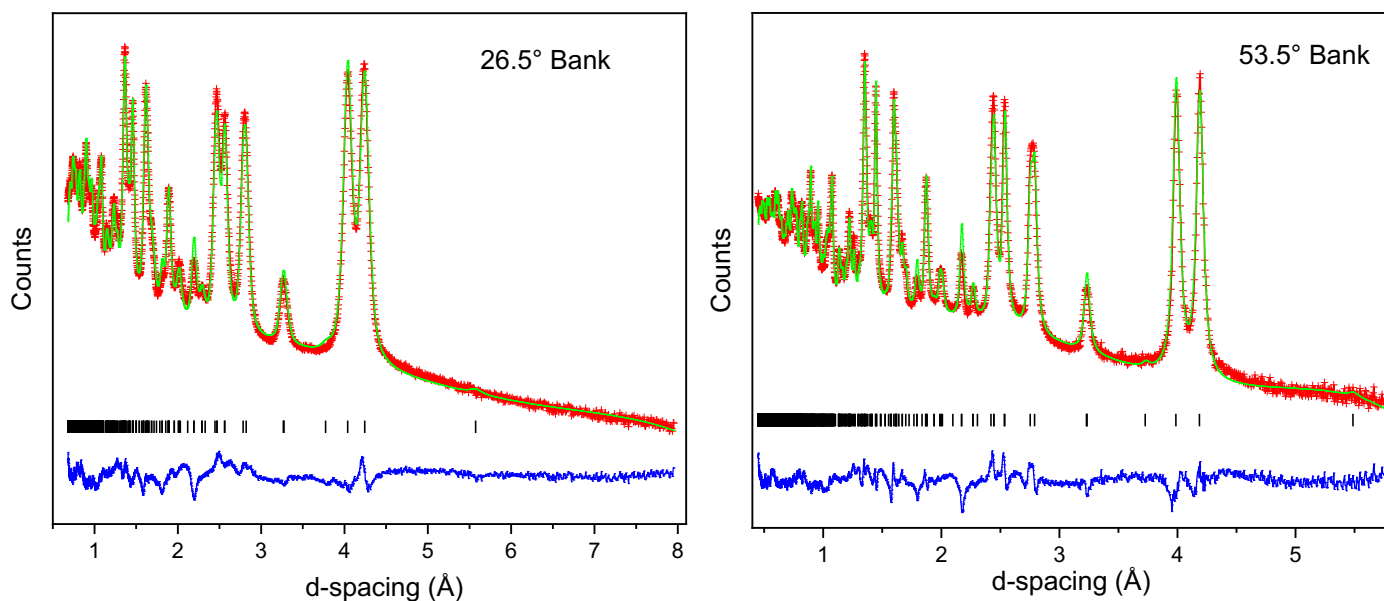


Figure 7.10. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ against NPD data, bank 26.5° (left), bank 53.5° (right)

Table 7.5. Parameters from the structural refinement of $\text{Li}_2\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ sample against neutron powder diffraction data

Atom	site	<i>x</i>	<i>y</i>	<i>z</i>	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	2 <i>a</i>	0.5	0.1513(17)	0.9888(29)	0.75(1)	0.33(12)
Li2	2 <i>a</i>	0.75	0.3486(17)	0.4888(29)	0.75(1)	0.33(12)
Li3	2 <i>a</i>	0.2400(66)	0.9226(27)	0.1259(51)	0.24(1)	0.33(12)
Li4	2 <i>a</i>	0.4931(71)	0.4226(27)	0.1259(51)	0.24(1)	0.33(12)
Ga1	2 <i>a</i>	0.0269(33)	0.1860(11)	0.9922(11)	1	0.99(9)
Fe1/Ge1	2 <i>a</i>	0.2674(32)	0.3297(90)	0.4907(73)	0.5/0.5	0.70(4)
O1	2 <i>a</i>	0.4909(31)	0.1582(11)	0.3919(11)	1	0.07(2)
O2	2 <i>a</i>	0.2745(34)	0.6554(12)	0.3837(13)	1	0.07(2)
O3	2 <i>a</i>	0.0190(32)	0.1911(10)	0.3847(11)	1	0.07(2)
O4	2 <i>a</i>	0.2486(31)	0.3262(12)	0.8472(49)	1	0.07(2)
$\text{Li}_2\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ – space group <i>Pn</i> (#7) $a = 6.4056(4) \text{ \AA}$, $b = 5.4501(2) \text{ \AA}$, $c = 5.0203(3) \text{ \AA}$, $\beta = 89.9638 (10)^\circ$ volume = 175.363 (16) $\text{\AA}^3$ Formula weight = 211.9935 g mol ⁻¹ , <i>Z</i> = 2 Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 1.88 \%$, $wR_p = 2.40 \%$						

Table 7.6. Table of bond lengths and BVS parameters for $\text{Li}_2\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ estimated from structural refinement against NPD data

Bonds	Average <M-O> ($\text{\AA}$)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1/Ge1-O	1.818(5)	3.423	3.232	
Ga1-O	1.902(8)			2.578

SXRD data collected from $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{GaO}_4$ indicated a structural rearrangement occurs on lithium insertion (Section 7.4.1). Based on this observation, the NPD data collected from $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ were indexed with a monoclinic unit cell with *Pn* symmetry, similar to the ordered T-LiFeO₂ structure¹⁵³. Thus prior to the structural refinement, a structural model based on the ordered T-LiFeO₂ structure was constructed where both the Fe sites were replaced with disordered Fe/Ga and Fe/Ge sites. This model was refined against the data to achieve good fits as shown in Figure 7.12 with crystallographic parameters given in Table 7.7.

To determine the location of the inserted lithium ions, Fourier difference maps were calculated during the structural refinement of the data against the aforementioned crystallographic model with “Pristine” composition (i.e., $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{GaO}_4$ with no additional

lithium). Figure 7.11 show a plot of the Fourier difference map showing the largest negative scattering density observed which were assigned to the locations of the inserted lithiums. It was found that the additional lithium ions are located in the vacant octahedral sites in the structure sharing faces with adjacent MO_4 ($M = \text{Fe/Ga/Ge}$) tetrahedra. Hence, during the structural determination, the additional lithium ions were initially placed in the $2a$ octahedral sites, and their positions and occupancy parameters were refined. The occupancy parameter of the pre-existing Li-sites were also refined. This refinement led to the composition of the final refined model as $\text{Li}_{2.6(1)}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, which is in good agreement with the lithium content determined from iodometric titrations and ICP-MS data (Appendix-I, Table 7a.3-7a.4). It was found that, upon lithiation in $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, the additional lithium ions not only fill the available vacancy in the existing Li-sites resulting the occupancy parameter 0.84(2) but also partially occupy the empty octahedral sites in the structure.

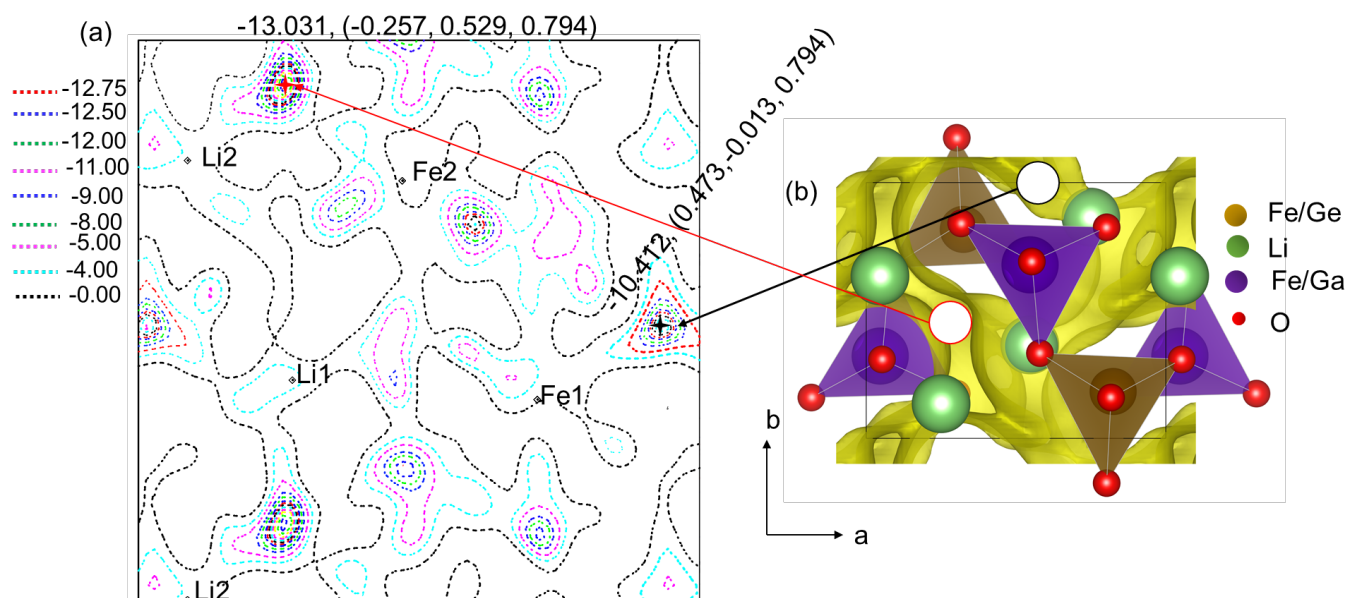


Figure 7. 11. Plot of Fourier difference map with centre of reference (0,0,0) and height from the centre 4.0 Å, calculated from the structural refinement of $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ against NPD data (a); ‘+’ signs indicate the highest negative scattering density observed in the Fourier difference map. (b) Bond Valence Energy Landscape (BVEL) map for lithium ions within $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ structure. Yellow isosurfaces represent a constant Bond Valence Sum (BVS) value for lithium ions, calculated with a percolation energy of 3 eV. The empty octahedral sites, shown by dotted circles, exhibit the highest density of lithium percolation channels.

The correlations between the highest negative scattering density and highest density of lithium percolations are indicated by red and black arrows.

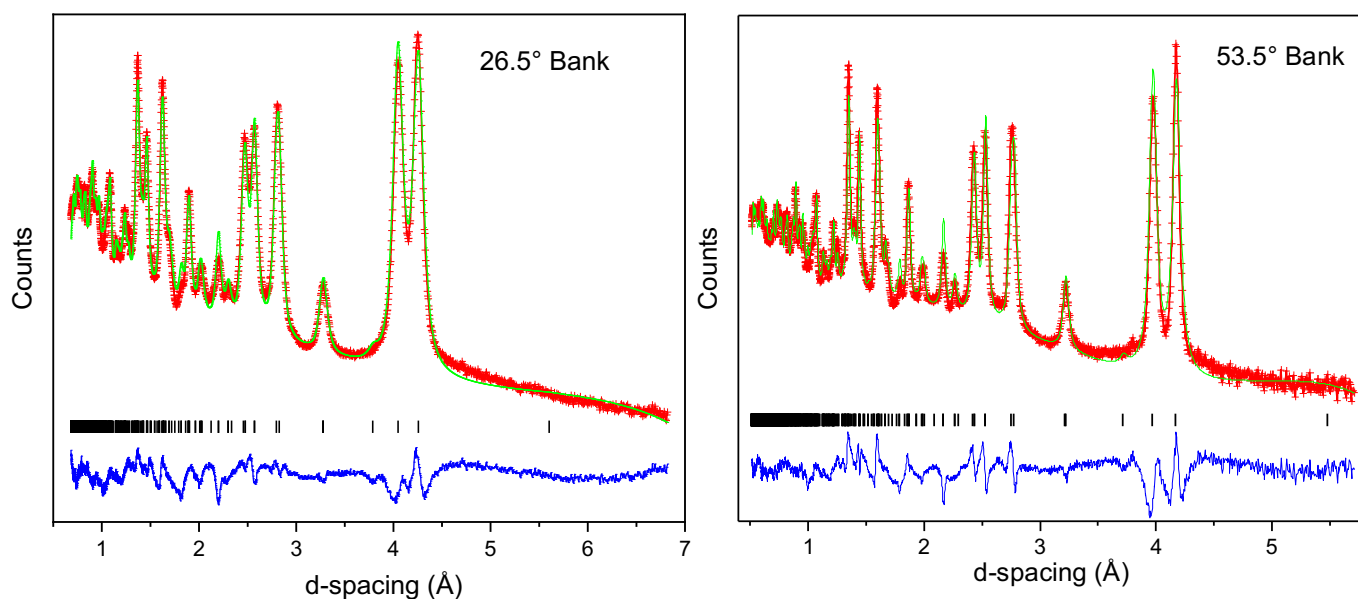


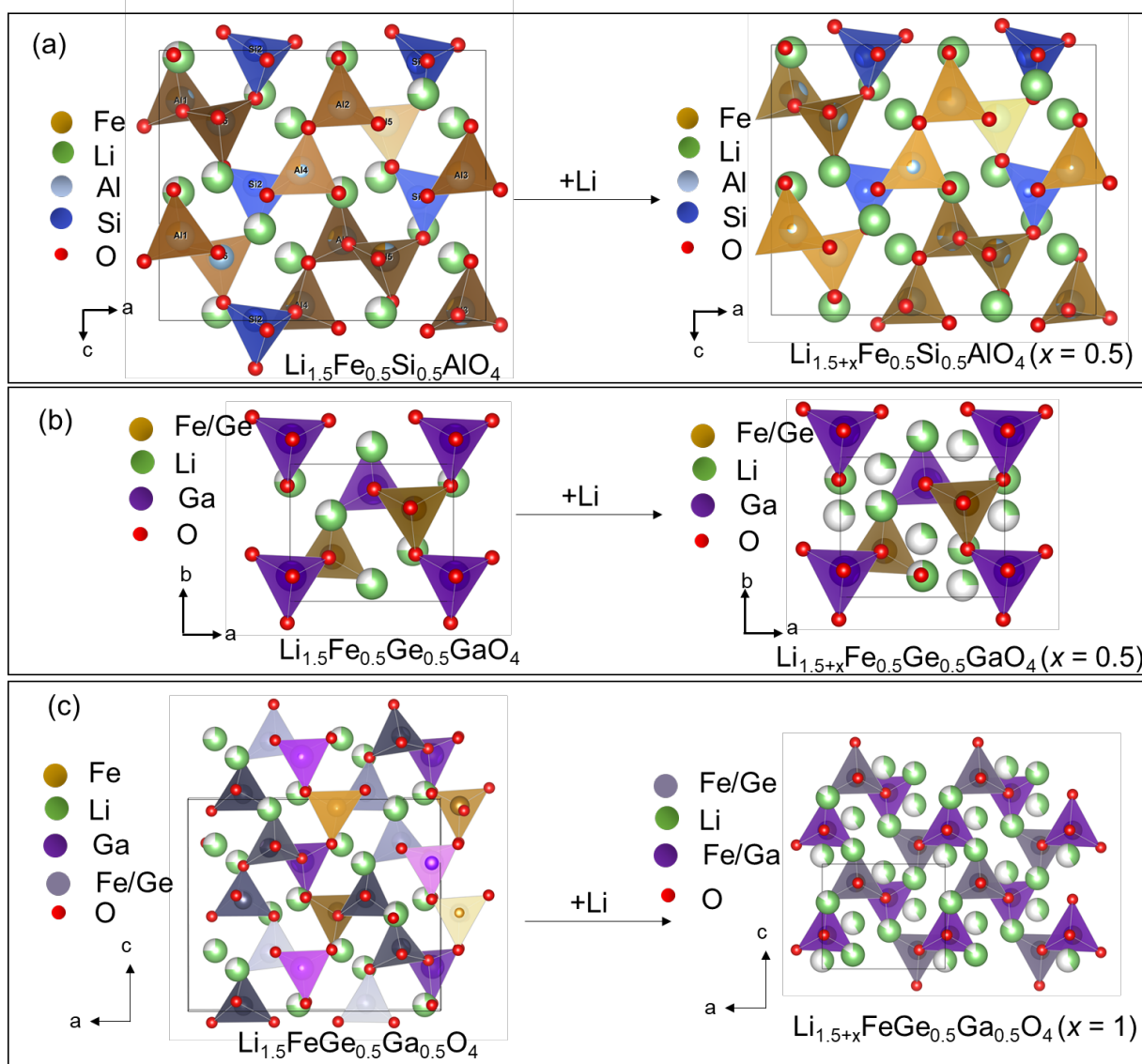
Figure 7.12. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ against NPD data, bank 26.5° (left), bank 53.5° (right)

Table 7.7. Parameters from the structural refinement of $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	2a	0.25	0.1350(19)	0	0.84(2)	0.9(3)
Li2	2a	0.5460(12)	0.3649(19)	0.5	0.84(2)	0.9(3)
Li3	2a	0.75	0.5634(29)	0	0.48(6)	0.9(3)
Li4	2a	0.5	0.9193(38)	0.5	0.48(6)	0.9(3)
Fe1/Ge1	2a	0.7749(20)	0.1779(18)	0.0353(22)	0.5/0.5	0.21(5)
Fe2/Ga1	2a	0.0399(22)	0.3216(19)	0.5682(21)	0.5/0.5	0.21(5)
O1	2a	0.2891(18)	0.1600(25)	0.4299(11)	1	0.58(3)
O2	2a	0.0663(13)	0.6579(24)	0.4789(11)	1	0.58(3)
O3	2a	0.8152(15)	0.1756(24)	0.4409(15)	1	0.58(3)
O4	2a	0.0327(19)	0.3208(24)	0.9330(15)	1	0.58(3)
$\text{Li}_{2.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ – space group Pn (#7) $a = 6.4064(4) \text{ \AA}$, $b = 5.4727(5) \text{ \AA}$, $c = 5.0325(4) \text{ \AA}$, $\beta = 89.6708(13)^\circ$ Volume = 176.445 (31) $\text{\AA}^3$ Formula weight = 215.351 g mol $^{-1}$, $Z = 2$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 3.04 \%$, $wR_p = 3.96 \%$						

Table 7.8. Table of bond lengths and BVS parameters for $\text{Li}_{2.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ estimated from structural refinement against NPD data

Bonds	Average $\langle M\text{-O} \rangle$ (Å)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1/Ge1-O	1.884(7)	2.997	2.764	
Fe2/Ga1-O	1.881(6)	2.889		2.65



A summary of the structural changes observed for $\text{Li}_{1.5+\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases due to lithium intercalation is shown in Figure 7.13. For $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, no structural change is observed. In other words, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ retains the $\gamma\text{-NaFeO}_2$ structure type of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ upon lithiation and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ retains the $\beta\text{-NaFeO}_2$ structure type of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ upon lithiation. The cation distributions of the corresponding pristine phases are also retained in reduced $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ on lithiation.

On the other hand, for lithiated $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, a rearrangement of the structure from $\gamma\text{-NaFeO}_2$ structure type to $\beta\text{-NaFeO}_2$ structure type is observed (Figure 7.13). It is found that the cation ordering in $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ also changed as a result of lithium intercalation. In the structure of pristine $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ described in Pc space group, out of eight MO_4 ($M = \text{Fe/Ge/Ga}$) tetrahedral sites, four sites are shared by Fe/Ge, two sites are independently occupied by Fe and the remaining two sites are independently occupied by Ga. Whereas, in the structure of lithiated $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ described in Pn space group, out of two MO_4 ($M = \text{Fe/Ge/Ga}$) tetrahedral sites, one tetrahedral site is shared by Fe/Ge and the other tetrahedral site is shared by Fe/Ga. Both the disorder of Fe/Ga and Fe/Ge cations is observed in $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ as a result of lithium intercalation.

NPD data additionally reveals that for $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, the vacant tetrahedral Li-sites ($2a$ site symmetry) are filled due to lithium insertion; on the other hand, for $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ the additional lithium inserted occupies the empty octahedral sites ($2a$ site symmetry) rather than filling the tetrahedral Li-vacancy already present in the structure. For $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, the additional lithium ions fill both the available vacancy of the tetrahedral sites in the structure as well as occupy the empty octahedral site in the structure.

Tables 7.4, 7.6, and 7.8 provide details on the $\langle M-O \rangle$ bond lengths and M -BVS parameters derived from the crystallographic model subsequent to structural refinement. In the case of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, an increase in $\langle \text{Fe-O} \rangle$ bond lengths and a concurrent decrease in Fe-BVS parameters are observed compared to the pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, respectively. This trend aligns with the anticipated reduction of the Fe-site resulting from lithium intercalation.

Conversely, for $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{Ga}_{0.5}\text{O}_4$, an intriguing decrease in Fe-O bond lengths and an increase in Fe-BVS are observed in comparison to $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{Ga}_{0.5}\text{O}_4$ (Table 7.6). This observation contradicts the expected trend, and its complexity is attributed to the presence of Fe/Ge disorder in the system. The NPD data, sensitive to changes in the average structure, likely captures the impact of this disorder, contributing to the unconventional observation.

7.4.3. X-ray absorption spectroscopy (XAS)

Fe-XANES: X-ray absorption near edge structure (XANES) data were collected from both lithiated ($\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{Ga}_{0.5}\text{O}_4$, $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$) and pristine ($\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{Ga}_{0.5}\text{O}_4$, $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$) $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ samples, in addition to reference materials Fe_2O_3 and FeO . The Fe K-edge XANES data from Fe_2O_3 and FeO were employed as references for Fe (III) and Fe (II), respectively. Figures 7.14, 7.15, and 7.16 present the normalized XANES data for the $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ samples, with a specific focus on changes in the iron K-edge energies induced by chemical lithium intercalation.

Fe K-edge XANES data from both pristine and lithiated $\text{Li}_{1.5+\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases, as depicted in Figures 7.14, 7.15, and 7.16, show a characteristic pre-edge feature at energies around ~ 7112 eV, indicative of the presence of FeO_4 tetrahedra in the structure. A comparison of the Fe K-edge between the pristine and lithiated phases reveals a shift towards lower energy for all lithiated samples ($\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{Ga}_{0.5}\text{O}_4$, $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$) in comparison to their respective pristine counterparts ($\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{Ga}_{0.5}\text{O}_4$,

$\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$). This shift in the Fe K-edge XANES data is consistent with the reduction of the Fe-site induced by lithium intercalation.

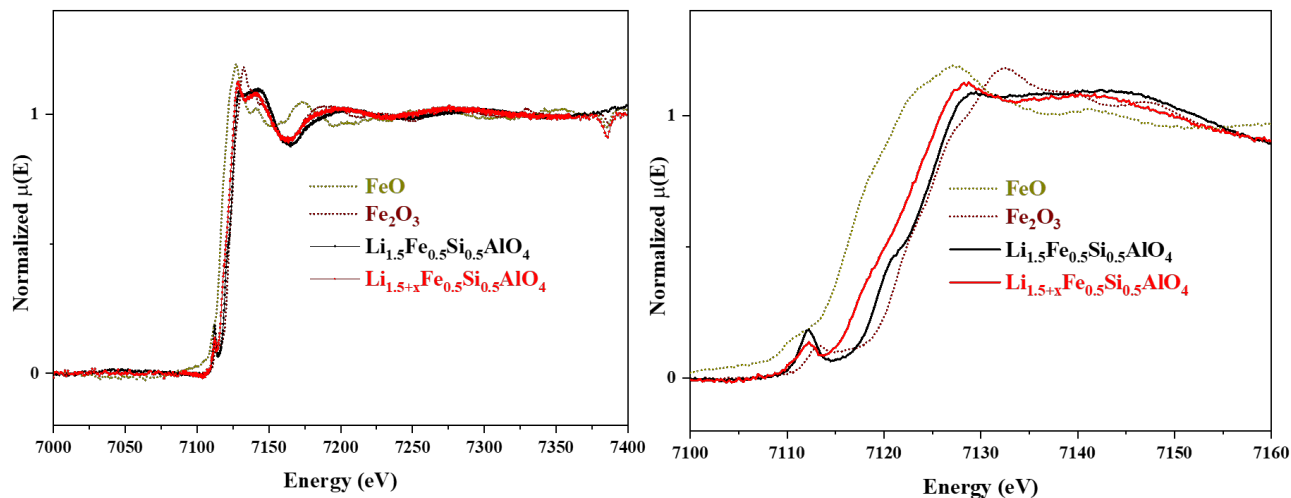


Figure 7.14. XANES data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ with references (dotted lines); normalization(left), Fe K-edge comparison(right).

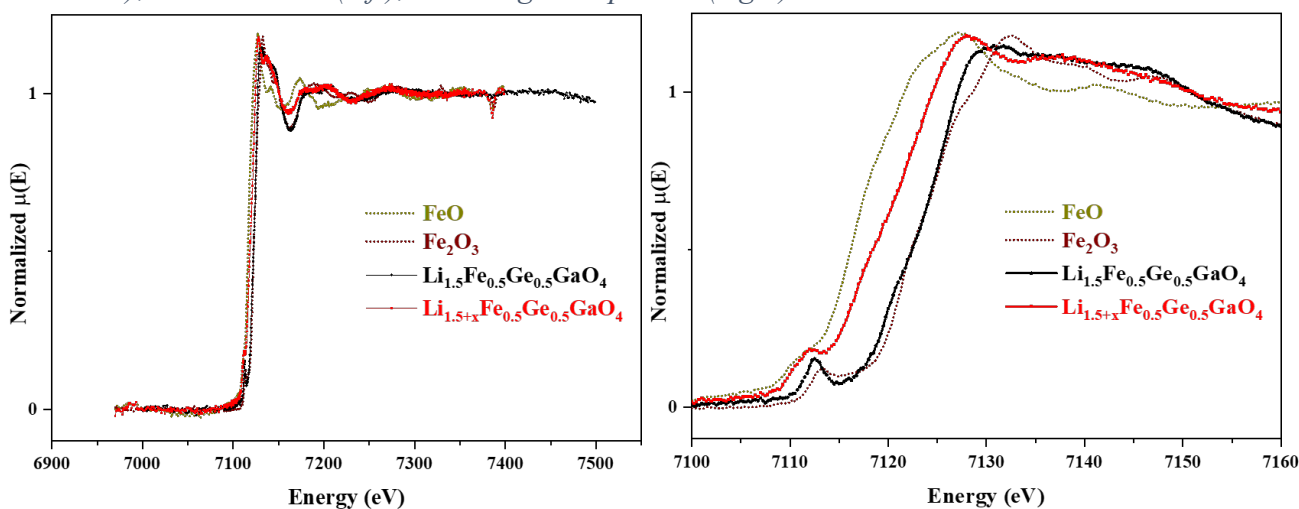


Figure 7.15. XANES data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ with references (dotted lines); normalization(left), Fe K-edge comparison (right).

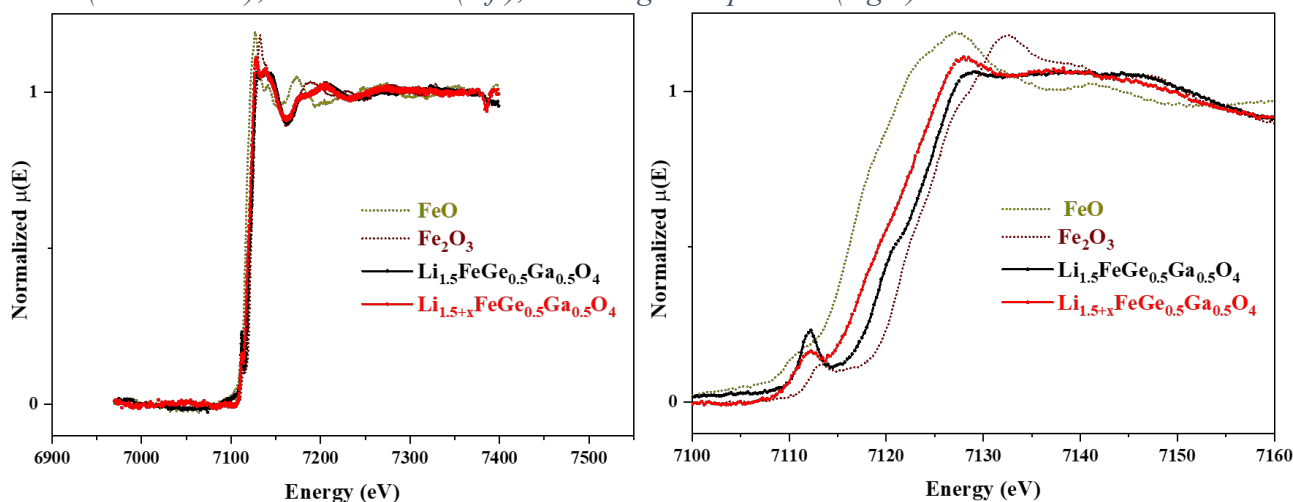


Figure 7.16. XANES data from $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ and $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ with references (dotted lines); normalization(left), Fe K-edge comparison (right).

EXAFS data: High-resolution X-ray absorption spectroscopy (XAS) data were collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, distinct from the data illustrated in Figure 7.15. These datasets were employed as extended X-ray absorption fine structure (EXAFS) data to examine the local structural modifications within the FeO_4 site induced by lithium insertion. The XAS data, at energies above the absorption edge, underwent conversion into various oscillations specific to the absorber atom, subsequently analyzed as EXAFS data.

The first shell of the EXAFS data, featuring the FeO_4 tetrahedra, derived from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, were carefully fitted by refining the crystallographic models obtained after the structural refinement of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ against NPD data. The resultant fit is shown in Figure 7.17, with the refined parameters given in Table 7.9.

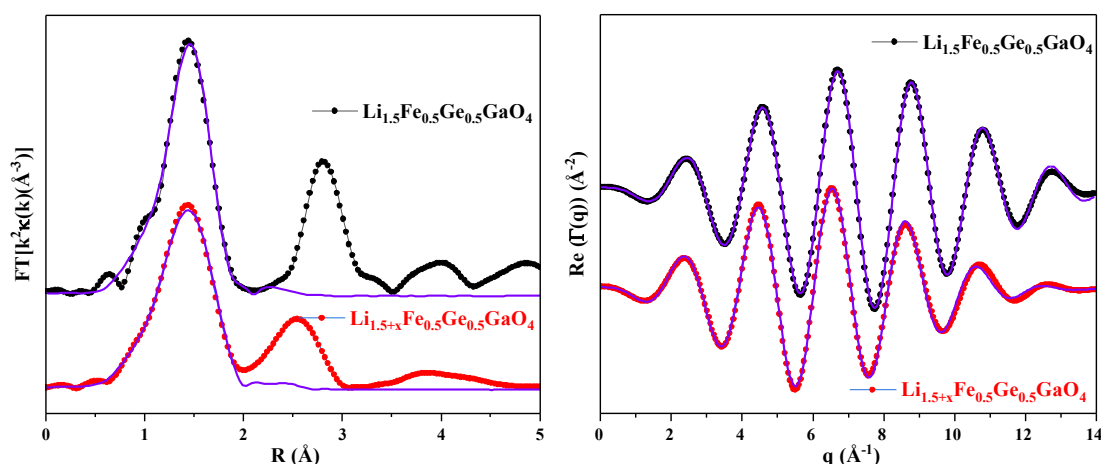


Figure 7. 17. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space

Table 7.9. Refined EXAFS parameter of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$

Sample	Bond	N	$R(\text{\AA})$	Debye-Waller Factor ($10^{-3} \text{\AA}^2$)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD ($\text{\AA}$)
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	Fe-O	4	1.882(4)	5.5(6)	0.3	2.868	1.835(7)
$\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	Fe-O	4	1.915(1)	8.9(2)	1.1	2.624	1.818(5)

The EXAFS data analysis provides a comprehensive comparison of the $\langle\text{Fe-O}\rangle$ bond lengths within the FeO_4 tetrahedra of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, as summarized in Table 7.9. Notably, there is an increase in the $\langle\text{Fe-O}\rangle$ bond length, progressing from 1.882(4) Å in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ to 1.915(1) Å in $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$. This increment of Fe-O bond lengths subsequent to lithium intercalation is consistent with the reductive lithium insertion in $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$.

7.4.4. Electrochemical cycling data

To investigate the electrochemical performance of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ cyclic voltammogram (CV) profile and galvanostatic charge-discharge capacity data were collected. As shown in Figure 7.18, CV data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ exhibits reversible redox features in the voltage window of 1.5-4.5 V with a reduction feature at 1.5 V and an oxidation feature at 3.0 V. A large polarization spanning more than 2 V is observed between the oxidation and reduction features. The area under both the features is well maintained up to the sixth cycle indicating large-scale cathode decomposition is not occurring.

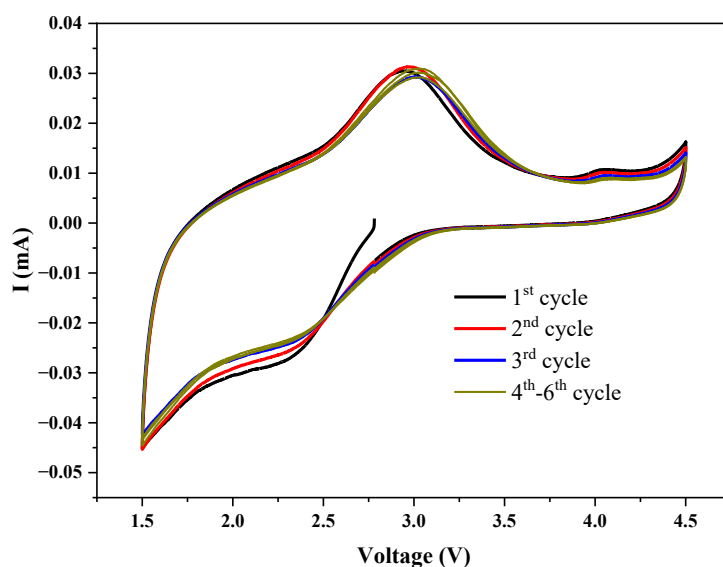


Figure 7. 18. Cyclic voltammogram profiles from $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ in the voltage range of 1.5-4.5 V

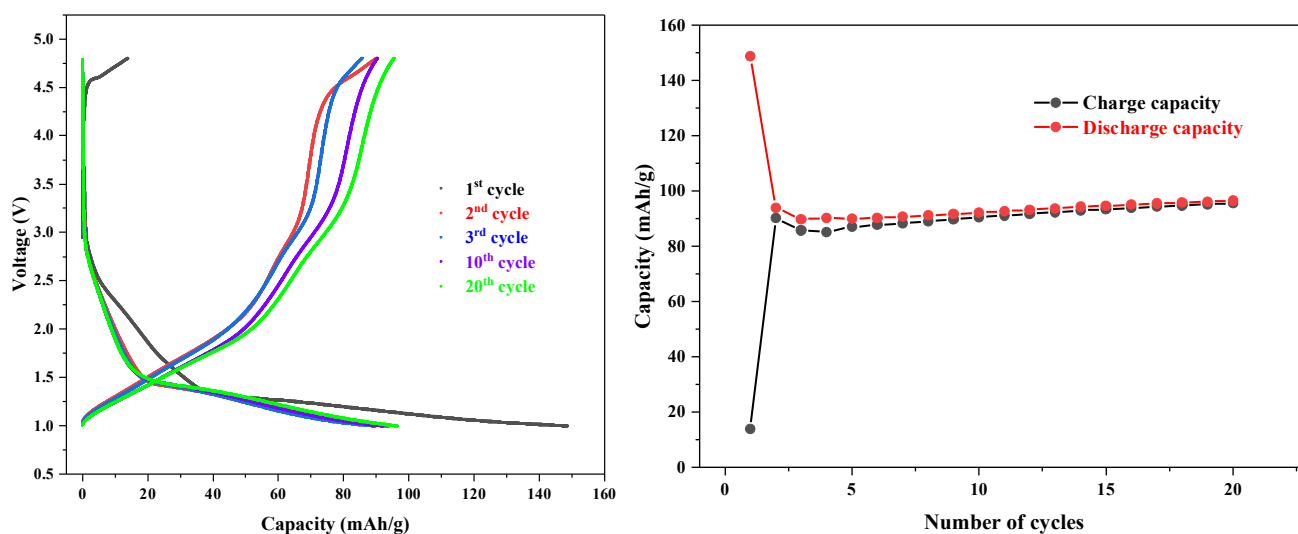


Figure 7. 19. Charge-discharge capacity profile from $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ sample in the voltage range of 1.0-4.8 V (left), Plot of capacity vs. the number of cycles (right)

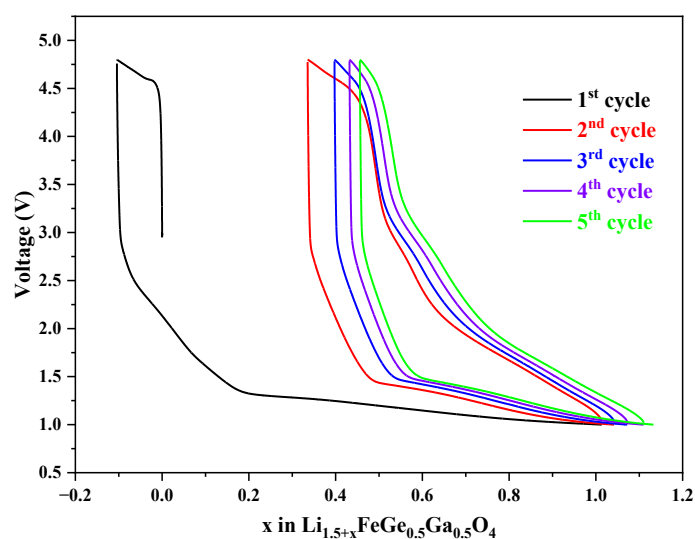


Figure 7. 20. Plot of voltage vs x, where x represents the amount of lithium being inserted, derived from the cycling data of $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ in the voltage range of 1-4.8V

Figures 7.19 and 7.20 present the charge-discharge capacity profile of $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ within the voltage range of 1-4.8 V. In the initial discharge cycle (4.8 V to 1.0 V), a capacity of 148.6 mAh/g is observed, equivalent to the insertion of 1.11 Li^+ per formula unit. This extent of lithium intercalation aligns well with the amount of intercalated lithium determined from NPD data (1 Li^+ /f.u., Section 7.4.2) and iodometric titrations (Appendix-I Table 7a.3).

Subsequent cycles exhibit a stable reversible capacity of approximately 100 mAh/g for up to 20 cycles, corresponding to cycling of 0.75 Li⁺ per formula unit. The capacity vs. number of cycles plot (Figure 7.19, right) shows an initial drop in capacity for the 1st -4th cycles, followed by a slight increase in observed capacity from the 5th-20th cycle. This increase in capacity can be attributed to the structural transformation observed from Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄ (described in *Pc* space-group) to lithiated Li_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄ (described in *Pn* space-group) as a result of chemical lithium intercalation (Section 7.4.2), which facilitates easier cycling of lithium in the voltage range of 1-4.8 V.

Figure 7.20 illustrates the electrochemical performance of Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄ in terms of lithium ions inserted into its structure. A close inspection of the data shows, in the first discharge cycle 1.1 Li⁺/f.u. is inserted (indicating the corresponding oxidation state of Fe^{1.91+}) but only 0.74 Li⁺/f.u. is extracted at the end of second charge cycle at 4.8 V (indicating the corresponding oxidation state of Fe^{2.64+}). This indicates the structure of Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄ attaining superior stability under reductive conditions and there is a reluctance of iron cations to be oxidised back to Fe³⁺. In subsequent cycles, cycling of ~0.75 Li⁺ per formula unit is observed, which is well maintained up to 20 cycles. Consequently, the cycling feature of Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄ is attributed to the change in iron oxidation state from Fe³⁺ → Fe²⁺, and then Fe²⁺ ↔ Fe^{2.x+}.

Nevertheless, a robust cycling capacity of 100 mAh/g is achieved for Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄, showcasing the stability of the tetrahedral-LiFeO₂ structure when iron sites are substituted with both Ge⁴⁺ and Ga³⁺.

7.4.5. Discussion for lithiated Li_{1.5+δ}Fe_{2-x-y}M_x^{III}N_y^{IV}O₄ phases

Structural determination from NPD data highlights distinct behaviours in lithiated Li_{1.5+x}Fe_{0.5}Si_{0.5}AlO₄, Li_{1.5+x}Fe_{0.5}Ge_{0.5}GaO₄, and Li_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄. Li_{1.5+x}Fe_{0.5}Si_{0.5}AlO₄ and

$\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ maintain their pristine structure type and the pristine cation ordering, while $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ undergoes structural rearrangement (Figure 7.9) from $\gamma\text{-NaFeO}_2$ type to $\beta\text{-NaFeO}_2$ type on lithium insertion. The distribution of cations in the structure of reduced $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ is also found to be different from pristine $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ as a result of lithium insertion.

In $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, additional lithium ions fill the partially occupied tetrahedral lithium sites, while in $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ the additional lithium ions occupy the empty octahedral site adjacent to MO_4 tetrahedra, sharing faces. In $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, additional lithium ions occupy both the tetrahedral site as well as octahedral sites in the structure. Structures of both $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, and $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ [$\beta\text{-NaFeO}_2$ structure type, uni-directional MO_4] contain more open channels thus the empty octahedral sites are available to be filled during lithium intercalation. On the other hand, structure of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ [$\gamma\text{-NaFeO}_2$ structure type, poly-directional MO_4] contains $\text{Fe}^{3+}/\text{Al}^{3+}$ and Si^{4+} atoms in more irregular fashion which prevents the access to the octahedral site for the additional lithium ions thus the vacancy present on the tetrahedral Li sites are filled in the structure during the lithium intercalation.

X-ray diffraction data from lithiated $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ after the treatment of I_2 in acetonitrile (Appendix-I, Figure 7a.2) shows retention of $\beta\text{-NaFeO}_2$ structure type, indicating the structural change from $\gamma\text{-NaFeO}_2$ type in $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ to $\beta\text{-NaFeO}_2$ type in $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ is irreversible in nature under the oxidising conditions used.

Fe K-edge XANES data from $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, and $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ indicate a reduction of Fe(III) to Fe(II) due to lithium insertion. Furthermore, EXAFS data from $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ reveals an increase in $\langle\text{Fe-O}\rangle$ bond

lengths and a decrease in Fe-BVS parameter, consistent with the Fe cations undergoing reduction due to lithium intercalation.

As discussed in Section 4.3, a complete structural decomposition was observed for $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ phases under reductive conditions. However, the structure of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ is found to be stable under reductive conditions, indicating substituting Si^{4+} for Fe^{3+} in $\text{LiFe}_{1-x}\text{Al}_x\text{O}_2$ phases is effective stabilising the structure under reductive conditions. The structural decomposition of $\text{Li}_{1+\delta}\text{Fe}_{1-x}\text{Al}_x\text{O}_2$ phases was attributed to the smaller size of Al^{3+} ($0.39 \text{ \AA}$)¹⁵⁴, causing severe strain in the structure when the FeO_4 site expands during reductive lithium insertion. However, a similar rationale can not explain the stabilisation of $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ indicating more subtle bonding interactions are at play for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$.

Electrochemical charge-discharge capacity data from $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ exhibit a reversible capacity of 100 mAh/g up to 20 cycles indicating stability of FeO_4 sites when substituted with Ge^{4+} and Ga^{3+} . Furthermore, the structural transformation from $\gamma\text{-NaFeO}_2$ to $\beta\text{-NaFeO}_2$ structure type observed in $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ during electrochemical cycling contributes to superior reversible capacities. This highlights the superiority of the $\beta\text{-NaFeO}_2$ structure type than the $\gamma\text{-NaFeO}_2$ structure type, as $\beta\text{-NaFeO}_2$ is characterised by unidirectional pointing of $(\text{Fe}/\text{M}/\text{N})\text{O}_4$ tetrahedra which channels the lithium cations better during the electrochemical cycling.

In the cycling data of $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, the change of oxidation state between $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{2.5+}$ is observed on the later cycles. The tendency to maintain the oxidation state of iron below 3 is rationalized by the expansion of the $\langle \text{Fe-O} \rangle$ bond that occurs during the lithium exchange reaction from $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ to $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ (Section 6.4). This enlargement of the $\langle \text{Fe-O} \rangle$ bond favours the presence of Fe(II) over Fe(III) in the structure, which influences the electrochemical behaviour during cycling.

Chapter 8 – Oxidation of $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases

8.1. Introduction

Nitronium tetrafluoroborate (NO_2BF_4) has an oxidation potential of 5.14 V vs the Li^+/Li couple¹¹⁵. Thus, oxidative delithiation reactions with nitronium tetrafluoroborate^{115,116} can be considered as the chemical equivalent of the electrochemical charge process of a cathode in a lithium ion battery. To achieve oxidative lithium deintercalation, $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ samples were treated with nitronium tetrafluoroborate in acetonitrile. The products obtained were characterized by SXRD, ICP-MS, NPD, XAS, RIXS and titration techniques. The analysis of these results is described in this chapter. In addition, electrochemical performances of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ are also discussed.

8.2. Experimental section

8.2.1. Chemical deintercalation

In a small Schlenk tube under a nitrogen atmosphere, approximately 500 mg of NO_2BF_4 (95+%, Merck Life Science) was dissolved in 10 mL of acetonitrile. Maintaining a molar ratio of 1:5 of $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4 : \text{NO}_2\text{BF}_4$, around 200 mg of $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ sample was added to the solution, and the tube was sealed with a glass cap. The tube was then transferred to an oil bath where the contents inside the tube were constantly stirred and heated at 50°C for 7 days. Following this period, the suspension obtained was filtered with excess acetonitrile solution, and the resulting powder was collected via vacuum filtration.

To check the reversibility of lithium deintercalation, the deintercalated sample ($\text{Li}_{1.5-x}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$) was treated with LiI (99.999%, Alfa Aesar) in the following manner. In a controlled nitrogen atmosphere, about 300 mg of LiI (99.999%, Alfa Aesar) was dissolved in 10 mL of acetonitrile within a small Schlenk tube. Maintaining a molar ratio of 1:10 between

$\text{Li}_{1.5-\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ and LiI, approximately 50-70 mg of $\text{Li}_{1.5-\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ sample was introduced into the solution, and the tube was then sealed with a glass cap. The sealed tube was placed in an oil bath where its contents were continuously stirred and heated at 50°C for 3 days. A noticeable change in the colour of the solution from colourless to yellow or dark brown was observed, indicating iodine release during the reaction. Following this reaction, the powder was collected through filtration. To quantify the released iodine, the filtrate was titrated against a standardized thiosulphate solution.

8.2.2. Electrochemical cycling

Coin cell preparation with the aliovalent LiFeO_2 samples as cathode is described in Section 7.2.3. To investigate the electrochemical performance, cyclic voltammogram profile and galvanostatic charge-discharge capacity measurements were conducted with the assembled coin cells.

8.3. Results and discussion

8.3.1. Synchrotron X-ray diffraction (SXR) data

Synchrotron X-ray diffraction (SXR) data collected from the chemically delithiated, aliovalent doped, LiFeO_2 samples henceforth referred to as $\text{Li}_{1.5-\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$, are shown in Figure 8.1. A close inspection of the data from $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, reveal retention of crystallinity, indicating this level of substitution is sufficient to inhibit the structural decomposition under oxidative conditions. On the other hand, a complete loss of crystallinity is observed for the SXR data from $\text{Li}_{1.5-x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, indicating structural decomposition upon delithiation. This observation is consistent with the instability of iron sites under oxidative conditions^{50,51,55,56,74,160,179,180} in the absence of adequate redox inactive elements coexisting with iron in the structure.

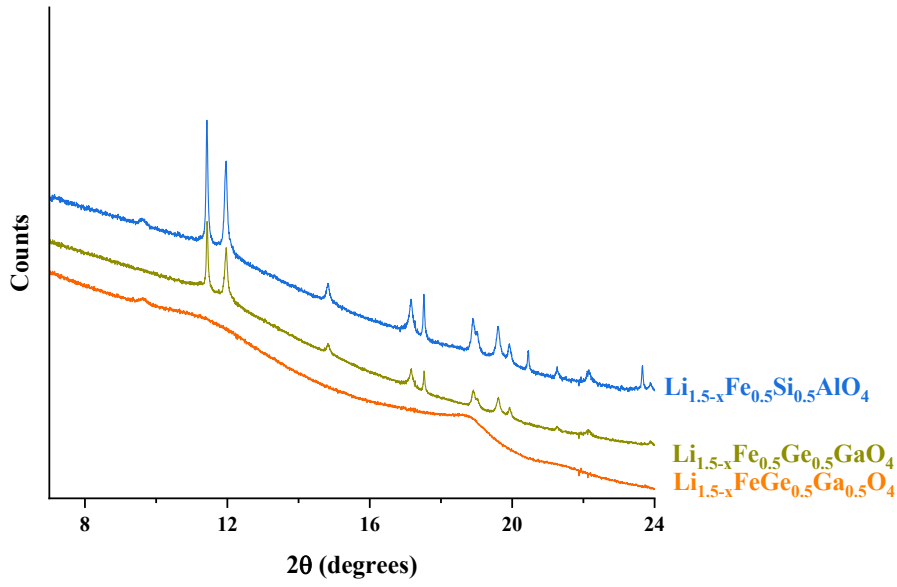


Figure 8. 1. Plot of SXRD data collected from the chemically oxidised aliovalent doped LiFeO_2 ($\text{Li}_{1.5-\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$) samples

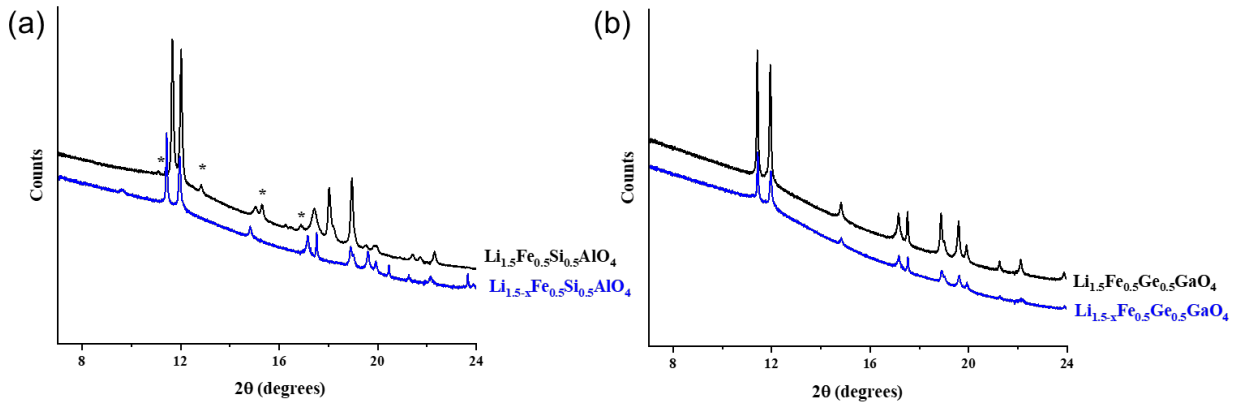


Figure 8. 2. Comparison of SXRD data collected from (a) $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (b) $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, * indicate reflections which can only be indexed using the unit cell parameters from the structure described in space group Pc

Figure 8.2 presents a comparison of SXRD data collected from pristine and oxidized $\text{Li}_{1.5-\delta}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases. A comparison of the SXRD data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ reveals that, $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ fails to retain reflections at $2\theta = 10.95$, 12.84 , and 15.317° , which were evident in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and indicative of a lower symmetry, and consistent with the adoption of the Pc space group (Figure 8.2, a). SXRD data

from delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ closely resemble the corresponding pristine materials (Figure 8.2, b). This comparison of SXRD data indicates that, while $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ maintain the pristine structural symmetry (same as $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$), $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ undergoes a structural rearrangement upon delithiation.

SXRD data from delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ was indexed on the basis of an orthorhombic unit cell with reflection conditions consistent with $Pna2_1$ space group (based on the reported disordered T-LiFeO₂ structure⁵⁵). Thus, crystallographic models described in the $Pna2_1$ space-group were constructed where the $4a$ Fe site contains a combination of Fe/Si/Al as per the composition. This model was refined against the data to achieve a good fit as shown in Figure 8.3 with crystallographic parameters given in Table 8.1. SXRD data from delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ is found to exhibit sharp reflections at $2\theta = 8.90, 20.5$ and 23.5° which were assigned to unknown impurity (indicated by * in Figure 8.3) formed during the chemical delithiation process.

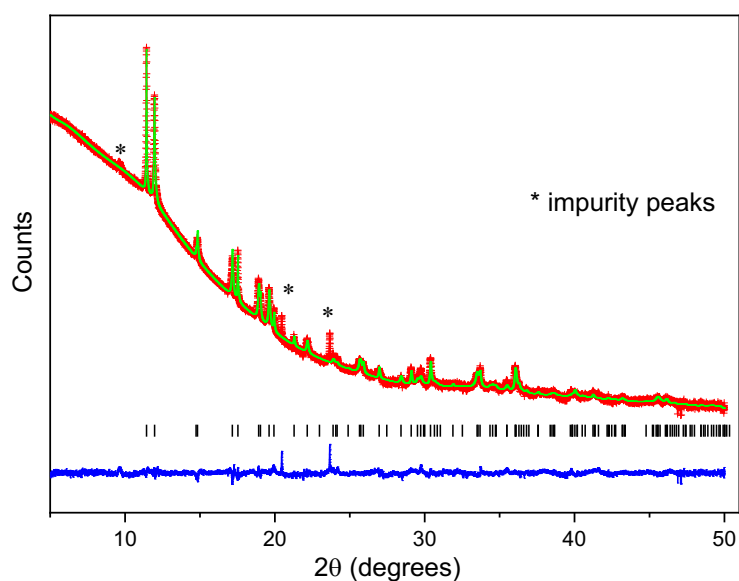


Figure 8. 3. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ against SXRD data. * indicates reflections associated with unknown impurity phase formed during the chemical delithiation

Table 8.1. Parameters from the structural refinement of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ sample against SXRD data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	4a	0.4356(3)	0.1475(32)	0.5180(32)	0.75	0.1
Al1/Si1/Fe1	4a	0.0802(5)	0.1361(5)	0	0.5/0.25/0.25	0.1
O1	4a	0.0492(13)	0.1198(14)	0.3583(10)	1	0.1
O2	4a	0.3748(12)	0.1843(11)	0.9045(12)	1	0.1
$\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ – space group $Pna2_1$ (#33) $a = 5.4269(6) \text{ \AA}$, $b = 6.4460(7) \text{ \AA}$, $c = 5.0314(5) \text{ \AA}$, volume = $176.014(35) \text{ \AA}^3$ Formula weight= 139.8865 g mol ⁻¹ , Z = 2 Radiation source: synchrotron, $\lambda = 0.826855 \text{ \AA}$ Temperature: 298 K $R_{\text{Bragg}} = 0.64 \%$, $R_p = 0.77 \%$, $wR_p = 1.20 \%$						

* B_{eq} parameters were fixed to 0.1 due to absorption issues

Table 8.2. Bond lengths and BVS parameter table for $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$

Bonds	$\langle M-O \rangle$ ($\text{\AA}$)	Average $\langle M-O \rangle$ ($\text{\AA}$)	Fe-BVS	Si-BVS	Al-BVS
Fe1/Al1/Si1-O	1.676(8)	1.779(8)	3.920	2.721	2.927
	1.699(8)				
	1.814(6)				
	1.931(9)				

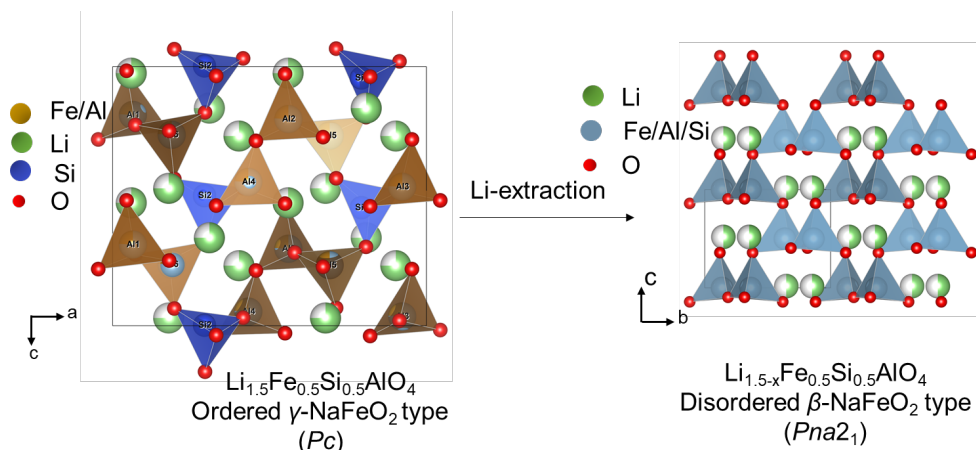


Figure 8. 4. Structural relationship from pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ to delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$

The $\langle\text{Fe-O}\rangle$ bond lengths and Fe-BVS parameters calculated from the refined crystallographic model obtained after the structural refinement of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, are given in Table 8.2. It shows an average of $\langle\text{Fe-O}\rangle$ bond length of 1.779(8) Å with Fe-BVS as 3.920 for $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ which is in good agreement with oxidation of Fe(III) to Fe(IV) in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ upon treatment with NO_2BF_4 .

Figure 8.4 summarises the structural change observed for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ on chemical delithiation. A close inspection of the structures reveals a structural rearrangement from the ordered $\gamma\text{-NaFeO}_2$ type in pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ to the disordered $\beta\text{-NaFeO}_2$ type structure in delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$. The SXRD data was fit with a structural model described in space group $Pna2_1$ with a complete disorder between Fe/Si/Al cations (Table 8.1). However, as the SXRD data can not distinguish between the neighbouring elements in the periodic table (e.g., Al and Si), the exact cation ordering in delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ phase remains uncertain from this structural refinement.

It is also worth pointing out that, although SXRD analysis of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ reveals the structural transformation, it does not reveal any information about the extent of lithium being deintercalated from the structure.

8.3.2. Neutron powder diffraction (NPD) data

To assist with structural determination, neutron powder diffraction (NPD) data were collected from delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ sample. A crystallographic model described in *Pn* space-group (similar to $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, Section 6.3.3) was refined against the data which resulted in a good fit as shown in Figure 8.5 with crystallographic parameters given in Table 8.3. Average $\langle\text{Fe-O}\rangle$ bond lengths and Fe-BVS parameters calculated from the refined model are given in Table 8.4.

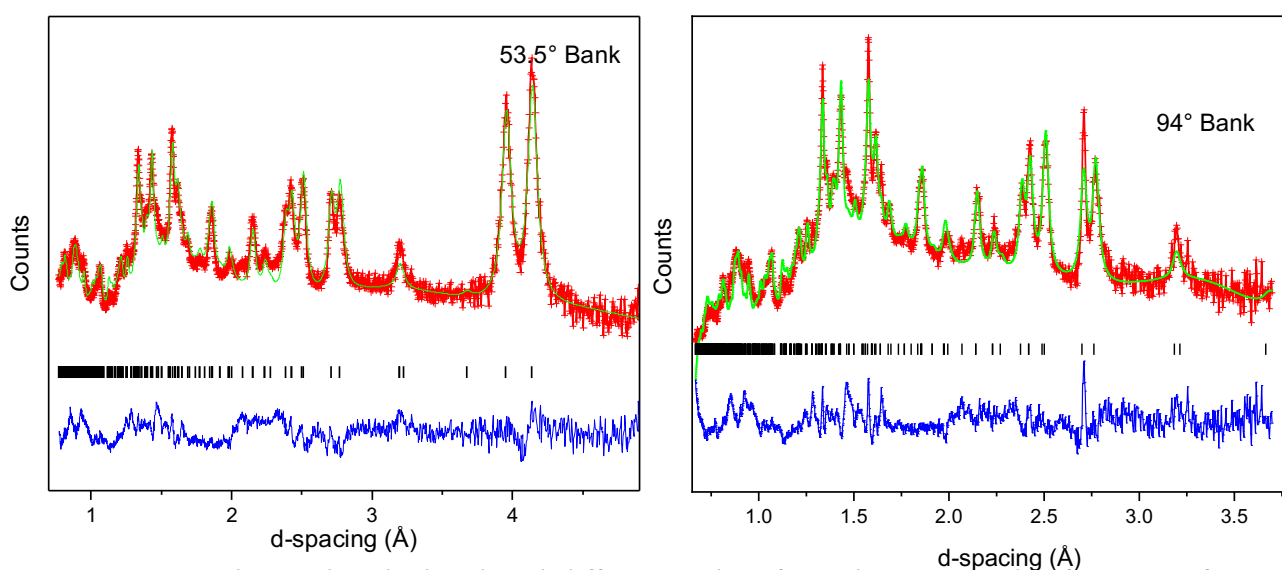


Figure 8. 5. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ against NPD data, bank 53.5° (left), bank 94° (right)

Table 8.3. Parameters from the structural refinement of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li1	2a	$\frac{1}{2}$	0.0876(61)	0	0.48(4)	0.81(8)
Li2	2a	$\frac{3}{4}$	0.4124(61)	$\frac{1}{2}$	0.48(4)	0.81(8)
Fe1/Ge1	2a	0	0.2107(23)	0	0.5/0.5	0.29(2)
Ga1	2a	0.2342(18)	0.3174(13)	0.4929(41)	1	0.26(1)
O1	2a	0.4813(33)	0.1595(39)	0.3362(33)	1	0.51(10)
O2	2a	0.2724(30)	0.6543(32)	0.4154(34)	1	0.51(10)
O3	2a	0.0219(47)	0.1501(41)	0.3694(34)	1	0.51(10)
O4	2a	0.2212(59)	0.3326(38)	0.8842(41)	1	0.51(10)
$\text{Li}_{0.96}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ – space group <i>Pn</i> (#7) $a = 6.4474(12) \text{ \AA}$, $b = 5.4116(9) \text{ \AA}$, $c = 5.0139(8) \text{ \AA}$, $\beta = 89.877(13)^\circ$ volume = 174.943 (54) $\text{\AA}^3$ Formula weight= 203.8485 g mol $^{-1}$, $Z = 2$ Radiation source: neutron, time of flight Temperature: 298 K $R_p = 1.71 \%$, $wR_p = 2.16 \%$						

Table 8.4. Bond lengths and BVS parameter table for $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$

Bonds	Average $\langle M-O \rangle$ (Å)	Fe-BVS	Ge-BVS	Ga-BVS
Fe1/Ge1-O	1.891(11)	2.830	2.747	
Ga1-O	1.856(17)			2.845

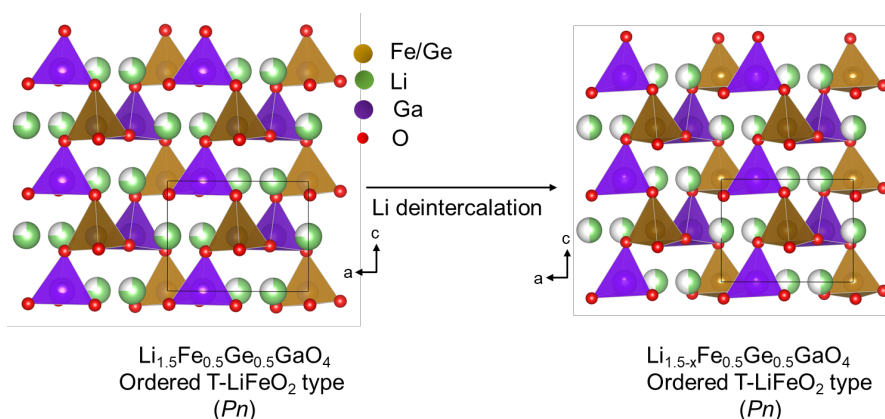


Figure 8. 6. Structural relationship from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ to $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$

During the structural determination, refinement of the occupancy parameters of the lithium sites resulted in a final composition of the refined model of $\text{Li}_{0.96}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ which is in good agreement with the lithium content determined from the ICP-MS analysis (Appendix-I Table8a.1). Figure 8.6 presents the structural relationship from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ to $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ upon delithiation. Comparison of the structures in the figure reveals that the ordered β -NaFeO₂ structure type of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ is retained in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ with an identical cation distribution in the MO_4 tetrahedral sites of the structure.

The $\langle \text{Fe-O} \rangle$ bond length determined from $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (Table 8.4) shows no significant change when compared with pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (Section 6.3.3, Table 6.13) indicating minimal change of iron oxidation state in the FeO_4 site when delithiated with the treatment of NO_2BF_4 .

8.3.3. X-ray absorption spectroscopy (XAS) data

Fe-XANES: X-ray absorption near edge structure (XANES) data were acquired from both delithiated ($\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$) and pristine ($\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$) $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ samples, in addition to reference materials Fe_2O_3 and SrFeO_3 . The Fe K-edge XANES data from Fe_2O_3 and SrFeO_3 were employed as references for Fe (III) and Fe (IV), respectively. Figures 8.7 and 8.8 present the normalized XANES data for the $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ samples, with a specific focus on changes in the iron K-edge energies induced by chemical lithium deintercalation.

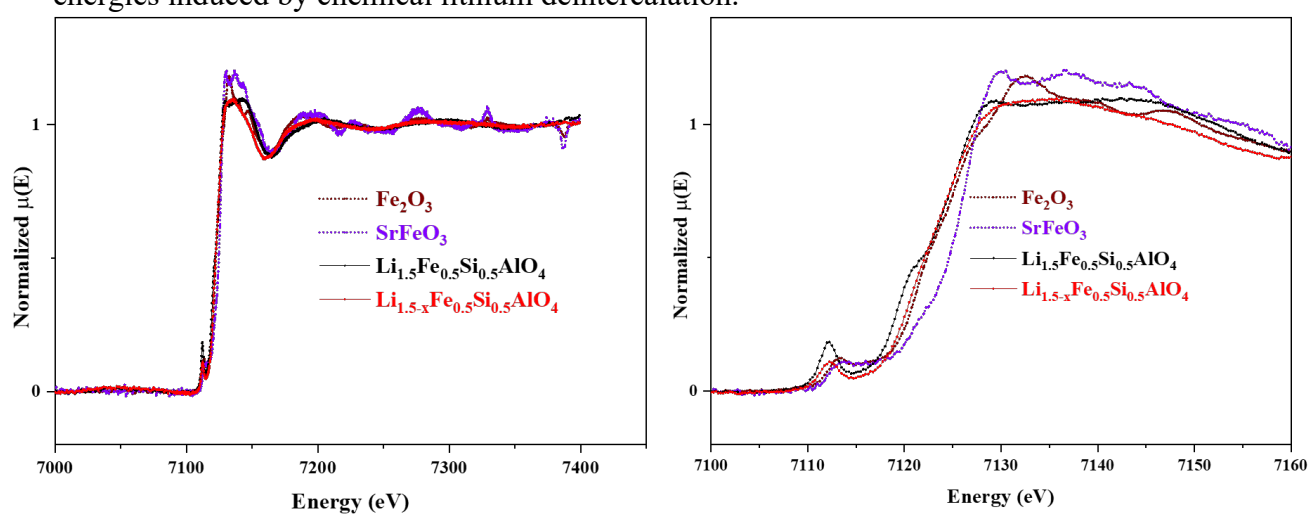


Figure 8.7. XANES data of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ with references (dotted lines); normalization(left), Fe K-edge comparison (right).

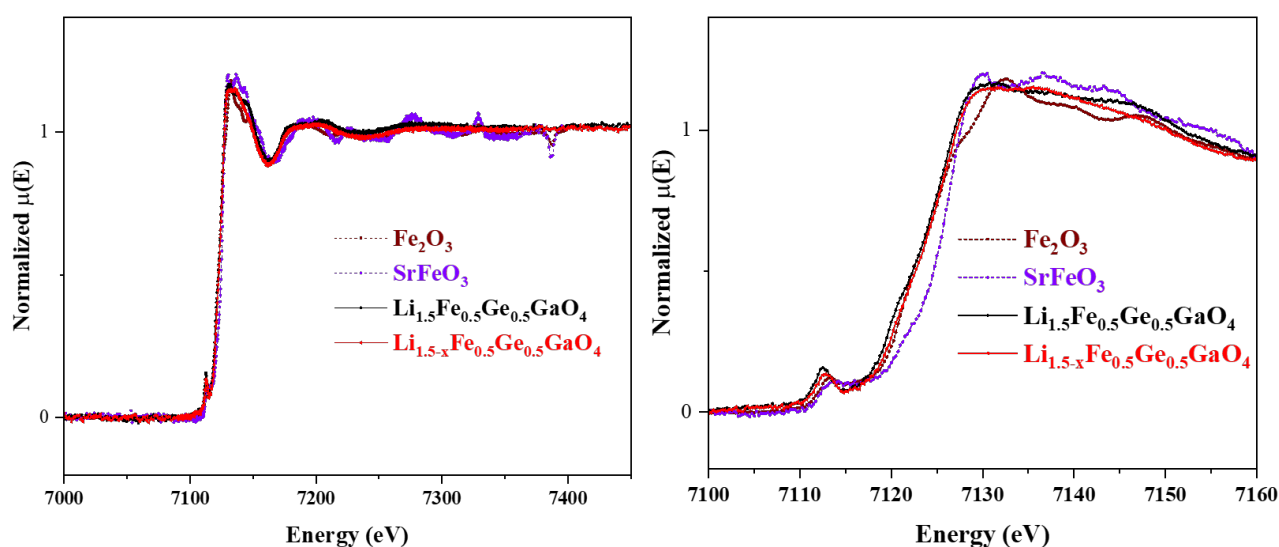


Figure 8.8. XANES data of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ with references (dotted lines); normalization(left), Fe K-edge comparison (right).

Fe K-edge XANES data from both pristine and delithiated $\text{Li}_{1.5-8}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases, as depicted in Figures 8.7 and 8.8, show a characteristic pre-edge feature at energies around ~ 7112 eV, indicative of the presence of FeO_4 tetrahedra in the structure. A comparison of the Fe K-edge between $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ reveals a small shift towards higher energy (Figure 8.6) which is consistent with oxidation of iron site upon exposure to NO_2BF_4 .

However, a comparison of Fe K-edge between $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ reveals no significant change in the energy of the absorption edge (Figure 8.8) indicating minimal degree of iron oxidation in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ due to chemical delithiation.

Fe-EXAFS: High-resolution X-ray absorption spectroscopy (XAS) data were collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, distinct from the data illustrated in Figure 8.7. These datasets were employed as extended X-ray absorption fine structure (EXAFS) data to examine the local structural modifications within the FeO_4 site induced by lithium extraction. The XAS data, at energies above the absorption edge, underwent conversion into various oscillations specific to the absorber atom, subsequently analysed as EXAFS data.

The first shell of the EXAFS data, featuring the FeO_4 tetrahedra, derived from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, were carefully fitted by refining the crystallographic models obtained from the structural refinement of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ against NPD data. The resultant fit is shown in Figure 8.9, with the refined parameters given in Table 8.5.

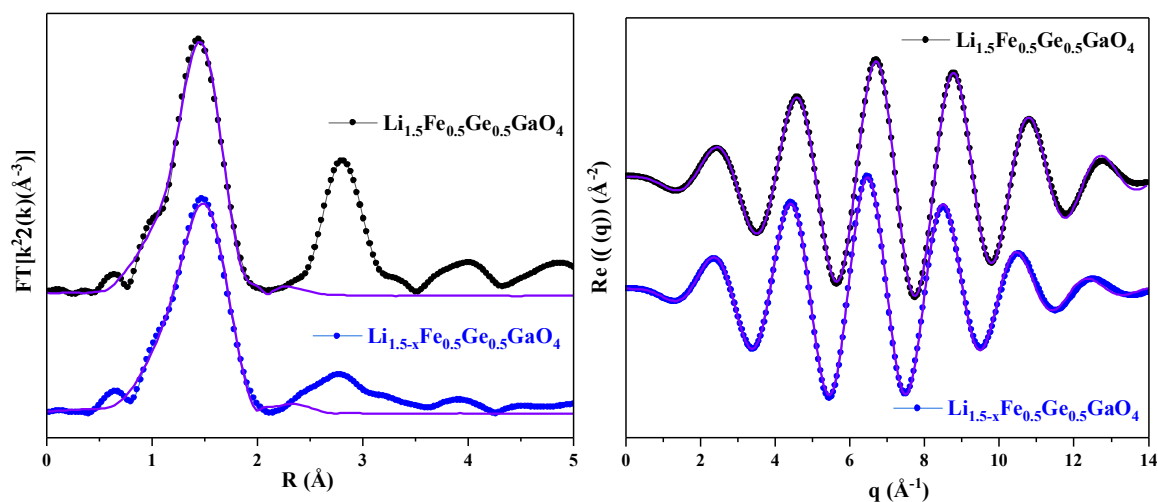


Figure 8. 9. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_2$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_2$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 8.5. Refined EXAFS parameters of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_2$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_2$

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD (Å)
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	Fe-O	4	1.882 (4)	5.5 (6)	0.3	2.868	1.835(7)
$\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	Fe-O	4	1.942 (5)	9.9 (8)	0.3	2.439	1.891(11)

The $\langle \text{Fe-O} \rangle$ bond lengths determined from the first shell fit of the EXAFS data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ reveal that, $\langle \text{Fe-O} \rangle$ bond length in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ is increased due to chemical delithiation (Table 8.5). A similar trend is also observed from the analysis of the NPD data. The $\langle \text{Fe-O} \rangle$ bond lengths and Fe-BVS parameter determined from the EXAFS analysis, provide no indication of Fe-oxidation in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ upon delithiation.

8.3.4. O K-edge X-ray absorption spectroscopy (XAS) data

O K-edge XAS data were collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ in fluorescence yield (FY) mode. The normalized data are presented below.

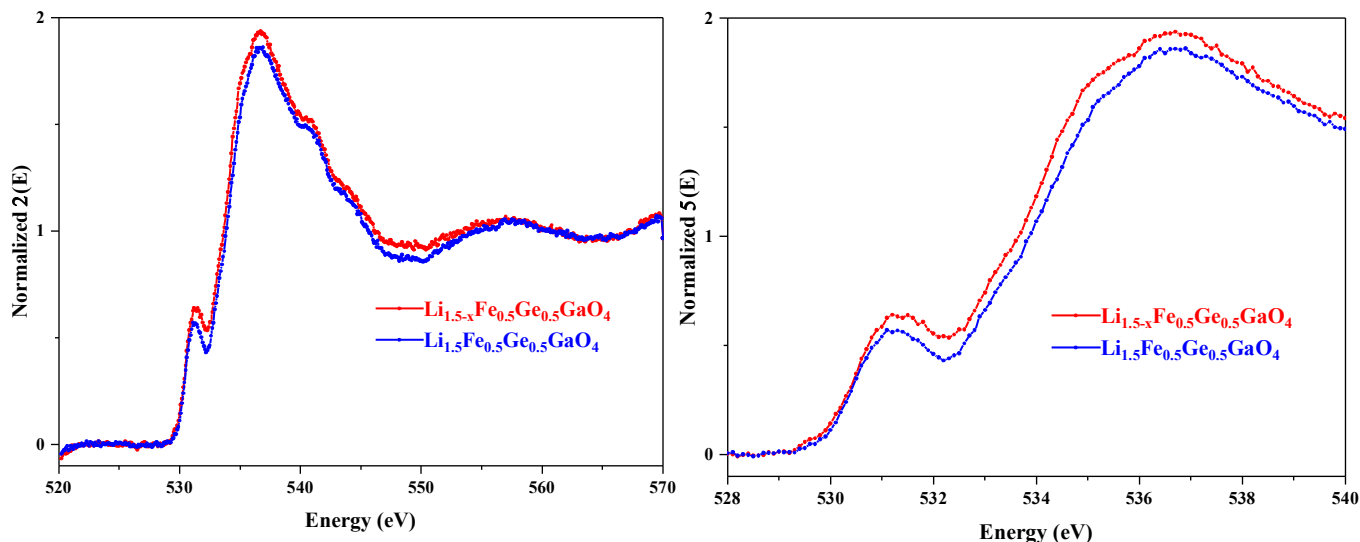


Figure 8. 10. Plot of O K-edge XAS of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$; Fluorescence mode data (a,b), Normalization (a), enlarged comparison (b)

As shown in Figure 8.10, the O K-edge XAS data collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ show a sharp feature at 531 eV which is assigned to the excitation of Oxygen 1s electron to the $\text{Fe}(3d)\text{-O}(2p)$ hybridised band⁸³. At energies higher than 533 eV the spectra exhibit broad features which are assigned to the excitation of Oxygen 1s electron to the $\text{Fe}(4s,4p)\text{-O}(2p)$ hybridised band⁸³.

Comparison of XAS data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ in FY mode [(a,b) Figure 8.10] show no shift in O K-edge energy for the sharp feature at 531 eV, however, a small increase in intensity can be noticed. Likewise, for the broad feature in the O K-edge spectra [(b) in Figure 8.10]) no shift in the energy but an enhancement in the overall feature with increased intensity is noticed for the oxidised material in comparison to the pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ sample. The intensity enhancement at an energy of 531 eV in O K-edge XAS data is consistent with oxygen oxidation in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ according to recent reports with the oxidation of other cathode materials^{89,156–159}.

8.3.5. RIXS data

Resonant inelastic X-ray scattering (RIXS) data were collected from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ to further investigate the oxidised oxygen species generated after chemical delithiation. The RIXS energy maps were constructed from multiple RIXS line scans with excitation energies ranging from 529 to 535 eV with a step size of 0.25 eV. In addition, RIXS line scan data were collected at an excitation energy of 531.75 eV.

Figure 8.10 show Resonant Inelastic X-ray Scattering (RIXS) energy maps of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$. In both $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, the main feature observed associated within the excitation energy range of 530.5-532 eV, is linked to the excitation of oxygen 1s electron to the Fe(3d)-O(2p) hybridized band⁹³.

From the mRIXS plot with the emission energy on the vertical axis and the excitation energy on the horizontal axis [Figures 8.11 (a, and c)], the observed intensities were integrated within the emission energy range of 522.5-525 eV. This integration resulted in the partial fluorescence yield (sPFY) data, illustrated in Figures 8.11 (b) and (d). A comparative analysis of the integrated fluorescence spectra between $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ reveals a clear distinction with an increased intensity for $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ at an excitation energy of 531 eV (Figure 8.12, a). This heightened intensity at the excitation energy of 531.5 eV is found to be linked with the emission energy of 523.75-524 eV, which is attributed to an intraband excitons of $\pi_u \rightarrow \sigma_u^*$ during the emission process⁹⁴ (Section 1.9).

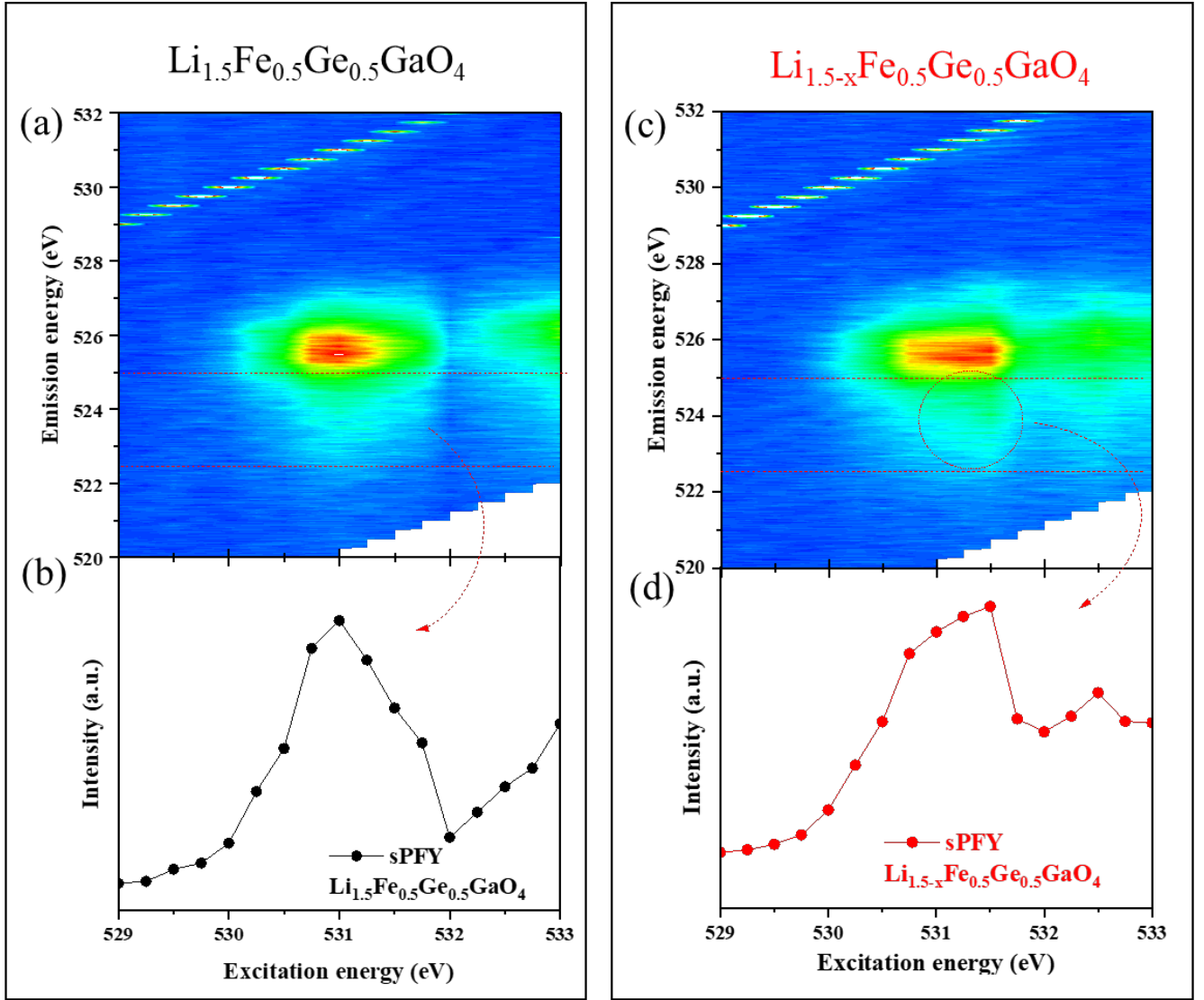


Figure 8. 11. Plot of mRIXS data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (a) and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (c) with vertical axis as Emission energy and horizontal axis as Excitation energy; Plot of corresponding integrated partial fluorescence yield (sPFY) data in the emission range of 522.5-525 eV vs excitation energy (b and d). Red circle in the mRIXS plot of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (c) shows enhanced intensity corresponding to the excitons of $\pi_u \rightarrow \sigma_u^*$ during the emission process⁹⁴

This increased intensity at emission energy ranging from 523.75 to 524 eV is also evident in the RIXS line scan spectra at an excitation energy of 531.75 eV, depicted in Figure 8.12 (b) (indicated with blue dotted circle). These findings strongly suggest the involvement of oxygen redox processes during the chemical delithiation of the material.

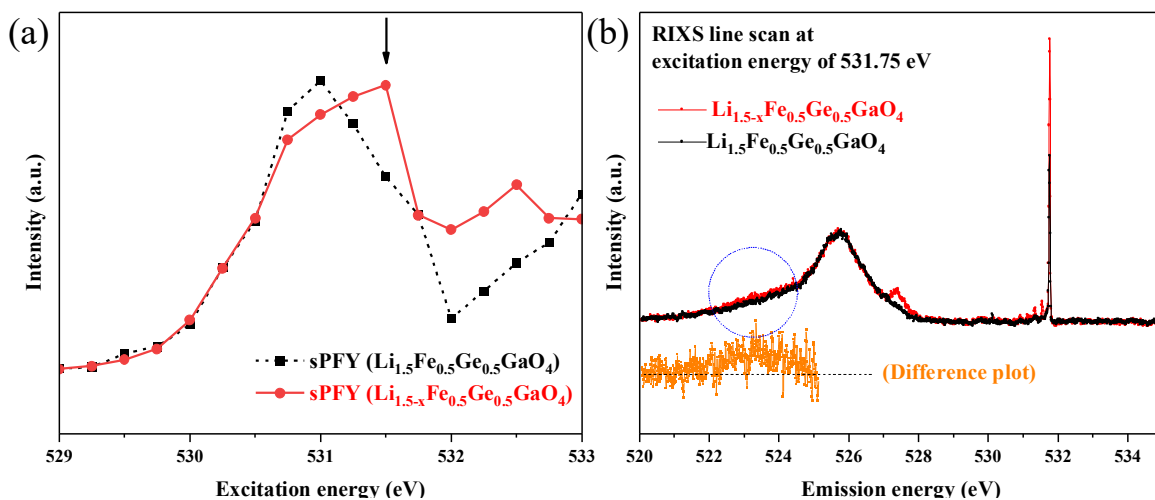


Figure 8. 12. (a): Comparison of sPFY data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (black dotted line) and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (red line). Arrow ($\downarrow$) indicates enhanced intensity for $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ at excitation energy of 531.5 eV. (b): RIXS line scan data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (black line) and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (red line), Highlighted area with blue dotted circle indicates the enhanced intensities at emission energy ~ 524 eV which is a characteristic trait of oxygen oxidation

8.3.6. Electrochemical cycling data

$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$

To investigate the electrochemical performance of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, cyclic voltammograms (CV) and galvanostatic charge-discharge measurements were performed. As shown in Figure 8.13 (a), CV data in the voltage range of 1.5-3.5 V show a discharge feature at ~ 1.8 V in the first cycle. The corresponding oxidation feature is observed at 2.5 V during the oxidation sweep. In the first six cycles a broad reversible feature is observed in the CV which is consistent with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$.

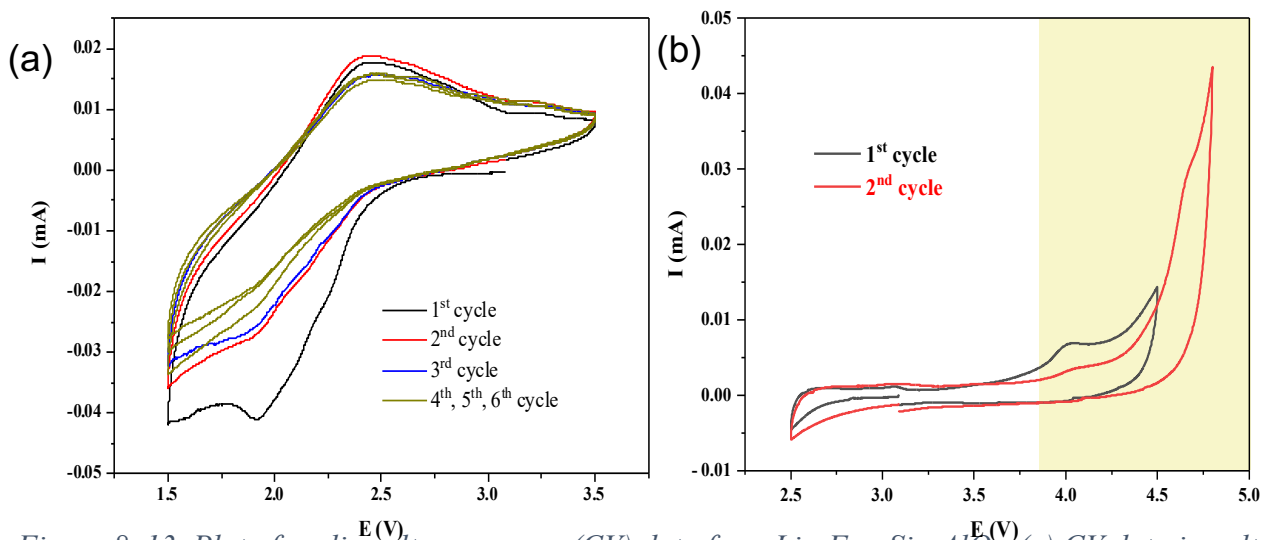


Figure 8. 13. Plot of cyclic voltammogram (CV) data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, (a) CV data in voltage range of 1.5-3.5 V in the first six cycles, (b) CV data in the voltage range of 2.5-4.8 V. Highlighted region indicates the irreversible oxidation feature observed during the cycling of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$.

CV data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ in the voltage range of 2.5-4.8 V (Figure 8.13, b) exhibit a large oxidation feature at voltages higher than 4.0 V, but the corresponding reduction peak is not observed indicating the electrochemical oxidation of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ being irreversible in nature.

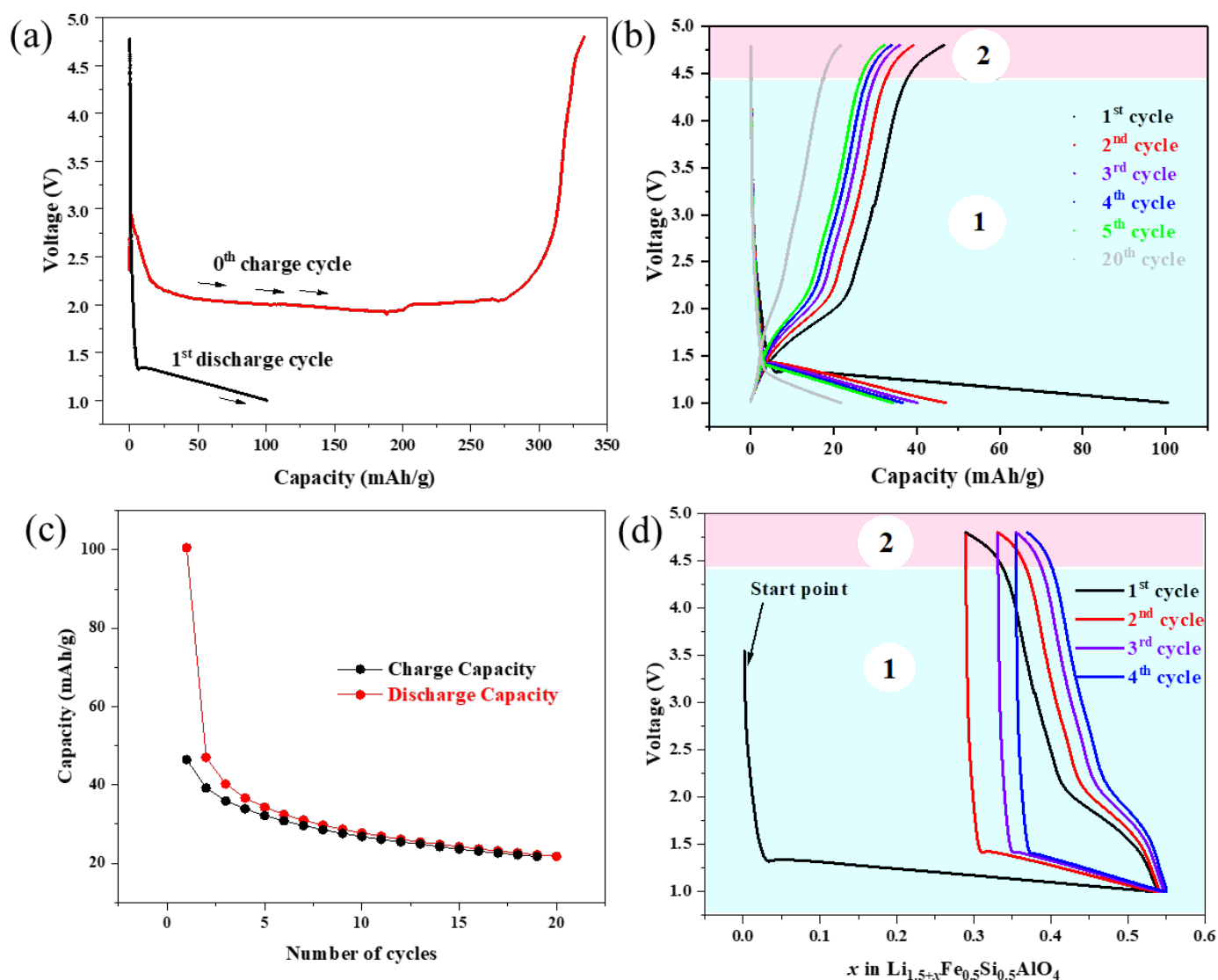


Figure 8. 14. Charge-discharge capacity profile of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ sample; (a) Voltage vs capacity plot with initial cycles, labelled as the 0th charge cycle with an unusual shape which is attributed to the phase transformation in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ upon delithiation. (b) Voltage vs capacity plot, excluding the 0th charge cycle (c) Plot of capacity vs number of cycles excluding the 0th charge cycle, (c) Plot of voltage vs the number of lithium being inserted (x) excluding the 0th charge cycle. Process1: charge-discharge within the voltage window of 1-4.5V, Process2: charge within the voltage window of 4.5-4.8 V.

Figure 8.14 displays the galvanostatic charge-discharge capacity profile data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ within the voltage range of 1-4.8 V. As shown in Figure 8.14 (a), the initial charge cycle, labelled as the 0th cycle, is anomalous. After an initial rise in potential from 2.4 V to 3V, there is an unexpected drop in potential from 3 V to 2 V, followed by a plateau which corresponds to a charge capacity of 300 mAh/g (Figure 8.14, a). Following this plateau, the potential rises again, reaching 4.8 V. This unusual behaviour during oxidation, especially the decline in potential, is attributed to the structural transformation of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ observed from a $\gamma\text{-NaFeO}_2$ to a $\beta\text{-NaFeO}_2$ structure type on delithiation, as detailed in Section 8.3.1.

As a result of this structural transformation on delithiation, the structural integrity of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ is not maintained, so the degree of lithiation of the material cannot be tracked by monitoring the current through the process. For instance, the observed charge capacity of 300 mAh/g is equivalent to the extraction of 1.6 Li^+ ion from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ which is unrealistic as it is more lithium than the sample contains. As a result, the actual amount of lithium extracted in the 0th charge cycle could not be determined. The Fe-XANES data collected from delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ shows no significant changes in the K-edge energy when compared with the pristine $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ (Section 8.3.3), indicating the delithiation in the 0th cycle is mainly associated with the oxidation of oxygen. Thus, it was assumed that at the end of the 0th charge cycle the oxidation state of iron in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ remained Fe^{+3} .

Subsequent charge discharge cycles performed on delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, shown in Figure 8.14 exhibit more conventional form, consistent with reversible insertion and removal of lithium. A capacity of 100 mAh/g is observed in the 1st discharge cycle which diminishes rapidly in the subsequent cycles (Figure 8.14, c). Close inspection of the charge profile reveals two separate processes. At low potential (1-4.5 V), an oxidation process (Process 1, Figure 8.14 b, d) is observed corresponding to 37 mAh/g in the 1st cycle, which is

attributed to the oxidation of iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$), in line with the analysis of the CV data in Figure 8.13. At potentials greater than 4.5 V, a second process (Process 2, Figure 8.14 b, d) occurs which contributes additional 10 mAh/g to the overall capacity. With reference to the CV data in Figure 8.13, this process is attributed to an irreversible oxidation associated with the Fe-O redox couple.

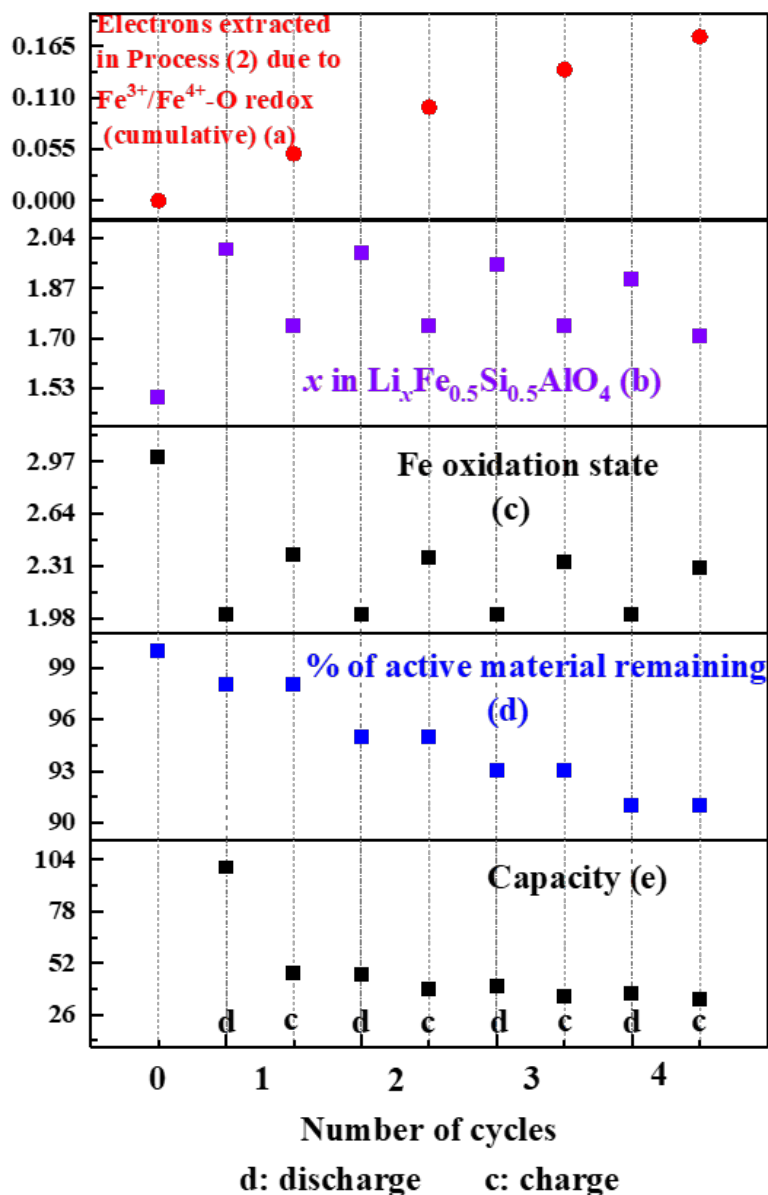


Figure 8. 15. Plot of various electrochemical features of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ derived from the plot of Voltage vs the amount of lithium inserted (x) in $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ (Figure 8.14, d). (a): Plot of number of cumulative electrons extracted in Process (2) due to combined $\text{Fe}^{3+}/\text{Fe}^{4+}$ -O redox against the number of cycles. (b): x in $\text{Li}_x\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ against the number of cycles, (c): variation of Fe oxidation state against the number of cycles. (d): % of active material remaining against the number of cycles. (e): Plot of capacity observed against the number of cycles.

In line with the analysis performed on the cycling data for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ in Section 5.4.6, we can track the different redox processes occurring in the $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ system by separating them into two process: Process 1, charge/discharge in the voltage range of $1 \leq V \leq 4.5$ which is attributed to $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox and, Process 2, charge in the voltage range of $4.5 \leq V \leq 4.8$ which is assigned to the irreversible Fe-O redox (Figure 8.14, b, d).

Figure 8.14, d, shows the initial discharge after the structural change from $\gamma\text{-NaFeO}_2$ structure to a $\beta\text{-NaFeO}_2$ structure, which yields a capacity of 100 mAh/g. If taken literally, this corresponds to the insertion of 0.54 Li^+ per formula unit, which would take the iron oxidation state below Fe^{2+} , which is chemically not reasonable. To avoid this, the excess 0.04 Li^+ per formula unit is assumed to decompose 2 mole% of the active material by reducing Fe^{2+} to elemental Fe. Thus, after the initial charge-discharge cycle, the cathode material has a composition of $\text{Li}_2\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ with the oxidation state of Fe(II).

The lithium insertion and extraction in the subsequent cycles, then can be analysed using the two processes at $1 \leq V \leq 4.5$ (Process 1) and $4.5 \leq V \leq 4.8$ (Process 2) as described above and shown in Figure 8.14 (b, and d). It is observed that, on charging, lithium is removed by oxidising both $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Fe-O redox processes. However, on reduction only the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple is reduced. It is also evident that, in the reduction step, more lithium is inserted than is required to reduce all the iron back to Fe(II). This again, is interpreted as the partial decomposition of the cathode (~2% in each discharge cycle).

Figure 8.15 tracks the different processes in the subsequent charge/discharge cycles i.e., the number of cumulative electrons extracted in Process (2), the amount of lithium (x) in $\text{Li}_x\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, the Fe-oxidation state, the percentage of the active material remaining, and the capacity against the number of cycles. It can be observed that the number of accumulated electrons due to Fe-O redox increases in each charge cycle. The iron oxidation state is found

to remain consistently below +3 when this irreversible Fe-O takes place. This demonstrates a preference towards maintaining Fe(II) in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ even when subjected to 4.8 V.

Approximately 2% of the $\text{Li}_x\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ active material is decomposed in each discharge cycle as a result the over-reduction, with the iron oxidation state cycling between $\text{Fe}^{2+}/\text{Fe}^{2.3(1)+}$. The observed capacity in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ (Figures 8.14 and 8.15) decline continuously and reaches 20 mAh/g in the 20th cycle. This capacity fading is attributed to both the irreversible loss of lithium ($\sim 0.05\text{Li}^+/\text{f.u.}$ in each cycle) due to Fe-O redox (major cause) and the decomposition of 2% active material in each discharge cycle due to over-reduction (minor cause).

The apparent stability of Fe(II) in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ can be explained due to the enlargement of the $\langle\text{Fe-O}\rangle$ bond, occurring during the cation exchange process from $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ to $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$. This enlarged $\langle\text{Fe-O}\rangle$ bond in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ favours the presence of Fe(II) and thus maintains the oxidation state of iron below +3 even when subjected to charge at a voltage of 4.8 V.

The continuous decomposition of 2% active material in each discharge cycle indicates that, substitutions of Fe cation by Al/Si cations in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ fails to completely stabilise the structure fully under reductive conditions.

Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄

The CV data from Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄, depicted in Figure 8.16 within the voltage range of 1.5-4.25 V, reveals two distinct processes. In the 1.5-3.2 V range, a broad reversible feature is evident with an oxidation peak at 2.75 V and a reduction peak at 1.9 V, indicative of the Fe³⁺/Fe²⁺ redox process. At voltages higher than 3.5 V, another broad oxidative feature is observed, which fades in subsequent cycles. Significantly, there is no evidence of any reduction feature for this high-voltage oxidative peak in the cyclic voltammogram profile, suggesting the electrochemical irreversibility of the oxidation at higher voltage.

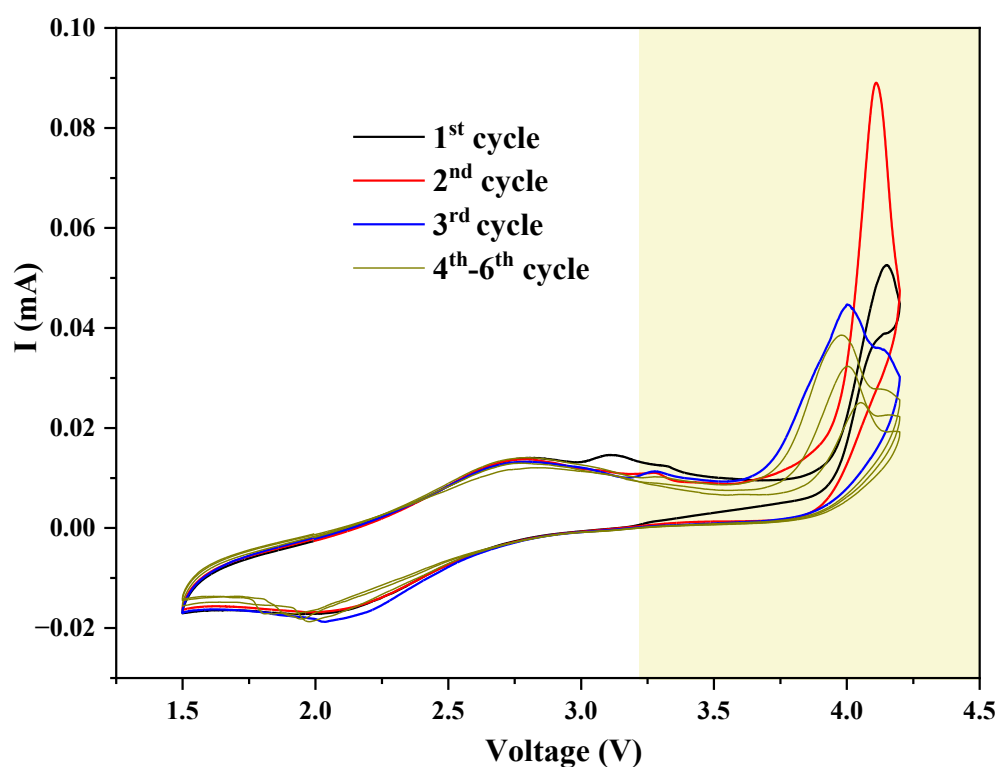


Figure 8. 16. CV data from Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄ in the voltage range of 1.5-4.25 V. Highlighted region indicates the irreversible oxidation feature.

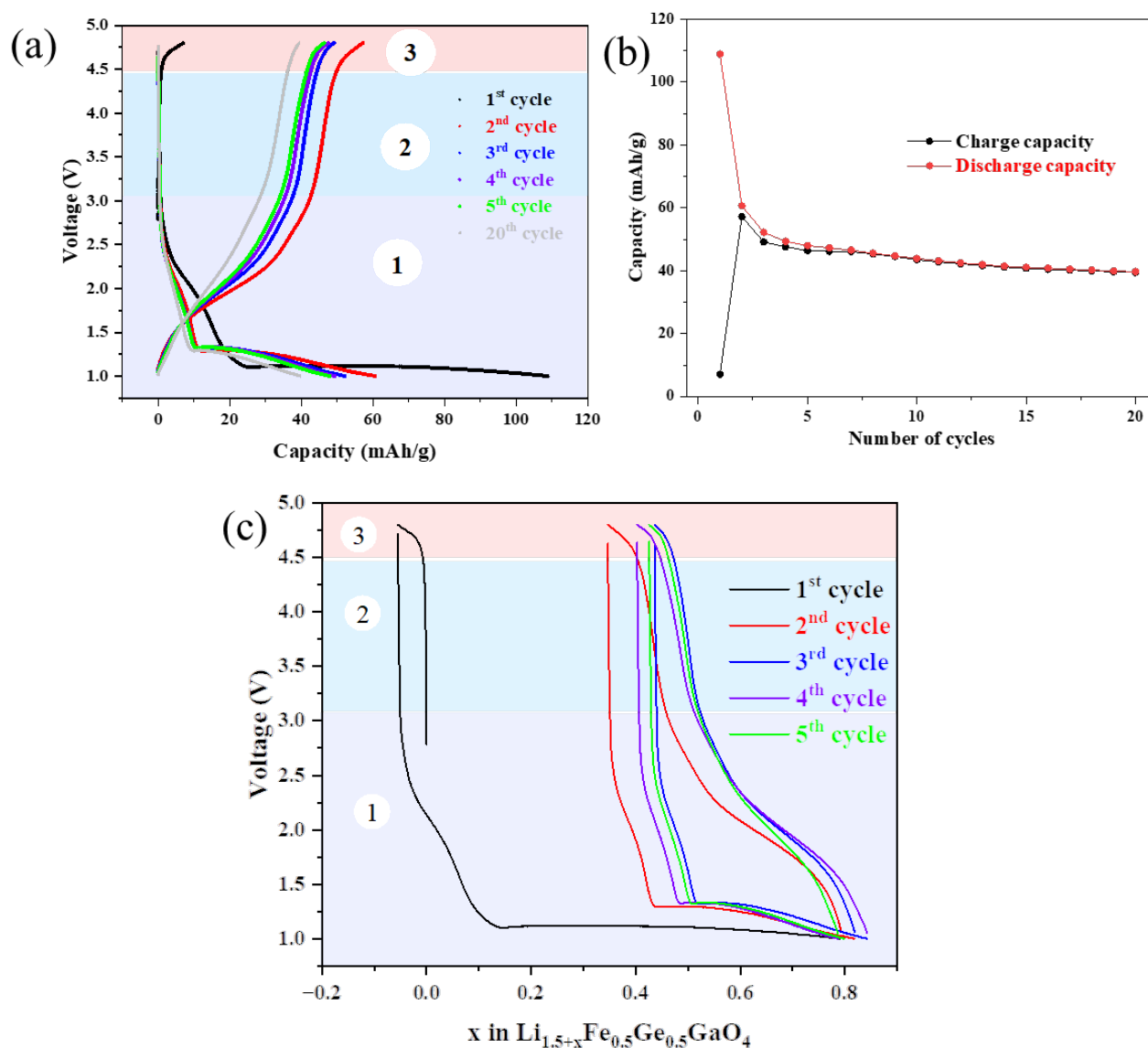


Figure 8.17. Charge-discharge capacity profile of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ sample; (a) Voltage vs capacity plot, (b) Capacity vs number of cycles, (c) voltage vs number of lithium being inserted (x), Process1: charge-discharge within the voltage window of 1-3.1V, Process2: redox inactive region within the voltage window of 3.1-4.5V. Process3: charge within the voltage window of 4.5-4.8 V.

The charge-discharge capacity profile data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ is presented in Figure 8.17. In the first discharge cycle, a discharge capacity of 108 mAh/g is observed which corresponds to the insertion of 0.83 Li^+ per formula unit. If taken literally, this insertion of 0.83 Li^+ will reduce iron below the oxidation state of +2, which is chemically not reasonable. Thus, to avoid this, it was assumed that the excess 0.33 Li^+ per formula unit decomposes 16.5 mol% of the active material by reducing Fe^{2+} to elemental iron. In the subsequent cycles, a stable reversible capacity of 40 mAh/g, equivalent to the cycling of 0.34 Li^+ per formula unit in each

cycle is evident (Figure 8.17, c). Similar to the analysis of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ (discussed earlier), the electrochemical data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ was divided into three process as: Process 1, reversible charge/discharge in the voltage range of $1 \leq V \leq 3.1$ associated with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox; Process 2, redox inactive region in the voltage range of $3.1 \leq V \leq 4.5$; and Process 3, irreversible charge process at voltages higher than 4.5 V associated with the Fe-O redox.

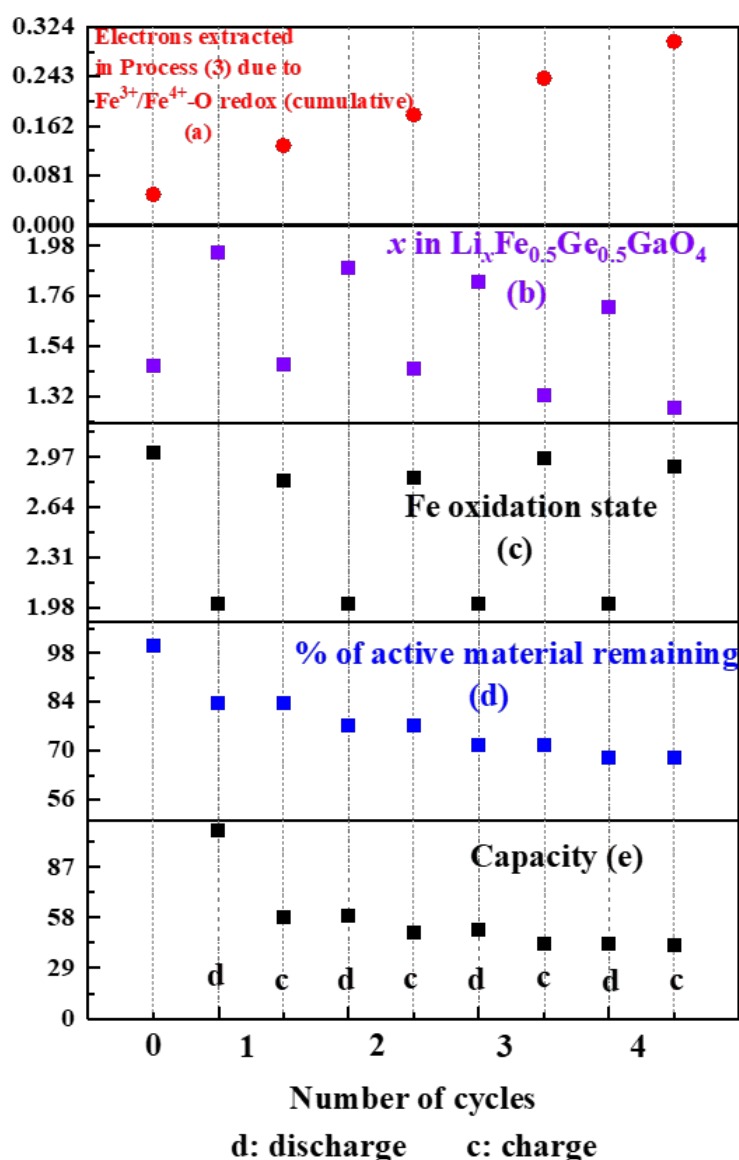


Figure 8. 18. Plot of various electrochemical features of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, derived from the plot of Voltage vs the amount of lithium inserted (x) in $\text{Li}_{1.5+x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (Figure 8.17, c). (a): Plot of number of cumulative electrons extracted in Process (3) due to combined $\text{Fe}^{3+}/\text{Fe}^{4+}$ -O redox against the number of cycles. (b): lithium content (x) in $\text{Li}_x\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (c): variation of Fe oxidation state against the number of cycles. (d): Plot of % of active material remaining against the number of cycles. (e) Plot of capacity observed against the number of cycles.

Figure 8.18 tracks the different processes in the charge/discharge cycles, i.e., the number of cumulative electrons extracted in Process (3), the amount of lithium (x) in $\text{Li}_x\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, the Fe-oxidation state, the percentage of the active material remaining and the capacity against the number of cycles. In the voltage range of 4.5-4.8 V (Process 3) a charge process is observed which corresponds to the irreversible extraction of $\sim 0.05 \text{ Li}^+$ in each cycle (Figures 8.17, c and 8.18, a). The repeated extraction of $\sim 0.05 \text{ Li}^+$ in each charge cycle, slowly depletes the lithium content of the material, but as shown in Figure 8.18, c, the Fe oxidation state continues to cycle between Fe(II) and Fe(III). Thus after ~ 6 -7 cycles the cathode material has a composition close to $\sim \text{Li}_{1.0}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ in the charged state, which is approximately the same composition of the sample prepared by oxidation with NO_2BF_4 (Section 6.4). The continued cycling of the cathode material between Fe(II) and Fe(III) (Figure 8.18, c) despite the irreversible loss of lithium in the high voltage process, suggests this irreversible loss is not the source of capacity loss.

During the discharge process, lithium insertion in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ leads to over-reduction of the active material which results in decomposition ($\text{Fe}^{2+} \rightarrow \text{Fe}^0$). Figure 8.18 shows that $\sim 30\%$ of active material is decomposed in the first four discharge cycles which can be attributed to the primary cause of the capacity fading in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$. Figure 8.18 also shows that, a fully reversible $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox in the voltage range of 1-3.1V is operational, indicating that $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ does not suffer from any strong preference towards Fe(II) unlike $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$. The capacity fading in the initial cycles can be attributed to both the irreversible $0.05 \text{ Li}^+/\text{f.u.}$ extraction in each cycle at $V > 4.5 \text{ V}$ (minor contribution) and the decomposition of the active material at $V < 3.1 \text{ V}$ due to the over reduction (major contribution). After the initial cycles, the decomposition of the active material is stopped progressively. This inhibition of the decomposition of the active material is consistent with the stable capacity ($\sim 40 \text{ mAh/g}$) observed in the later cycles.

The analysis of the charge-discharge profile data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ reveals, despite the initial capacity loss and partial decomposition of the active material, a stable and reversible capacity of ~ 40 mAh/g is observed in the later cycles. A comparison of the $\langle\text{Fe-O}\rangle$ bond lengths of $\text{Na}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (1.83(4) Å) and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ (1.882(4) Å) shows an elongation of the $\langle\text{Fe-O}\rangle$ in the latter compound compared to the former (Section 6.4). This elongation implies a preference for Fe(II) over Fe(III) in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ upon lithiation. Surprisingly, contrary to this expectation, no such preference is observed, as fully reversible $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox is evident in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ during cycling. This observation indicates there are more subtle bonding interaction in play for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ which contributes to this distinct behaviour in the electrochemical data.

A comparison of the electrochemical data of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ reveals different mechanisms are contributing to capacity loss. In $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, the primary cause of capacity decline is the irreversible Li^+ loss associated with the Fe-O redox process. Conversely, in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, the primary factor leading to capacity reduction is linked to the decomposition of the active material triggered by over-reduction ($\text{Fe}^{2+} \rightarrow \text{Fe}^0$).

8.3.7. Discussion for oxidation of $\text{Li}_{1.5-8}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ phases

Analysis of the SXRD data from delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, reveal that a structural transformation from the γ - NaFeO_2 structure type in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ to the β - NaFeO_2 structure type in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ as a result of treatment with NO_2BF_4 . This structural transformation of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ upon delithiation, is also evident in the charge process of the electrochemical data.

X-ray diffraction data from delithiated $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ after the treatment of LiI in acetonitrile (Appendix-I, Figure 8a.1) shows retention of β - NaFeO_2 structure type, indicating

the structural change from γ -NaFeO₂ type in Li_{1.5}Fe_{0.5}Si_{0.5}AlO₄ to β -NaFeO₂ type in Li_{1.5-x}Fe_{0.5}Si_{0.5}AlO₄ is irreversible in nature under the lithiating conditions used.

The Fe-BVS values calculated from the refined structural model of Li_{1.5-x}Fe_{0.5}Si_{0.5}AlO₄, indicates a small degree of iron oxidation upon delithiation (Section 8.3.1) which is further supported by the Fe K-edge XANES data. Although O K-edge XAS and RIXS data were not collected for Li_{1.5}Fe_{0.5}Si_{0.5}AlO₄ and Li_{1.5-x}Fe_{0.5}Si_{0.5}AlO₄, the extent of change in the Fe K-edge energy in the XANES data and the observed irreversible electrochemical features suggest a combination of Fe³⁺/Fe⁴⁺ redox and participation of oxygen redox during the delithiation process.

Analysis of the NPD data collected from Li_{1.5-x}Fe_{0.5}Ge_{0.5}GaO₄ reveals the retention of the pristine structure and the pristine cation ordering of Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄ in delithiated Li_{1.5-x}Fe_{0.5}Ge_{0.5}GaO₄. Reversible intercalation in Li_{1.5-x}Fe_{0.5}Ge_{0.5}GaO₄ via the treatment with LiI is consistent with the analysis of the ICP-MS and iodometric titration data (Appendix-I Tables 8a.1-8a.2). Fe-XANES, O K-edge XAS, and RIXS data confirm that the delithiation process in Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄ to be primarily associated with oxygen oxidation.

Notably, this delithiation process is only chemically reversible and electrochemical irreversibility remains a common feature in doped LiFeO₂ samples, with approximately 0.05 lithium irreversibly extracted at high voltages ($E > 4V$) in each cycle, providing additional 10-15 mAh/g capacities to the overall capacities during the charge process. The observed irreversibility can be attributed to the slow kinetics of the involved redox processes.

The electrochemical cycling behaviour observed for both Li_{1.5}Fe_{0.5}Si_{0.5}AlO₄, and LiFe_{0.5}Ge_{0.5}GaO₄ is found to be associated with the reduction of Fe³⁺ to Fe²⁺ during the lithium insertion in the first discharge cycle with partial decomposition of the active material. In the case of Li_{1.5}Fe_{0.5}Si_{0.5}AlO₄, the irreversible Li⁺ loss due to anion redox in each cycle is observed

as the main cause for the capacity fading. On the contrary, in the case of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$, the primary cause of capacity fading is the decomposition of the active material in the initial cycles. After the initial decomposition and the capacity loss, a stable percentage of the active material and a stable capacity (40 mAh/g) is maintained for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ in the later cycles.

In the case of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, the change in iron oxidation state during the electrochemical cycling was observed as $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ (during 1st discharge) and $\text{Fe}^{2+x+} \leftrightarrow \text{Fe}^{2+}$ (subsequent charge/discharge cycles) in the voltage range of 1-4.8 V. However, in the case of $\text{LiFe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ the change of iron oxidation state observed as $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ in the voltage range of 1-3.1 V. In other words, $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ shows a preference towards maintaining Fe(II) (even at 4.8V), however $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ shows no such preference. This behaviour is hard to explain only on the basis of enlargement of $\langle \text{Fe-O} \rangle$ bond lengths, as for both the samples, this enlargement during the cation exchange process is observed from $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ to $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$ (Section 6.4). This behaviour further indicates that, there are more subtle bonding interactions are at play for the aliovalent doped LiFeO_2 samples which influences the electrochemical behaviours of these samples.

In the electrochemical cycling data of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{LiFe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ both are found to be decomposing partially when subjected to reductive conditions indicating, substitution of iron cations by Si/Al or Ga/Ge cations in LiFeO_2 do not fully stabilise the structure under reductive conditions.

Chapter 9 – Synthesis, characterization, reduction and oxidation of $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases ($A = \text{Na}$ or Li)

9.1. Introduction

The synthesis, crystal structure and magnetic properties of $\text{Na}_3\text{Fe}_5\text{O}_9$ were first reported by C. Romers et al.¹⁸¹ The crystal structure of $\text{Na}_3\text{Fe}_5\text{O}_9$ consists of a linked network of two tetrahedral FeO_4 units ($8f$ site symmetry) and one octahedral FeO_6 unit ($4e$ site symmetry) as shown in Figure 9.1 and thus can be considered as a composite of $\alpha\text{-NaFeO}_2$ ($R\bar{3}m$) and $\beta\text{-NaFeO}_2$ ($Pna2_1$). Adjacent FeO_6 units share edges to form chains which run parallel to the c -axis. The Fe-O framework contains vacant channels, labelled A, B, C, and D in Figure 9.1, which can accommodate additional cations (e.g. Na^+).

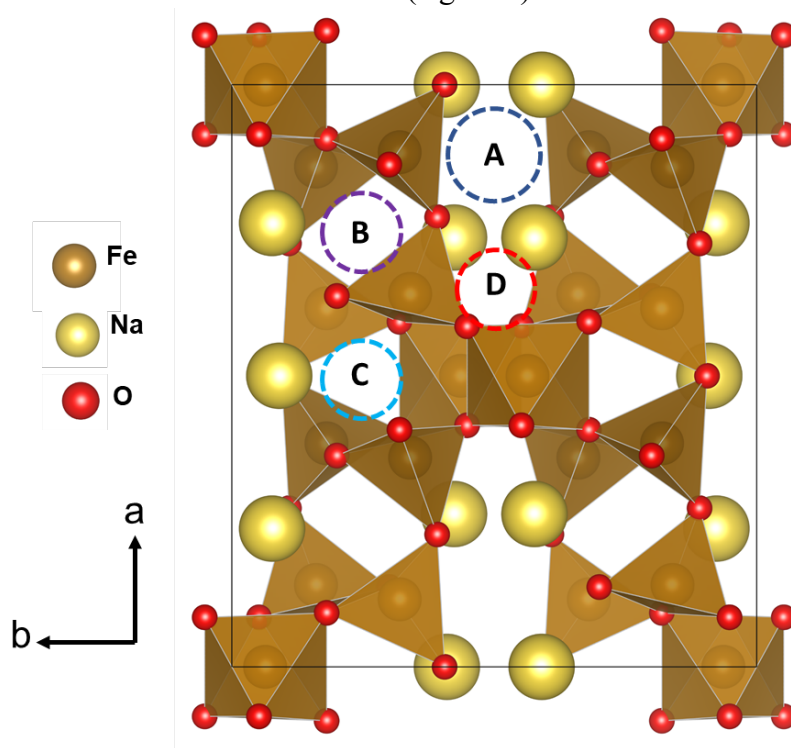


Figure 9. 1. The structure of $\text{Na}_3\text{Fe}_5\text{O}_9$, A, B, C, and D represents vacant channels

Gallium-substituted $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases were synthesized, and sodium within the material was replaced by lithium through ion exchange reactions, resulting in the corresponding

$\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases. For reductive lithium insertion and oxidative lithium extraction, $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases were treated with *n*-butyl lithium (*n*-BuLi) and nitronium tetrafluoroborate (NO_2BF_4), respectively, with electrode potentials of 1.04 V and 5.14 V vs the Li^+/Li redox couple.^{115,116,155} The products obtained were characterised by SXRD, NPD, XAS, ICP-MS, Mössbauer, XAS, and RIXS techniques, which are described in this chapter. Additionally, the electrochemical performance of $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ is also discussed.

9.2. Experimental section

9.2.1. Synthesis of $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

Samples of $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ ($0 \leq x \leq 5$) were synthesized by a high-temperature ceramic synthesis method as described in Section 2.1.1. Suitable ratios of Na_2CO_3 (>99%, BDH chemicals), Fe_2O_3 (99.105%, Alfa Aesar), Ga_2O_3 (99.99% Alfa Aesar) were weighed, ground and calcined in air at 750 °C for 12 hours. The powders were then reground and pressed into 13 mm pellets which were heated at 1100 °C for 24 hours. The grinding, pellet pressing and reheating cycles were continued until a pure $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phase was obtained. The addition of an extra 5-10 mol percent of Na_2CO_3 during the later heating cycles facilitated the preparation of the pure samples

9.2.2. Synthesis of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

After obtaining pure $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples, low-temperature topochemical cation exchange reactions were performed to obtain the corresponding $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases. Initially ten mole equivalents of LiCl (98+%, Alfa Aesar) or LiBr (99%, Alfa Aesar) was added to a 250 mL round bottom flask containing ~ 150 mL of *n*-hexanol, then the $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ sample was added. A water condenser was attached to the flask and the apparatus was heated at 165 °C for 48 hours, using an oil bath, with constant stirring of the *n*-hexanol suspension. After heating, the contents of the flask were filtered and then washed with methanol. Finally, the cation exchanged product was collected by vacuum filtration and transferred into a glovebox.

9.2.3. Lithium intercalation into $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases

Approximately 200 mg of each $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ sample was placed into a small Schlenk tubes under a nitrogen atmosphere and 6-8 mL of a 1.6 M *n*-BuLi in *n*-hexanes solution (Merck life sciences) was added, maintaining a 1:5 molar ratio of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ to *n*-BuLi. The tube was securely sealed using a glass cap, and the contents were stirred at room temperature for a duration of 48 hours. This process resulted in a colour transformation of the powder from orange/dark brown to black. The resulting black suspension was then subjected to filtration and washed with excess toluene under a nitrogen environment. Finally, the black powder obtained was dried under vacuum and transferred into an argon-filled glove-box.

To check the reversibility of lithium intercalation, the samples were exposed to a known concentration of iodine in acetonitrile. Following the reaction, the remaining iodine was titrated against a standardized thiosulfate solution.

9.2.4. Lithium deintercalation from $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$

In a small Schlenk tube under a nitrogen atmosphere, approximately 500 mg of NO_2BF_4 (95+%, Merck Life Science) was dissolved in 10 mL of acetonitrile. Maintaining a molar ratio of 1:5 of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$: NO_2BF_4 , around 200 mg of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ sample was added to the solution, and the tube was sealed with a glass cap. The tube was transferred to an oil bath where the contents of the tube were constantly stirred and heated at 50°C for 7 days. Following this period, the suspension obtained was filtered with excess acetonitrile solution, and the resulting powder was collected via vacuum filtration.

To check the reversibility of lithium deintercalation, the deintercalated sample ($\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$) was treated with LiI (99.999%, Alfa Aesar) in the following manner. In a controlled nitrogen environment, about 300 mg of LiI (99.999%, Alfa Aesar) was dissolved in 10 mL of acetonitrile within a small Schlenk tube. Preserving a molar ratio of 1:10 between $\text{Li}_{3-\delta}\text{Fe}_{5-x}$

$x\text{Ga}_x\text{O}_9$ and LiI, approximately 50-70 mg of the $\text{Li}_{3-8}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ sample was introduced into the solution, and the tube was sealed with a glass cap. The sealed tube was then placed in an oil bath where its contents were continuously stirred and heated at 50°C for 3 days. A noticeable change in the colour of the solution from colourless to yellow or dark brown was observed, indicating iodine release during the reaction. Following this reaction, the powder was collected through filtration. To quantify the released iodine, the filtrate was titrated against a standardized thiosulphate solution.

9.2.5. Electrochemical cycling

A mixture with a 80:10:10 mass ratio of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$: carbon black : polyvinylidene fluoride (PVDF) was weighed and ground into a fine powder. 0.3 mL of 1-methyl-2-pyrrolidone (NMP) was then added and the mixture was mechanically shaken until a homogeneous viscous slurry was obtained. The slurry was poured onto a carbon-coated aluminium foil and first dried in air and then heated for 12 hours at 80°C in a vacuum oven. The dry slurry cast was cut into 12 mm disc cathodes and transferred into the glovebox. A coin cell was assembled using Cambridge Energy Solutions SS316 CR2032 coin cell cases, a lithium chip (15.6 mm diameter, 0.25 mm thick), a Whatman glass fiber membrane separator (16mm diameter), and the cast cathode. The separator was soaked with 10 μL of electrolyte and the coin cell was sealed. Cyclic voltammograms and charge-discharge capacity profile measurements were conducted after assembling the coin cell.

9.3. Characterization results and discussion for $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases

9.3.1. Structural characterization of $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$

Synchrotron X-ray diffraction (SXRD) and Neutron powder diffraction (NPD)

SXRD data were collected from $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases where x is 0, 1, 2, 3, 4 and 5. A series of crystallographic models were constructed based on the reported structure of $\text{Na}_3\text{Fe}_5\text{O}_9$ ¹⁸¹, described in space group $C2/c$, but with the $8f$ and $4e$ sites containing a combination of Fe/Ga cations appropriate to the sample composition. These models were then refined against the corresponding SXRD data to achieve good fits. Fitted diffraction data from the refinement of $\text{Na}_3\text{Fe}_5\text{O}_9$ are shown in Figure 9.2 with crystallographic data in Table 9.1. For other $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases, the same is given in Appendix-I Figures and Tables 9a.1-9a.3.

The similar X-ray scattering powers of Fe^{3+} and Ga^{3+} make the characterisation of any Fe/Ga order challenging. To assist with structural refinement, neutron powder diffraction data was collected from $\text{Na}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ and $\text{Na}_3\text{Fe}_2\text{Ga}_3\text{O}_9$. During the structural refinement, it was found that the best fit to the data was achieved using a model with $4e$ octahedral site containing exclusively iron and $8f$ tetrahedral site containing a combination of iron and gallium. The structural refinement plots and the corresponding refined crystallographic parameters are given in Figures 9.3, 9.4 and Table 9.2 and 9.3 for $\text{Na}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ and $\text{Na}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ respectively. $\langle\text{Fe}-\text{O}\rangle$, $\langle\text{Ga}-\text{O}\rangle$ bond lengths and bond valance sums calculated from the refined models of $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ ($0 \leq x \leq 5$) phases are given in Tables 9.5 and 9.6 respectively.

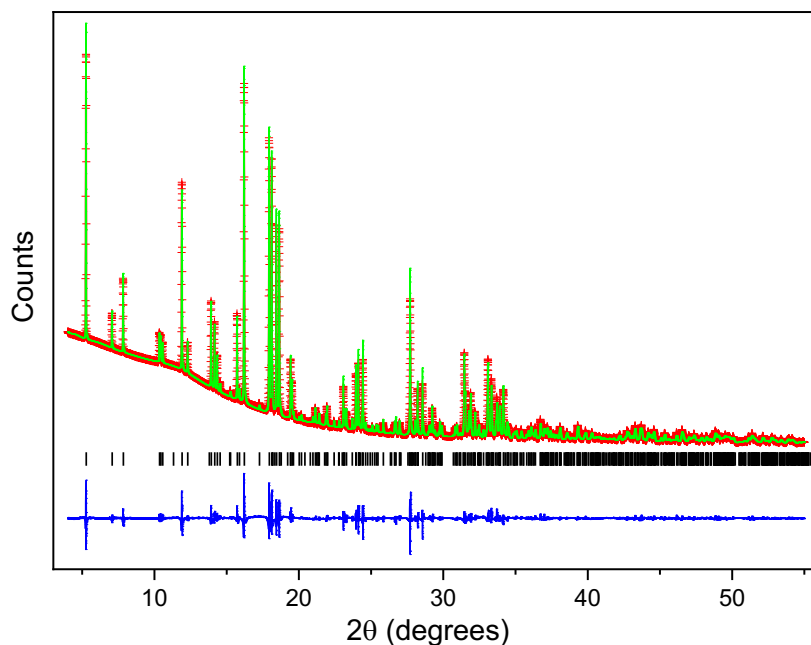


Figure 9. 2 Observed, calculated and difference plots from the structural refinement of $\text{Na}_3\text{Fe}_5\text{O}_9$ against SXRD data.

Table 9.1. Parameters from the structural refinement of $\text{Na}_3\text{Fe}_5\text{O}_9$ sample against SXRD collected at room temperature

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1	8f	0.1156(1)	0.3198(1)	0.2167(2)	1	0.45(1)
Fe2	8f	0.3597(1)	0.3388(1)	0.2829(2)	1	0.45(1)
Fe3	4e	0	0.0640(1)	1/4	1	0.45(1)
Na1	8f	0.2382(3)	0.0772(3)	0.2296(8)	1	1.01(5)
Na2	4e	0	0.5924(4)	1/4	1	1.01(5)
O1	8f	0.0825(3)	0.0548(4)	0.9227(9)	1	0.71(4)
O2	8f	0.3664(3)	0.2049(4)	0.1231(1)	1	0.71(4)
O3	8f	0.2274(3)	0.3874(3)	0.3266(9)	1	0.71(4)
O4	8f	0.4065(3)	0.3171(4)	0.6115(9)	1	0.71(4)
O5	4e	0	0.3990(5)	1/4	1	0.71(4)
$\text{Na}_3\text{Fe}_5\text{O}_9$ – space group $C2/c$ (#15) $a = 13.4031(1) \text{ \AA}$, $b = 12.0794(1) \text{ \AA}$, $c = 5.2985(4) \text{ \AA}$, $\beta = 89.1689(4)^\circ$ volume = $857.748(13) \text{ \AA}^3$ Formula weight= 492.2 g mol^{-1} , $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 2.02 \%$, $wR_p = 3.20 \%$, $R_{\text{Bragg}} = 1.43$						

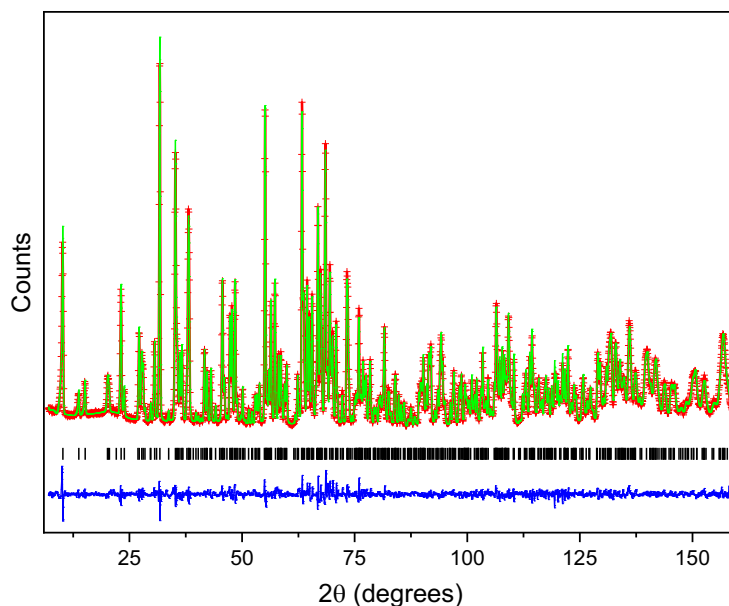


Figure 9. 3 Observed, calculated and difference plots from the structural refinement of $\text{Na}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ against NPD data

Table 9.2. Parameters from the structural refinement of $\text{Na}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1/Ga1	8f	0.1156(1)	0.3178(1)	0.2185(3)	0.5/0.5	0.086(32)
Fe2/Ga2	8f	0.3590(1)	0.3389(1)	0.2804(3)	0.5/0.5	0.086(32)
Fe3	4e	0	0.0638(1)	1/4	1	0.201(39)
Na1	8f	0.2409(2)	0.0758(3)	0.2307(8)	1	0.30(1)
Na2	4e	0	0.5922(5)	1/4	1	0.30(1)
O1	8f	0.0833(1)	0.0528(2)	0.9244(4)	1	0.192(35)
O2	8f	0.3653(1)	0.2030(2)	0.1279(4)	1	0.603(42)
O3	8f	0.2276(1)	0.3907(2)	0.6137(4)	1	0.440(40)
O4	8f	0.4054(1)	0.3185(2)	0.6137(4)	1	0.165(36)
O5	4e	0	0.4032(2)	1/4	1	0.535(60)
$\text{Na}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ – space group $C2/c$ (#15) $a = 13.3036(1) \text{ \AA}$, $b = 12.0849(1) \text{ \AA}$, $c = 5.2725(1) \text{ \AA}$, $\beta = 89.0917 (6)^\circ$ volume = $847.576 (15) \text{ \AA}^3$ Formula weight = $519.94 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, $\lambda = 1.59432 \text{ \AA}$ Temperature: 298 K $R_p = 3.08 \%$, $wR_p = 4.06 \%$, $R_{\text{Bragg}} = 1.21$						

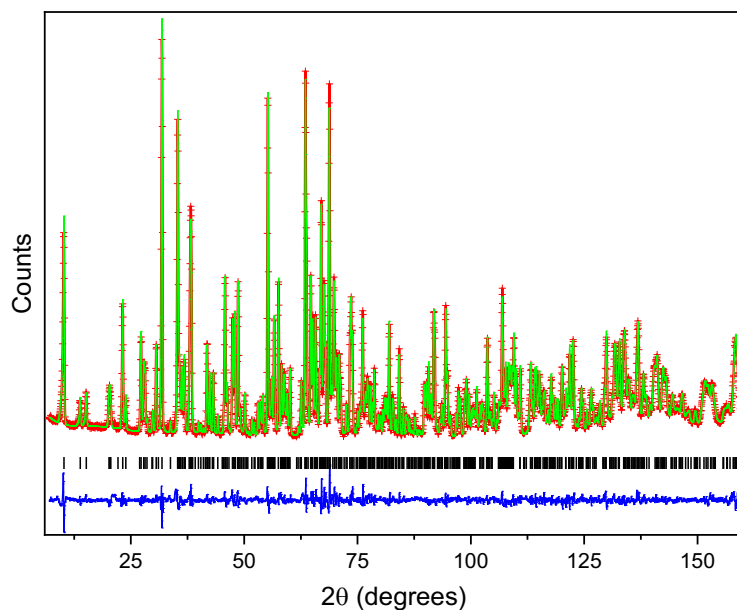


Figure 9. 4. Observed, calculated and difference plots from the structural refinement of $\text{Na}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ against NPD data

Table 9.3. Parameters from the structural refinement of $\text{Na}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1/Ga1	8f	0.1157(1)	0.3170(1)	0.2186(2)	0.25/0.75	0.103(24)
Fe2/Ga2	8f	0.3586(1)	0.3389(1)	0.2799(3)	0.25/0.75	0.103(24)
Fe3	4e	0	0.0641(1)	1/4	1	0.302(36)
Na1	8f	0.2408(2)	0.0759(3)	0.2322(7)	1	0.40(11)
Na2	4e	0	0.5903(4)	1/4	1	0.52(13)
O1	8f	0.0835(1)	0.0529(1)	0.9241(4)	1	0.218(36)
O2	8f	0.3651(1)	0.2029(1)	0.1276(4)	1	0.521(39)
O3	8f	0.2275(1)	0.3906(2)	0.3305(4)	1	0.357(3)
O4	8f	0.4058(1)	0.3188(2)	0.6124(4)	1	0.247(37)
O5	4e	0	0.4018(2)	1/4	1	0.427(56)
$\text{Na}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ – space group $C2/c$ (#15) $a = 13.2484(1) \text{ \AA}$, $b = 12.0830(1) \text{ \AA}$, $c = 5.2556(1) \text{ \AA}$, $\beta = 89.0555 (6)^\circ$ volume = $841.225 (14) \text{ \AA}^3$ Formula weight = $530.65 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, $\lambda = 1.59432 \text{ \AA}$ Temperature: 298 K $R_p = 2.99 \%$, $wR_p = 4.06 \%$, $R_{\text{Bragg}} = 1.21$						

Table 9.4. Table of cell parameters extracted from structural refinement against SXRD and NPD data from Na₃Fe_{5-x}Ga_xO₉ samples

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Volume (Å ³)
Na ₃ Fe ₅ O ₉	13.40310(11)	12.07939(10)	5.29852(4)	89.1689(4)	857.748(13)
Na ₃ Fe ₄ GaO ₉	13.35438(4)	12.08397(3)	5.28615(1)	89.1298(2)	852.950(4)
Na ₃ Fe ₃ Ga ₂ O ₉	13.3036(1)	12.0849(1)	5.2725(1)	89.0917(6)	847.576(15)
Na ₃ Fe ₂ Ga ₃ O ₉	13.2484(1)	12.0830(1)	5.2556(1)	89.0555(7)	841.225(14)
Na ₃ FeGa ₄ O ₉	13.19296(7)	12.07248(8)	5.23349(3)	89.0363(4)	833.431(9)
Na ₃ Ga ₅ O ₉	13.14071(8)	12.04941(8)	5.20678(3)	89.0464(4)	824.316(9)

Table 9.5. Table of bond distance calculated from structural refinement against SXRD and NPD data from Na₃Fe_{5-x}Ga_xO₉ samples

<M-O>	site	Na ₃ Fe _{5-x} Ga _x O ₉					
		<i>x</i> =0	<i>x</i> =1	<i>x</i> =2	<i>x</i> =3	<i>x</i> =4	<i>x</i> =5
		Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)
Fe1-O	8 <i>f</i>	1.846(2)	1.857(2)	1.846(4)	1.851(2)	1.871(2)	1.820(2)
Ga1-O	8 <i>f</i>						
Fe2-O	8 <i>f</i>	1.858(1)	1.866(2)	1.880(2)	1.848(2)	1.855(2)	1.857(1)
Ga2-O	8 <i>f</i>						
Fe3-O	4 <i>e</i>	2.044(2)	2.029(2)	2.031(2)	2.033(2)	1.977(1)	2.038(1)
Ga3-O	4 <i>e</i>						

Table 9.6. Table of bond valence sum calculated from structural refinement against SXRD and NPD data from Na₃Fe_{5-x}Ga_xO₉ samples

<M-O>	site	Na ₃ Fe ₅ O ₉	Na ₃ Fe ₄ GaO ₉	Na ₃ Fe ₃ Ga ₂ O ₉	Na ₃ Fe ₂ Ga ₃ O ₉	Na ₃ FeGa ₄ O ₉	Na ₃ Ga ₅ O ₉
		BVS	BVS	BVS	BVS	BVS	BVS
Fe1-O	8 <i>f</i>	3.174	3.075	3.162	3.121		
Ga1-O	8 <i>f</i>		2.853	2.819	2.862	2.759	3.149
Fe2-O	8 <i>f</i>	3.064	3.007	2.882	3.143		
Ga2-O	8 <i>f</i>		2.780	2.816	2.857	3.089	2.845
Fe3-O	4 <i>e</i>	2.774	2.888	2.878	2.879	3.330	
Ga3-O	4 <i>e</i>						2.825

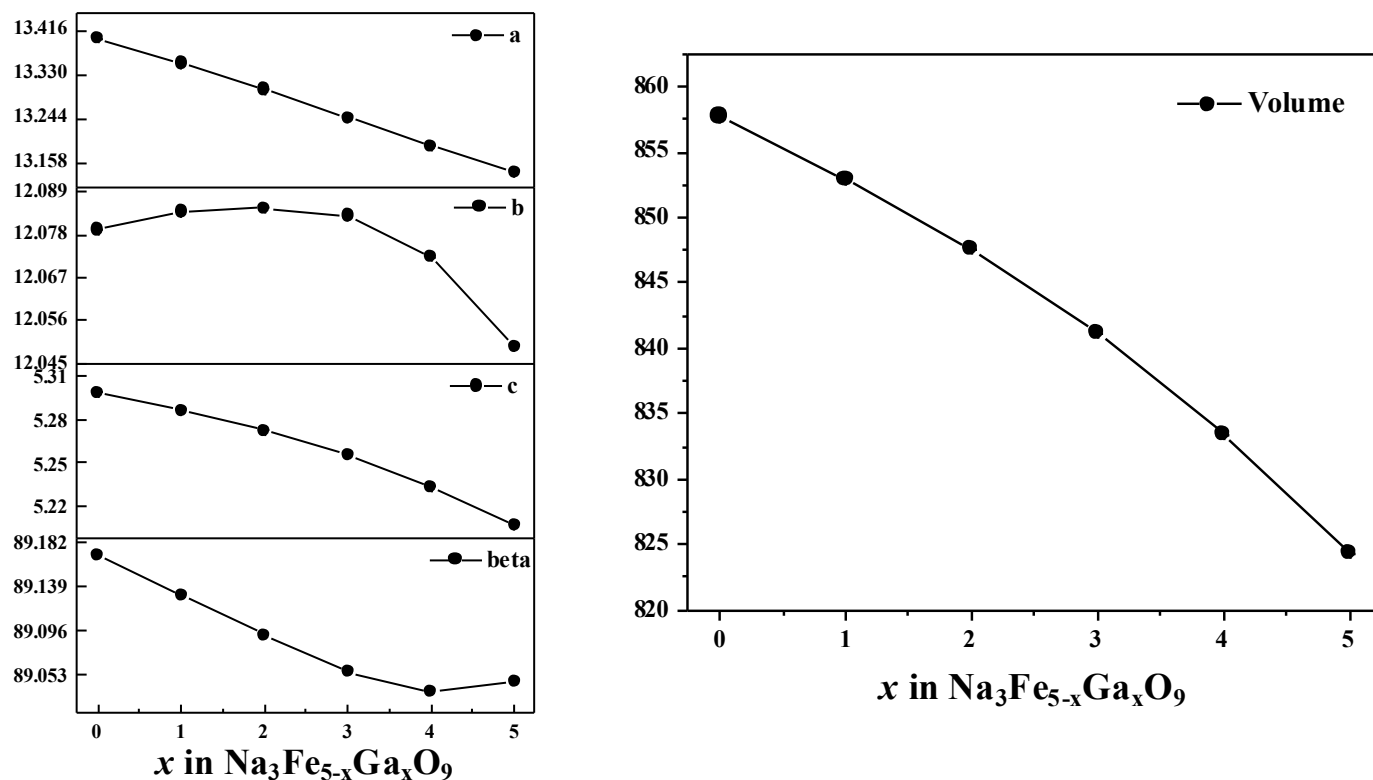


Figure 9. 5. Plot of lattice parameters as a function of composition for $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples. Error bars are smaller than the plotted points

9.3.2. Structural characterization of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$

Synchrotron X-ray diffraction (SXRD) data and Neutron powder diffraction (NPD)

SXRD data were collected from the $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases prepared by cation exchange from the corresponding $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases. A series of crystallographic models described in space group $C2/c$ were constructed based on the models of the corresponding $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases described above, but the sodium replaced with lithium. These models were then refined against the corresponding SXRD data to achieve good fits as shown in Appendix-I (Figures 9a.4-9a.7). Close inspection of the SXRD data from $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ reveal, for $x = 0$, a series of broad diffraction features consistent with the presence of the LiFe_5O_8 spinel phase, so this was added as a second phase during the refinement. For samples with $x = 3, 4$ and 5 , a series of small diffraction peaks consistent with the presence of LiGaO_2 was observed and so this was also added as a second phase during the refinement for the corresponding samples.

To assist with structural refinement, NPD data were collected from $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$. NPD data of $\text{Li}_3\text{Fe}_5\text{O}_9$ showed additional peaks corresponding to magnetic scattering and presence of a LiFe_5O_8 impurity phase. The combination of a chemical impurity (LiFe_5O_8), which is also magnetically ordered, and a complex magnetic structure made the solution of the magnetic structure challenging, so this part of the data was excluded during the refinement as shown in Figure 9.6.

NPD data of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ was found to be devoid of any magnetic reflections. However small intensities consistent with the presence of LiGaO_2 were observed which was added as a secondary phase during the refinement. Similar to $\text{Na}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, refinement of the NPD data was performed with the $4e$ site containing iron and the $8f$ site containing combination of iron and gallium which yielded as good fit as shown in Figure 9.7 with crystallographic details given in Table 9.8.

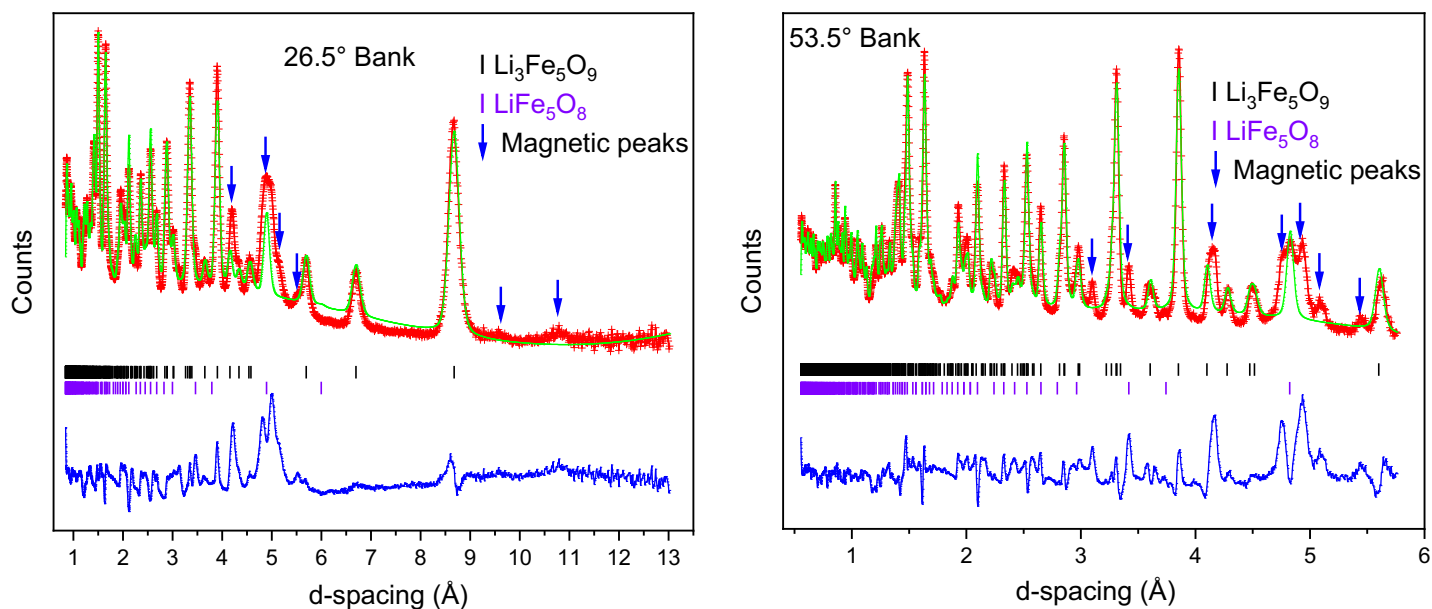


Figure 9. 6. Observed, calculated and difference plots from the structural refinement of $\text{Li}_3\text{Fe}_5\text{O}_9$ against NPD data, 26.5° Bank (left), 53.5° Bank (right)

Table 9.7. Parameters from the structural refinement of $\text{Li}_3\text{Fe}_5\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1	$8f$	0.1220(3)	0.3333(5)	0.2936(10)	1	0.05(5)
Fe2	$8f$	0.3615(4)	0.3335(5)	0.2178(11)	1	0.05(5)
Fe3	$4e$	0	0.0632(7)	1/4	1	0.05(5)
Li1	$8f$	0.2484(22)	0.0844(32)	0.1923(51)	1	1.5(5)
Li2	$4e$	0	0.5915(49)	1/4	1	1.5(5)
O1	$8f$	0.1011(6)	0.1821(8)	0.1291(17)	1	0.7(1)
O2	$8f$	0.3652(6)	0.1838(8)	0.3616(16)	1	0.7(1)
O3	$8f$	0.2224(5)	0.4110(8)	0.1429(14)	1	0.7(1)
O4	$8f$	0.4274(5)	0.4483(7)	0.4092(13)	1	0.7(1)
O5	$4e$	0	0.4027(12)	1/4	1	0.7(1)
$\text{Li}_3\text{Fe}_5\text{O}_9$ – space group $C2/c$ (#15) $a = 13.1759(12) \text{ \AA}$, $b = 11.1993(9) \text{ \AA}$, $c = 5.2725(4) \text{ \AA}$, $\beta = 90.8853(70)^\circ$ volume = $777.940(121) \text{ \AA}^3$ Formula weight = $444.0525 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 6.33 \%$, $wR_p = 9.02 \%$						
Crystallographic parameters of LiFe_5O_8 added as a secondary phase during the refinement LiFe_5O_8 – space group $P4_332$ (#212) $a = b = c = 8.3410(5) \text{ \AA}$, volume = $580.318(117)$ weight % = 20						

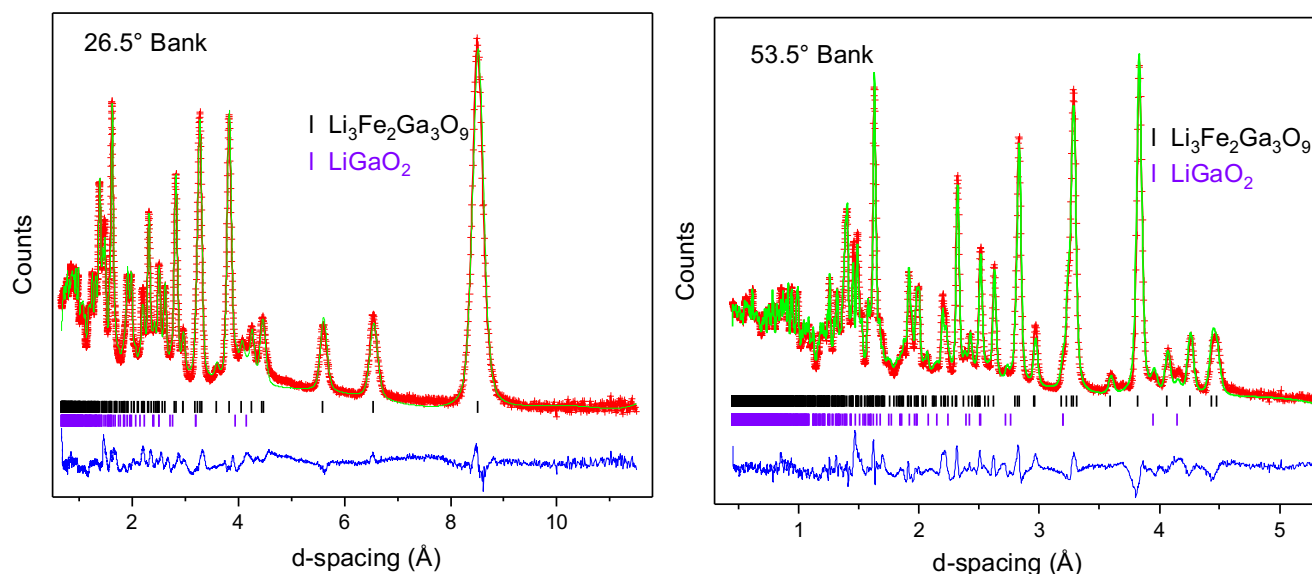


Figure 9. 7. Observed, calculated and difference plots from the structural refinement of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ against NPD data

Table 9.8. Parameters from the structural refinement of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1/Ga1	8f	0.1187(2)	0.3338(2)	0.2962(4)	0.25/0.75	0.11(4)
Fe2/Ga2	8f	0.3553(2)	0.3329(2)	0.2129(4)	0.25/0.75	0.11(4)
Fe3	4e	0	0.0676(3)	1/4	1	0.29(1)
Li1	8f	0.2426(9)	0.0682(14)	0.1944(25)	1	3.1(3)
Li2	4e	0	0.6136(17)	1/4	1	3.1(3)
O1	8f	0.1010(2)	0.1901(3)	0.1250(6)	1	0.07(2)
O2	8f	0.3645(2)	0.1813(3)	0.3560(6)	1	0.07(2)
O3	8f	0.2286(2)	0.4090(3)	0.1517(5)	1	0.07(2)
O4	8f	0.4199(2)	0.4438(3)	0.4158(5)	1	0.07(2)
O5	4e	0	0.4203(4)	1/4	1	0.07(2)
$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ – space group $C2/c$ (#15) $a = 13.0724(3) \text{ \AA}$, $b = 11.1879(3) \text{ \AA}$, $c = 5.2304(1) \text{ \AA}$, $\beta = 90.8639(18)^\circ$ volume = $764.880(39) \text{ \AA}^3$ Formula weight = $485.45 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 4.25 \%$, $wR_p = 5.66 \%$						
Crystallographic parameters of LiGaO_2 added as a secondary phase during the refinement LiGaO_2 – space group $Pna2_1$ (#33) $a = 5.4407(6) \text{ \AA}$, $b = 6.3986(7) \text{ \AA}$, $c = 5.0158(5) \text{ \AA}$, volume = $174.617(106) \text{ \AA}^3$ weight % = 3						

Table 9.9. Table of cell parameters extracted from structural refinement against SXRD and NPD data from $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å ³)
$\text{Li}_3\text{Fe}_5\text{O}_9$	13.2171(1)	11.2173(1)	5.2811(4)	90.9514(6)	782.873(11)
$\text{Li}_3\text{Fe}_4\text{GaO}_9$	13.1594(1)	11.2033(1)	5.2653(1)	90.8879(3)	776.181(4)
$\text{Li}_3\text{Fe}_3\text{Ga}_2\text{O}_9$	13.1261(1)	11.1978(1)	5.2501(1)	90.9016(3)	771.595(8)
$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$	13.0804(1)	11.1916(1)	5.2328(1)	90.8661(4)	765.955(7)
$\text{Li}_3\text{FeGa}_4\text{O}_9$	13.0369(1)	11.1796(1)	5.2116(1)	90.8359(7)	759.517(16)
$\text{Li}_3\text{Ga}_5\text{O}_9$	12.9919(2)	11.1574(2)	5.1846(1)	90.7778(12)	751.485(28)

Table 9.10. Table of bond distance calculated from structural refinement against SXRD and NPD data from $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

<M-O>	site	$\text{Li}_3\text{Fe}_5\text{O}_9$	$\text{Li}_3\text{Fe}_4\text{GaO}_9$	$\text{Li}_3\text{Fe}_3\text{Ga}_2\text{O}_9$	$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$	$\text{Li}_3\text{FeGa}_4\text{O}_9$	$\text{Li}_3\text{Ga}_5\text{O}_9$
		Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)
Fe1-O	8f	1.868(4)	1.858(3)	1.844(3)	1.855(2)	1.863(3)	1.859(4)
Ga1-O	8f						
Fe2-O	8f	1.885(3)	1.884(3)	1.870(2)	1.875(2)	1.884(3)	1.883(4)
Ga2-O	8f						
Fe3-O	4e	2.014(4)	2.020(3)	2.011(2)	1.989(3)	1.931(4)	2.032(5)
Ga3-O	4e						

Table 9.11. Table of bond-valence-sum calculated from structural refinement against SXRD and NPD data from $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

<M-O>	site	$\text{Li}_3\text{Fe}_5\text{O}_9$	$\text{Li}_3\text{Fe}_4\text{GaO}_9$	$\text{Li}_3\text{Fe}_3\text{Ga}_2\text{O}_9$	$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$	$\text{Li}_3\text{FeGa}_4\text{O}_9$	$\text{Li}_3\text{Ga}_5\text{O}_9$
		BVS	BVS	BVS	BVS	BVS	BVS
Fe1-O	8f	2.990	3.074	3.178	3.085		
Ga1-O	8f		2.841	2.924	2.859	3.023	2.977
Fe2-O	8f	2.881	2.903	2.972	2.936		
Ga2-O	8f		2.686	2.746	2.934	2.859	2.753
Fe3-O	4e	3.013	2.967	3.031	3.227	3.761	
Ga3-O	4e						2.952

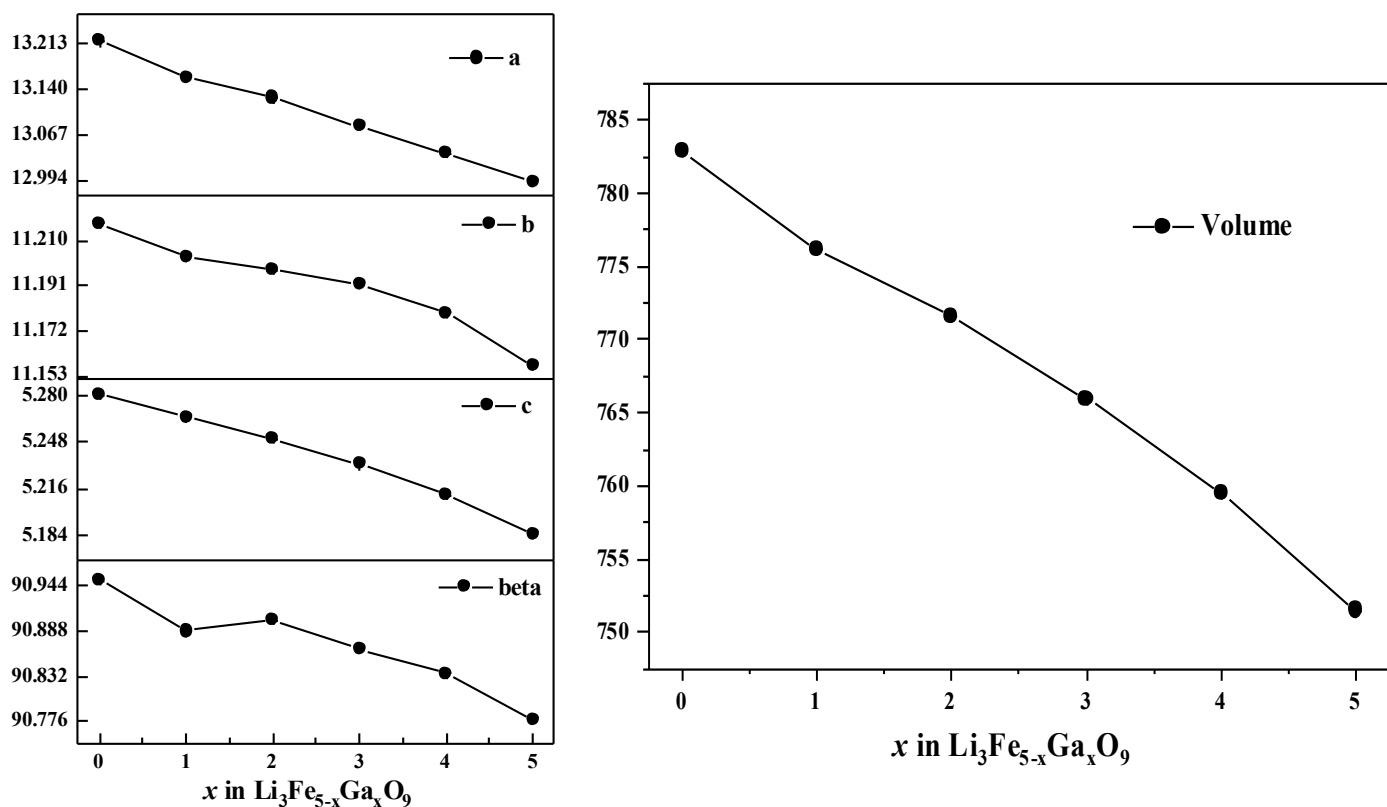


Figure 9. 8. Plot of cell parameters as a function of composition for $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples; Error bars are smaller than the plotted points

9.3.3. Discussion for $\text{A}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ ($\text{A}=\text{Na}, \text{Li}$)

Structural refinements against SXRD and NPD data of $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases, reveal that complete solid solutions can be prepared of $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and that these phases then can be converted to the corresponding $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases. The decline in lattice parameters with increasing gallium substitution (Figure 9.5 and 9.9) can be explained on the basis of smaller ionic radii of Ga^{3+} ($0.47 \text{ \AA}$)¹⁵⁴ compared to Fe^{3+} ($0.49 \text{ \AA}$)¹⁵⁴ which is in good agreement with Vegard's law.

In $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases, a preferential occupancy of gallium towards the $8f$ tetrahedral site and of iron towards the $4e$ octahedral site is observed which is maintained in the corresponding $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases after exchange of the sodium by lithium. Thus, it can be

assumed that in $\text{Na}_3\text{FeGa}_4\text{O}_9$ and $\text{Li}_3\text{FeGa}_4\text{O}_9$, a complete ordering between the iron and gallium site is present.

In $\text{Na}_3\text{Fe}_5\text{O}_9$, exchange of the sodium ions is associated with iron migration in the $C2/c$ structure resulting in the formation of LiFe_5O_8 spinel. The iron migration is stopped by addition of gallium which provides rigidity to the structure. However, for gallium rich samples 2-3 weight % LiGaO_2 is produced along with the exchanged $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$.

The NPD data obtained from $\text{Li}_3\text{Fe}_5\text{O}_9$, alongside previous reports on $\text{Na}_3\text{Fe}_5\text{O}_9$ ¹⁸¹, suggests that both $\text{Na}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_5\text{O}_9$ exhibit magnetic ordering at room temperature. Moreover, the introduction of gallium into other $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases appears to reduce the magnetic ordering. This observation aligns with the incorporation of non-magnetic gallium into the system.

9.4. Characterization results and discussion for lithiated $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

9.4.1. Synchrotron X-ray diffraction (SXRD)

SXRD data were collected from lithiated $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, henceforth referred to as $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, were indexed on the basis of monoclinic unit cells ($C2/c$) similar to the corresponding $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases. Crystallographic models based on $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ structures were refined against the SXRD data which yielded a rapid convergence as shown in Appendix-I (Figures 9a.8-9a.10).

The SXRD pattern collected from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ exhibited additional broad reflections associated with the presence of $\text{Li}_{1+x}\text{Fe}_5\text{O}_8$ and metallic iron, which were added as a secondary phase during the refinement process (see Figure 9.9). In contrast, SXRD data from $\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$ show no evidence of $\text{Li}_{1+x}\text{Fe}_5\text{O}_8$ or metallic iron, indicating that the addition of gallium restrained the formation of metallic iron and the spinel phase (Figure 9.9).

Figure 9.10 shows variation of lattice parameters of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ as a function of gallium concentration. In comparison to $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases exhibit, a decrease along a and increase along both b and c axis for $4 \geq x \geq 0$. Further structural characterization of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ with neutron powder diffraction data will be discussed in Section 9.4.2.

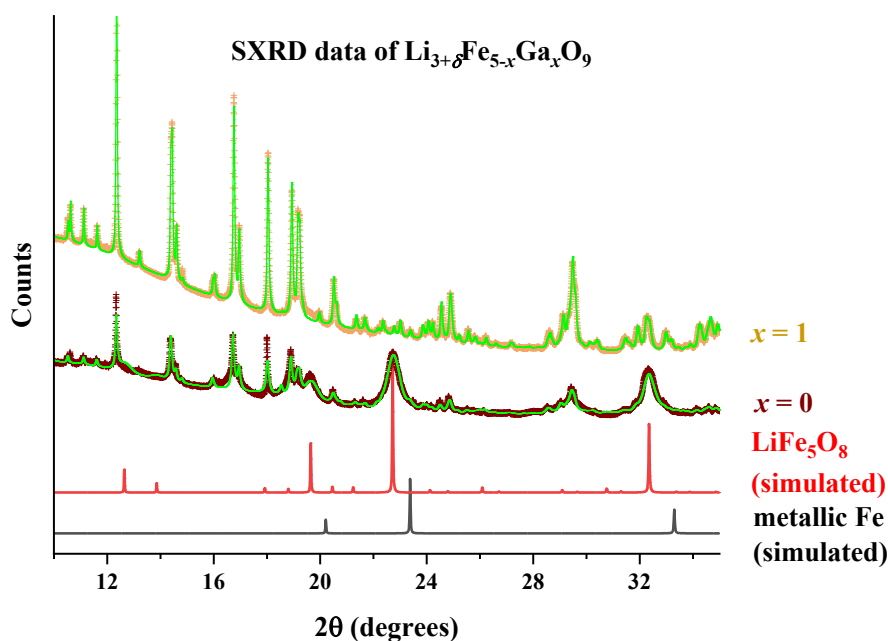


Figure 9. 9. Observed and calculated (green line) SXR D data from $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases for $x = 0, 1$; red and black line indicates simulated pattern of LiFe_5O_8 and metallic iron respectively; For $\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$, no peaks associated to LiFe_5O_8 and metallic iron was observed

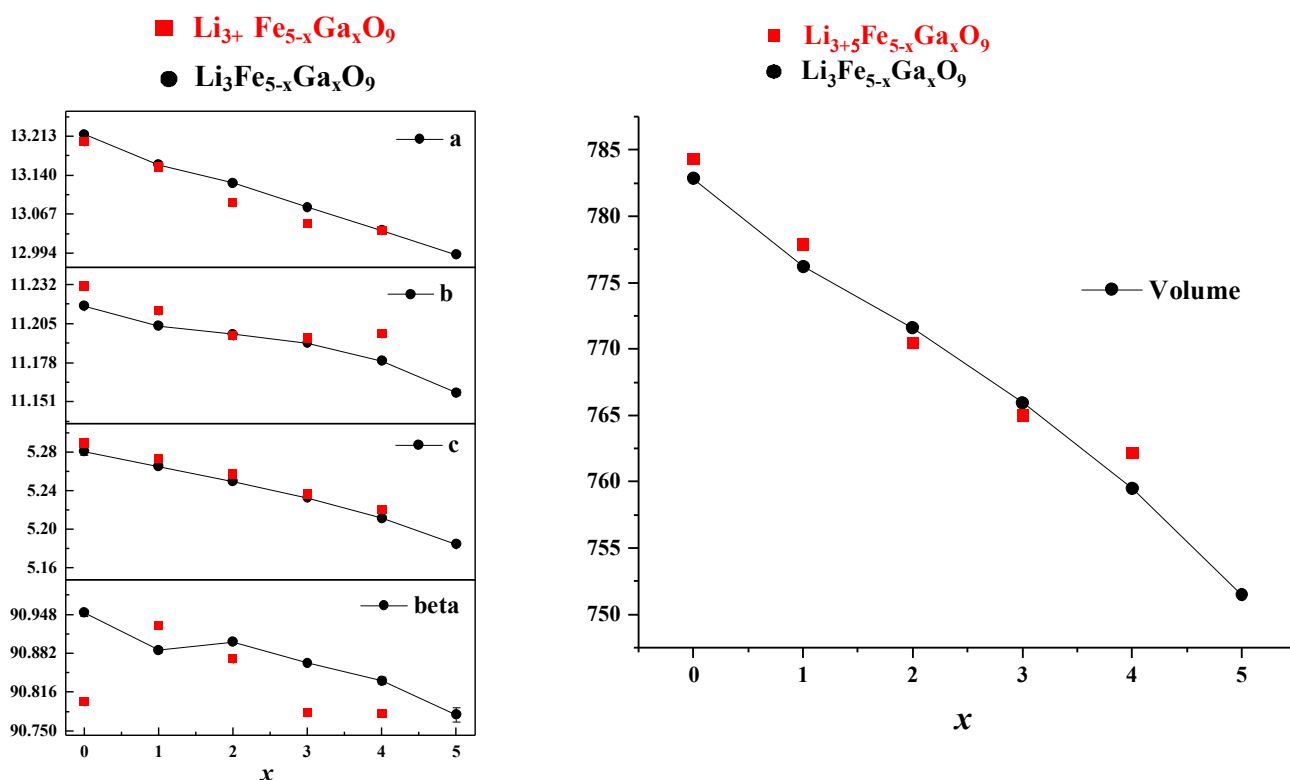


Figure 9. 10. Plot of lattice parameters as a function of compositions for $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases determined from structural refinement against SXR D data; Error bars are smaller than the plotted points

9.4.2. Neutron powder diffraction (NPD) data

To assist with structural determination, neutron powder diffraction (NPD) data were collected from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$. Crystallographic models, based on parent $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ structures, were refined against the data, resulting in convergence, as illustrated in Figures 9.12 and 9.14, with detailed structural parameters in Tables 9.12 and 9.13, respectively. To determine the location of the additionally inserted lithium, Fourier difference maps were computed from the data, and the positions with the highest negative scattering density were assigned to the inserted lithium ions in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$, as depicted in Figure 9.11 and 9.13, respectively.

As outlined in Section 9.1, structures of $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases contain four distinct vacant channels (A- $8f$, B- $4d$, C- $4e$, and D- $8f$ site) running parallel to the c axis of the unit cell. During structural refinement, additional lithium ions were placed in these channels based on the highest negative scattering density, and the positions and occupancies of lithium atoms were refined, resulting in the final compositions of $\text{Li}_{5.75}\text{Fe}_5\text{O}_9$ and $\text{Li}_{4.75}\text{Fe}_2\text{Ga}_3\text{O}_9$, which is in good agreement with lithium content determined from ICP-MS and iodometric titration data (Appendix-I Tables 9a.14, 9a.15, 9a.17).

For $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, additional lithium ions were found to partially occupy channel B ($4d$ site), C ($4e$ site), and D ($8f$ site). Conversely, in the case of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$, additional lithium ions were found to preferentially occupy channels A ($8f$ site), B ($4d$ site), and D ($8f$ site), as shown in Figure 9.15.

Similar to $\text{Li}_3\text{Fe}_5\text{O}_9$ (Section 9.3.2), NPD data from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ revealed additional reflections associated with the magnetic scattering of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, along with the presence of the $\text{Li}_{1+x}\text{Fe}_5\text{O}_8$ impurity phase. The cell parameters of the spinel impurity phase matched those of the previously reported reduced $\text{Li}_{1+x}\text{Fe}_5\text{O}_8^{111}$, indicating simultaneous lithium insertion in

both $\text{Li}_3\text{Fe}_5\text{O}_9$ and LiFe_5O_8 when treated with *n*-BuLi. Due to the presence of this impurity, which is also magnetically ordered, the magnetic structure determination of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ was excluded during the refinement process.

Tables 9.15-9.16 present the cell parameters, $\langle\text{Fe-O}\rangle$, and Fe-BVS parameters for $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases obtained from structural refinement against SXRD and NPD data. Upon close examination of the bond lengths in the octahedral FeO_6 (*4e* site) in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, an unexpected decrease in $\langle\text{Fe-O}\rangle$ and an increase in Fe-BVS parameters are observed in comparison to $\text{Li}_3\text{Fe}_5\text{O}_9$. This indicates that there is no reduction of the Fe3 site (*4e* site) in $\text{Li}_3\text{Fe}_5\text{O}_9$ upon reduction. However, for other Fe sites (*4e* and *8f*) in $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, an increase in $\langle\text{Fe-O}\rangle$ and a decrease in Fe-BVS, compared to $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, are observed, which is consistent with the reduction of the iron site due to reductive lithium insertion.

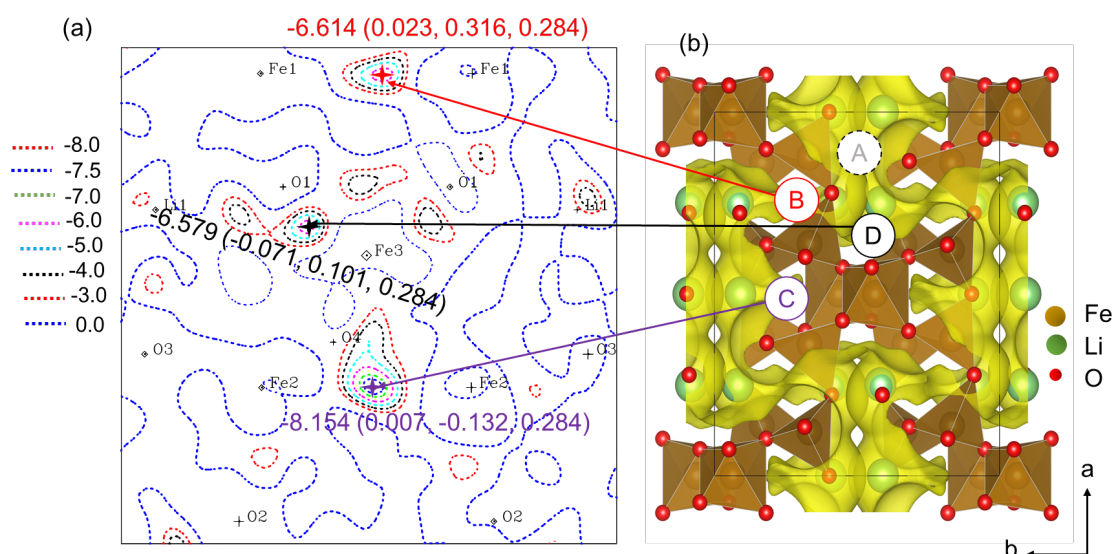


Figure 9. 11. Plot of Fourier difference map with the centre of reference (0,0,0) and height from the centre 1.5 Å, calculated from the structural refinement of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ against NPD data (a); ‘+’ signs indicate the highest negative scattering density observed in the Fourier difference map. (b) Bond Valence Energy Landscape (BVEL) map for lithium ions within $\text{Li}_3\text{Fe}_5\text{O}_9$ structure. Yellow isosurfaces represent a constant Bond Valence Sum (BVS) value for lithium ions, calculated with a percolation energy of 3 eV. The available empty sites for additional lithium are shown by white circles (A, B, C and D), which exhibit the highest density of lithium percolation channels.

The correlations between the highest negative scattering density and the highest density of lithium percolations are indicated by red (B), black (D) and purple (C) arrows. The Fourier difference map of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ data does not show any negative scattering density correlated with the highest density of lithium percolation channel A.

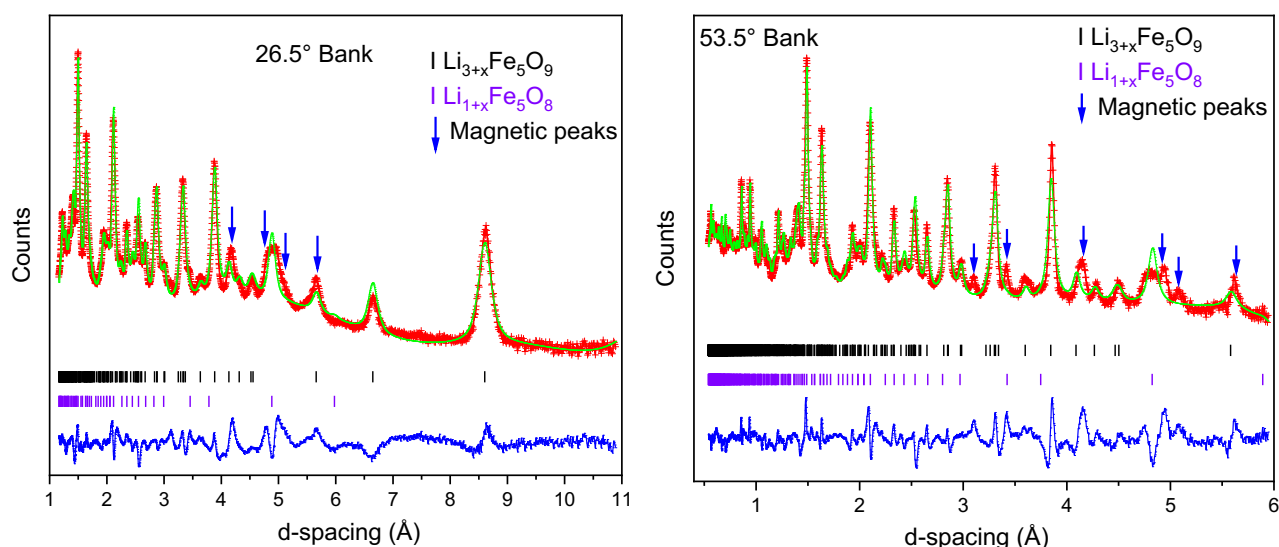


Figure 9.12 Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ against NPD data, 26.5° Bank (left) and 53.5° Bank (right)

Table 9.12. Parameters from the structural refinement of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1	8f	0.1178(6)	0.3314(7)	0.2927(17)	1	0.74(10)
Fe2	8f	0.3579(8)	0.3318(8)	0.2056(2)	1	0.74(10)
Fe3	4e	0	0.0642(12)	$\frac{1}{4}$	1	0.74(10)
Li1	8f	0.2439(33)	0.0785(42)	0.2013(85)	1	1.1(6)
Li2	4e	0	0.6167(55)	$\frac{1}{4}$	1	1.1(6)
Li3	8f	0.8562(53)	0.0132(65)	$\frac{1}{4}$	0.69(7)	1.1(6)
Li4	4d	$\frac{3}{4}$	$\frac{1}{4}$	0	0.67(12)	1.1(6)
Li5	4e	0	$\frac{3}{4}$	$\frac{1}{4}$	0.68(11)	1.1(6)
O1	8f	0.0972(9)	0.1733(14)	0.1271(28)	1	0.77(13)
O2	8f	0.3787(11)	0.1826(12)	0.3522(29)	1	0.77(13)
O3	8f	0.2211(9)	0.4102(14)	0.1685(26)	1	0.77(13)
O4	8f	0.4427(9)	0.4459(12)	0.3986(23)	1	0.77(13)
O5	4e	0	0.3921(17)	$\frac{1}{4}$	1	0.77(13)
$\text{Li}_{5.75}\text{Fe}_5\text{O}_9$ — space group $C2/c$ (#15) $a = 13.2025(27) \text{ \AA}$, $b = 11.2309(22) \text{ \AA}$, $c = 5.2902(10) \text{ \AA}$, $\beta = 90.7995(20)^\circ$ volume = $784.338(268) \text{ \AA}^3$ Formula weight= $463.14 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 4.39\%$, $wR_p = 6.11\%$						
Crystallographic parameters of $\text{Li}_{1+x}\text{Fe}_5\text{O}_8$ added as a secondary phase during the refinement $\text{Li}_{1+x}\text{Fe}_5\text{O}_8$ — space group $P4_332$ (#212) $a = b = c = 8.3893(5) \text{ \AA}$, volume = $590.453(169) \text{ \AA}^3$ mass fraction weight % = 26.2						

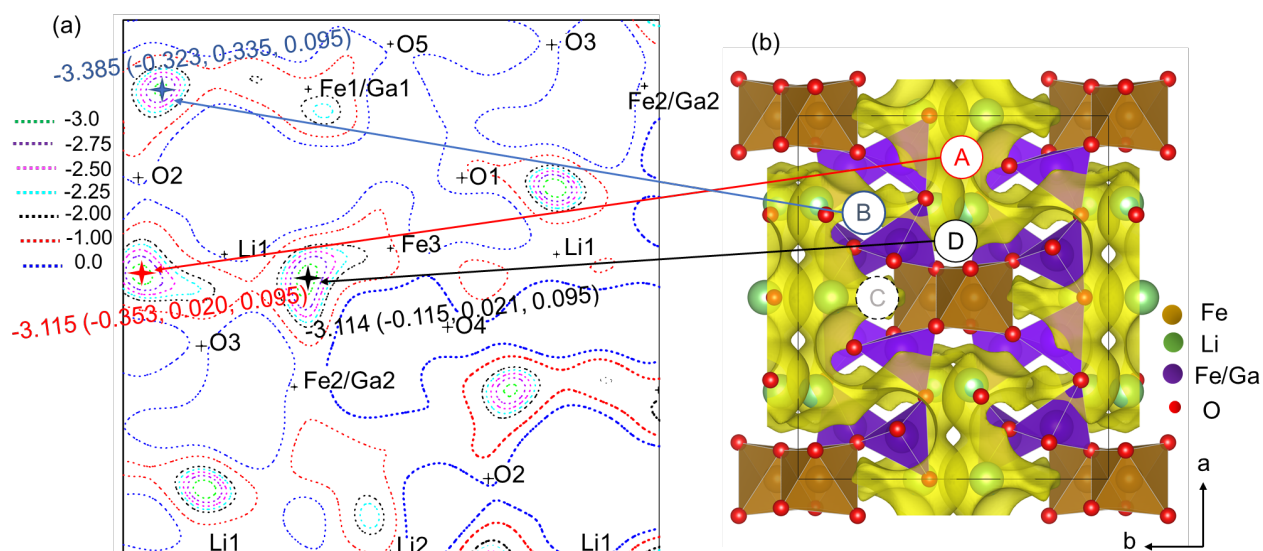


Figure 9. 13. Plot of Fourier difference map with the centre of reference (0,0,0) and height from the centre 0.5 Å, calculated from the structural refinement of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ against NPD data (a); '+' signs indicate the highest negative scattering density observed in the Fourier difference map. (b) Bond Valence Energy Landscape (BVEL) map for lithium ions within $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ structure. Yellow isosurfaces represent a constant Bond Valence Sum (BVS) value for lithium ions, calculated with a percolation energy of 3 eV. The available empty sites for additional lithium are shown by white circles (A, B, C and D), which exhibit the highest density of lithium percolation channels.

The correlations between the highest negative scattering density (a) and the highest density of lithium percolations (b) are indicated by red (A), black (D) and blue (B) arrows. The Fourier difference map of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ data does not show any negative scattering density correlated with the highest density of lithium percolation channel C.

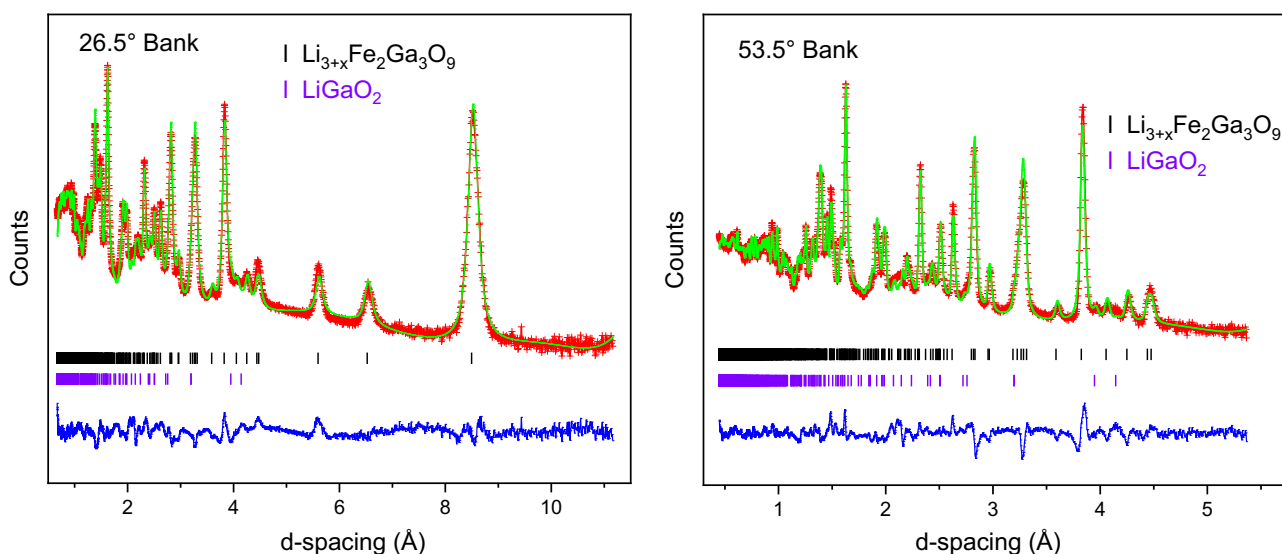


Figure 9. 14. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ against NPD data, 26.5° Bank (left) and 53.5° Bank (right)

Table 9.13. Parameters from the structural refinement of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1/Ga1	8f	0.1173(2)	0.3344(3)	0.2883(6)	0.25/0.75	0.58(6)
Fe2/Ga2	8f	0.3582(3)	0.3373(3)	0.2109(6)	0.25/0.75	0.39(5)
Fe3	4e	0	0.0665(4)	$\frac{1}{4}$	1	0.37(6)
Li1	8f	0.2460(13)	0.0697(19)	0.1321(31)	1	1.0(2)
Li2	4e	0	0.5591(30)	$\frac{1}{4}$	1	1.0(2)
Li3	8f	0.6139(30)	0	$\frac{1}{8}$	0.42(3)	1.0(2)
Li4	4d	$\frac{3}{4}$	$\frac{1}{4}$	0	0.23(3)	1.0(2)
Li5	8f	0.8594(31)	0.0394(36)	$\frac{1}{4}$	0.32(2)	1.0(2)
O1	8f	0.1028(3)	0.1822(4)	0.1270(8)	1	0.22(2)
O2	8f	0.3605(3)	0.1848(4)	0.3591(8)	1	0.22(2)
O3	8f	0.2280(3)	0.4115(4)	0.1585(6)	1	0.22(2)
O4	8f	0.4176(3)	0.4404(4)	0.4077(6)	1	0.22(2)
O5	4e	0	0.4146(5)	$\frac{1}{4}$	1	0.22(2)
$\text{Li}_{4.75}\text{Fe}_2\text{Ga}_3\text{O}_9$ – space group $C2/c$ (#15) $a = 13.0506(6) \text{ \AA}$, $b = 11.1948(5) \text{ \AA}$, $c = 5.2368(2) \text{ \AA}$, $\beta = 90.7817(19)^\circ$ volume = $765.028(66) \text{ \AA}^3$ Formula weight= $497.6075 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 2.84 \%$, $wR_p = 3.79\%$						
Crystallographic parameters of LiGaO_2 added as a secondary phase during the refinement LiGaO_2 – space group $Pna2_1$ (#33) $a = 5.4407(6) \text{ \AA}$, $b = 6.3986(7) \text{ \AA}$, $c = 5.0158(5) \text{ \AA}$, volume = $174.617(106) \text{ \AA}^3$ weight % = 5						

Table 9.14. Table of cell parameters extracted from structural refinement against SXRD and NPD data from $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

	$a (\text{\AA})$	$b (\text{\AA})$	$c (\text{\AA})$	$\beta (^\circ)$	Volume ($\text{\AA}^3$)
$\text{Li}_{3+x}\text{Fe}_5\text{O}_9$	13.2025(27)	11.2309(22)	5.2902(10)	90.7995(20)	784.338(268)
$\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$	13.1552(1)	11.2137(1)	5.2735(6)	90.9292(11)	777.852(17)
$\text{Li}_{3+x}\text{Fe}_3\text{Ga}_2\text{O}_9$	13.0888(6)	11.1967(5)	5.2577(2)	90.8724(3)	770.442(64)
$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$	13.0506(6)	11.1948(5)	5.2368(2)	90.7817(19)	765.028(66)
$\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$	13.0373(2)	11.1982(2)	5.2208(1)	90.7804(12)	762.182(21)

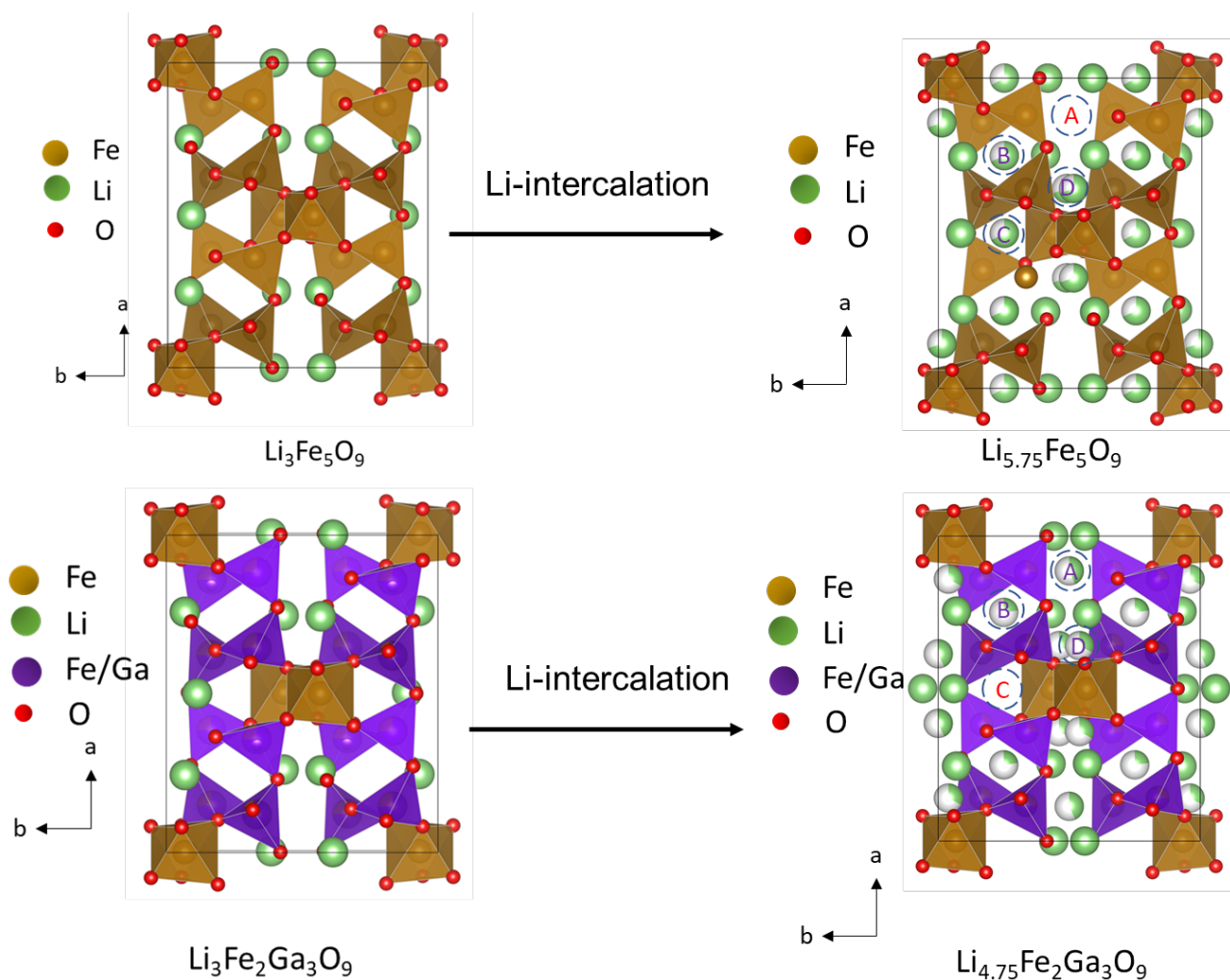


Figure 9. 15. Schematics of lithium insertion in $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, A, B, C and D represents different channels for lithiums in the structure

Table 9.15. Table of bond distance calculated from structural refinement against SXRD and NPD data from $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

<M-O>	Site	$\text{Li}_{3+x}\text{Fe}_5\text{O}_9$	$\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$	$\text{Li}_{3+x}\text{Fe}_3\text{Ga}_2\text{O}_9$	$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$	$\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$
		Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)
Fe1-O	8f	1.886(12)	1.843(4)	1.808(7)	1.868(6)	1.860(8)
Ga1-O	8f					
Fe2-O	8f	1.916(18)	1.888(6)	1.811(4)	1.882(6)	1.737(4)
Ga2-O	8f					
Fe3-O	4e	1.872(18)	2.023(5)	1.968(6)	2.007(6)	1.910(7)
Ga3-O	4e					

Table 9.16. Table of bond-valence-sum calculated from structural refinement against SXR and NPD data from $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

<M-O>	site	$\text{Li}_{3+x}\text{Fe}_5\text{O}_9$	$\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$	$\text{Li}_{3+x}\text{Fe}_3\text{Ga}_2\text{O}_9$	$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$	$\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$
		BVS	BVS	BVS	BVS	BVS
Fe1-O	8f	3.393	3.200	3.745	3.170	
Ga1-O	8f		2.959	3.463	2.931	2.830
Fe2-O	8f	2.657	2.859	3.584	3.013	
Ga2-O	8f		2.644	3.313	3.013	2.420
Fe3-O	4e	4.733	2.942	3.509	3.097	3.990
Ga3-O	4e					

9.4.3. Mössbauer spectroscopy

Room temperature ^{57}Fe Mössbauer data were collected from $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ phases. Data from $\text{Li}_3\text{Fe}_5\text{O}_9$ indicate magnetic ordering at room temperature and were fitted with three sextets (Figure 9.16, Table 9.17). Structure of $\text{Li}_3\text{Fe}_5\text{O}_9$ consists of tetrahedral FeO_4 and octahedral FeO_6 in a 4:1 ratio, which can be simplified as $\text{Li}_3[\text{Fe}_4]_{\text{Td}}[\text{Fe}]_{\text{Oh}}\text{O}_9$. Sextets 1 and 2 correspond to the tetrahedral FeO_4 site in $\text{Li}_3\text{Fe}_5\text{O}_9$, while Sextet 3 is assigned to the octahedral FeO_6 site in $\text{Li}_3\text{Fe}_5\text{O}_9$. The combined spectral area for the tetrahedral and octahedral Fe sites is largely consistent with the ratio of these iron sites in $\text{Li}_3\text{Fe}_5\text{O}_9$. The necessity of two sextets for the tetrahedral iron site is attributed to slightly distinct nature of the two tetrahedral iron sites in $\text{Li}_3\text{Fe}_5\text{O}_9$.

The magnetic ordering observed in $\text{Li}_3\text{Fe}_5\text{O}_9$ persists in lithiated $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$. The ^{57}Fe Mössbauer data from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ can be considered as a combination of lithiated $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ and unreacted $\text{Li}_3\text{Fe}_5\text{O}_9$. The data were fitted with one doublet and three sextets. Doublet 1 and Sextet 1 are assigned to the tetrahedral FeO_4 and octahedral FeO_6 sites in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, respectively. The chemical shift (CS) and quadrupole splitting (Δ) observed for Doublet 1 (FeO_4 in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$) are consistent with the presence of diamagnetic Fe(II)^{182} , supporting the reduction of FeO_4 observed in the NPD analysis (Section 9.4.3). The chemical shift and

quadrupole splitting for Sextet 1 are consistent with Fe(III), indicating no reduction of FeO₆ in Li₃Fe₅O₉, as observed in the NPD analysis. Sextet 2 and Sextet 3 are assigned to the tetrahedral FeO₄ and octahedral FeO₆ sites respectively in unreacted Li₃Fe₅O₉, consistent with the presence of Fe(III).

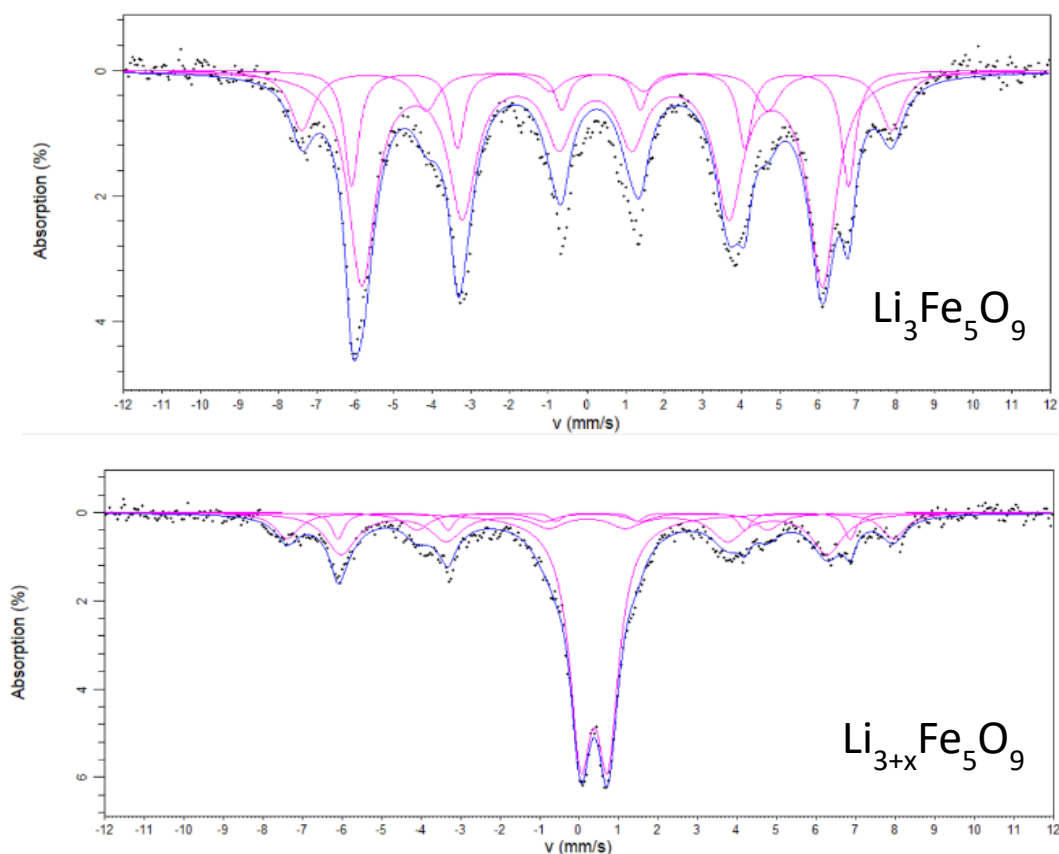


Figure 9.16. ⁵⁷Fe Mössbauer spectra collected from Li₃Fe₅O₉ (top) and Li_{3+x}Fe₅O₉ (bottom)

Table 9.17. Table of hyperfine parameters extracted from the fits to ⁵⁷Fe Mössbauer spectra collected from Li₃Fe₅O₉ and Li_{3+x}Fe₅O₉

	CS (mm/s) [± 0.02]	Δ (mm/s) [± 0.02]	B _{eff} (T)	HWHM (mm/s) [±0.02]	Spectral Area (%) [±2]	Fe-site
Li ₃ Fe ₅ O ₉						
Sextet 1	0.18	-0.05	37	0.43	65.5	FeO ₄
Sextet 2	0.36	-0.01	39.4	0.22	18.5	FeO ₄
Sextet 3	0.26	0	47.4	0.37	16	FeO ₆
Li _{3+x} Fe ₅ O ₉						
Doublet 1	0.38	0.69	0	0.34	51.96	FeO ₄ [Li _{3+x} Fe ₅ O ₉]
Sextet 1	0.31	-0.03	47.5	0.375	13.6	FeO ₆ [Li _{3+x} Fe ₅ O ₉]
Sextet 2	0.17	-0.04	38.1	0.476	27.4	FeO ₄ [Li ₃ Fe ₅ O ₉]
Sextet 3	0.41	-0.03	40.2	0.187	7.0	FeO ₆ [Li ₃ Fe ₅ O ₉]

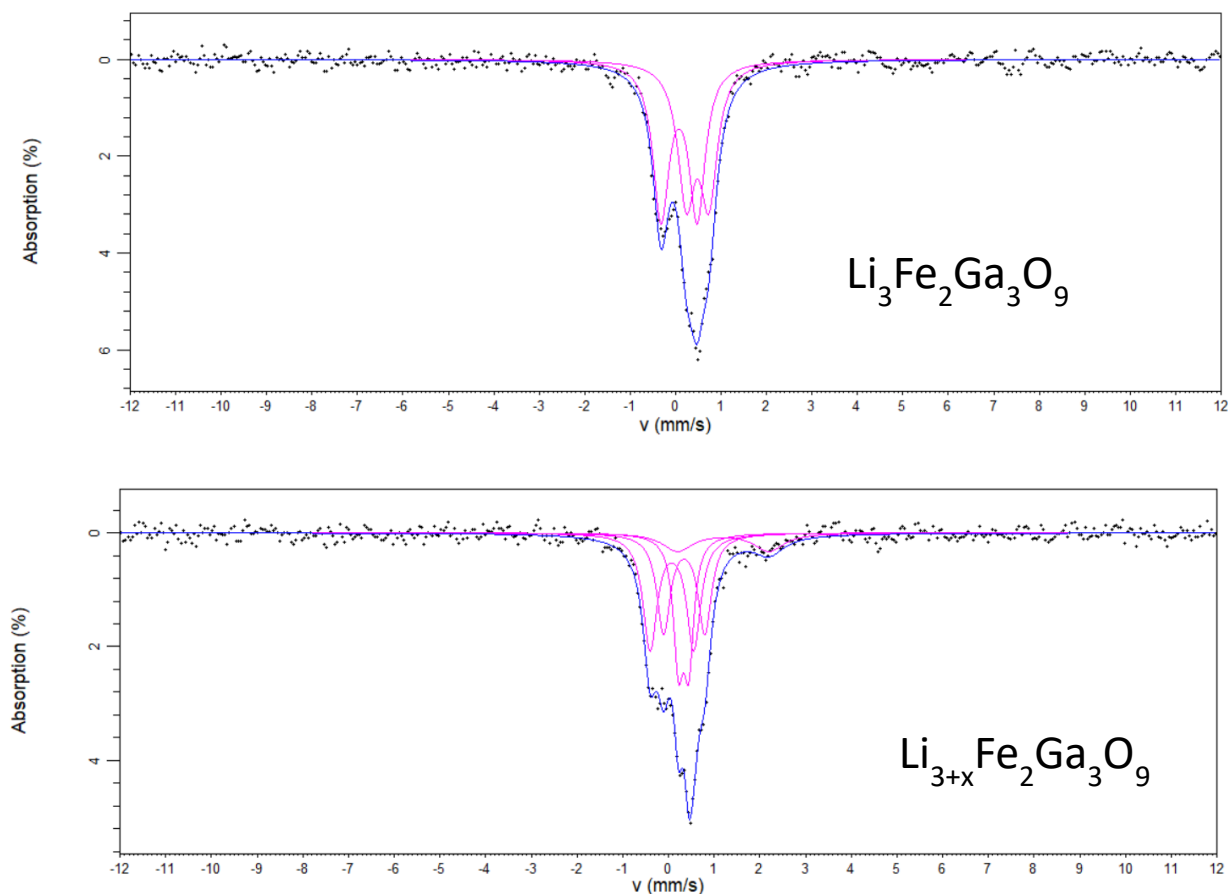


Figure 9.17. ^{57}Fe Mössbauer spectra collected from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ (top) and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ (bottom)

Table 9.18. Table of hyperfine parameters extracted from the fits to ^{57}Fe Mössbauer spectra collected from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$

	CS (mm/s) [± 0.02]	Δ (mm/s) [± 0.02]	HWHM (mm/s) [± 0.02]	Spectral Area (%) [± 2]	Fe-site
$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$					
Doublet 1	0.07	0.79	0.21	52.6	FeO_4
Doublet 2	0.48	0.49	0.23	47.4	FeO_6
$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$					
Doublet 1	0.35	0.9	0.18	28	FeO_4 [$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$]
Doublet 2	1.2	2	0.4	11.6	FeO_6 [$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$]
Doublet 3	0.08	0.95	0.19	34.4	FeO_4 [$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$]
Doublet 4	0.33	0.23	0.13	25.7	FeO_6 [$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$]

^{57}Fe Mössbauer data from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ show no magnetic ordering at room temperature, indicating that the addition of gallium suppresses magnetic ordering of $\text{Li}_3\text{Fe}_5\text{O}_9$. The fit and corresponding parameters are presented in Figure 9.17 and Table 9.18. The structure of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ contains a combination of $(\text{Fe}/\text{Ga})\text{O}_4$ tetrahedra and FeO_6 octahedra, and the composition can be simplified as $\text{Li}_3[\text{Fe}/2\text{Ga}]_{\text{Td}}[\text{Fe}]_{\text{Oh}}\text{O}_9$. The Mössbauer spectrum from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ was fitted with two doublets, where Doublet 1 is assigned to FeO_4 and Doublet 2 is assigned to FeO_6 (Table 9.18), both consistent with Fe^{3+} .

The Mössbauer spectrum obtained from $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ was fitted using four doublets (Figure 9.17). Doublets 1 and 2 were assigned to iron in FeO_4 and FeO_6 environments respectively within $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$. Doublets 3 and 4 were attributed to iron in FeO_4 and FeO_6 environments originating from the unreacted $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ present concurrently with lithiated $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$. The CS and Δ values of Doublet 1 were found to be consistent with Fe^{2+} in a tetrahedral environment¹⁸² (similar to $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, as described above). The CS and Δ values from Doublet 2 strongly indicate the presence of Fe^{2+} in the FeO_6 site of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ ^{75,183,184}. This observation is consistent with the reduction of iron in both FeO_4 and FeO_6 sites of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ matching the analysis of NPD data from $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ (Section 9.4.2).

Doublets 3 and 4 were found to be consistent with FeO_4 and FeO_6 environments representing Fe^{3+} in $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$.

9.4.4 X-ray absorption spectroscopy

9.4.4.1. Fe-XANES data

To investigate the change in oxidation state of iron in $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ after reductive lithium insertion, Fe K-edge XANES data were collected from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_5\text{O}_9$,

$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ along with FeO and Fe_2O_3 to act as references for Fe (II) and Fe (III) K-edges respectively. The normalized data are presented below.

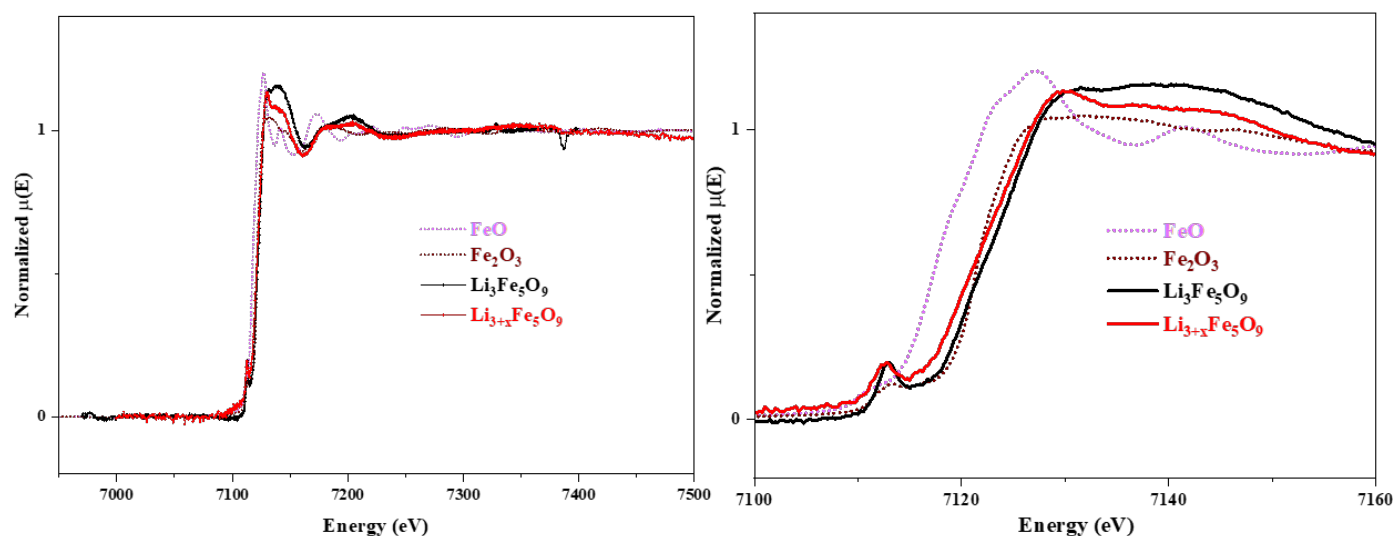


Figure 9. 18. XANES data of $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ with references (dotted lines); normalization (left), enlarged comparison (right).

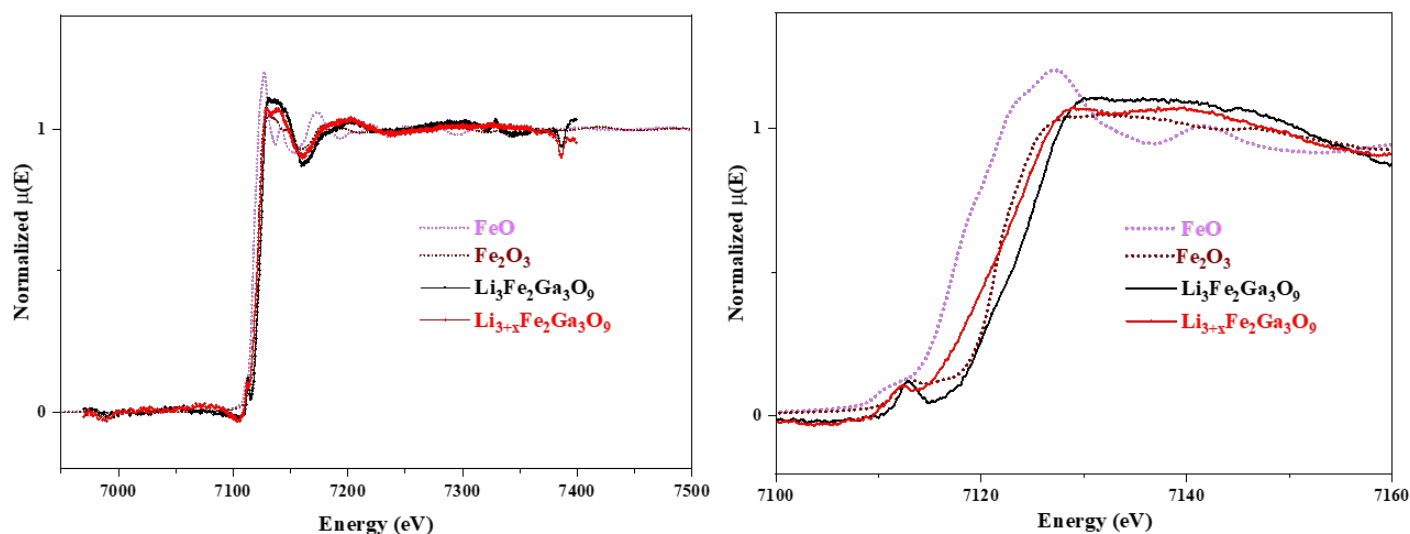


Figure 9. 19. XANES data of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ with references (dotted lines); normalization (left), enlarged comparison (right).

As depicted in Figure 9.18 and 9.19, XANES data from $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ (both in pristine and reduced states) exhibit a pre-edge feature at an energy of approximately 7112 eV, attributed to the characteristic tetrahedral iron environment in the structures. Upon closer examination of the data, it is evident that both lithiated $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$

show a shift of the Fe K-edge to lower energy in comparison to $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, consistent with the reduction of the iron site in the structure upon exposure to *n*-BuLi.

A comparison of the Fe K-edge energy between $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ reveals a modest difference of 0.75 eV. In contrast, when comparing the Fe K-edge energy $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$, a more substantial difference of approximately 2.1 eV is observed. This significant shift in the Fe K-edge towards lower energy for $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$, in comparison to $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, suggests a greater extent of reduction from Fe(III) to Fe(II) in the former. The magnitude of this energy shift is also in line with the number of lithium ions intercalated, as determined during the structural refinement against NPD data. This observation suggests that the reduction process from Fe(III) to Fe(II) is more pronounced in $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ compared to $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$.

9.4.4.2. EXAFS data

High-resolution X-ray absorption spectroscopy (XAS) data, distinct from the datasets presented in Figures 9.18 and 9.19, were collected from $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$. These datasets served as extended X-ray absorption fine structure (EXAFS) data to examine the local structural modifications within the FeO_4 and FeO_6 sites induced by lithium insertion. The XAS data, above the absorption edge, underwent conversion into various oscillations specific to the absorber atom and were subsequently analyzed as EXAFS data.

The first shell of the EXAFS data, encompassing both the FeO_4 tetrahedra and FeO_6 octahedra, derived from $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$, was carefully fitted by refining the crystallographic models obtained post the structural refinement against NPD data.

In the unit cell of $\text{Li}_3\text{Fe}_5\text{O}_9$, there exist 20 iron atoms, with 16 situated in two tetrahedral sites having a site symmetry of $8f$, and the remaining 4 located in the octahedral site with a site symmetry of $4e$. The presence of iron in multiple sites exhibiting distinct coordination environments led to the fitting of the EXAFS data of the first shell in R space as follows: (1) Tetrahedral Fe-O bond with a contribution of $4 \times (\frac{16}{20}) = 3.2$, and (2) Octahedral Fe-O bond with a contribution of $6 \times (\frac{4}{20}) = 1.2$.

The same approach was maintained for $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$, which resulted in rapid convergence to the data, as shown in Figures 9.20 and 9.21 with the refined parameters provided in Table 9.19 and 9.20.

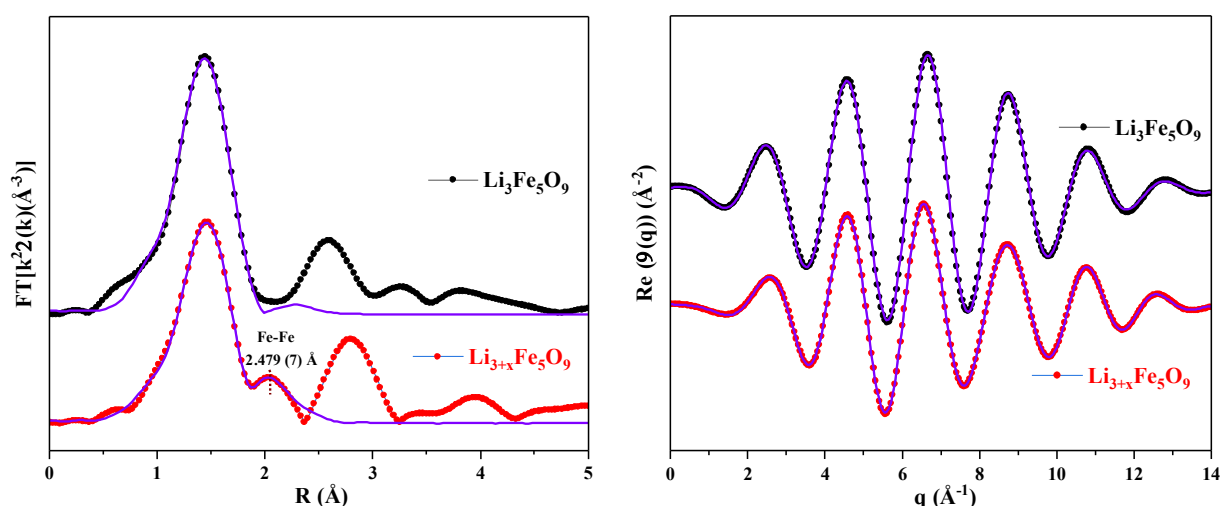


Figure 9. 20. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 9.19. Refined EXAFS parameters for $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD (Å)
$\text{Li}_3\text{Fe}_5\text{O}_9$	Fe-O	3.2	1.870(2)	4.2(4)	0.31	2.963	1.876(4)
	Fe-O	1.2	2.003(2)	2.5(9)		3.102	2.014(4)
$\text{Li}_{3+x}\text{Fe}_5\text{O}_9$	Fe-O	3.2	1.927(4)	11.6(1)	0.36	2.542	1.901(18)
	Fe-O	1.2	1.957(2)	2.14(1)		3.513	2.007(6)
	Fe-Fe	1.2	2.479(7)	5.13(3)			

As shown in Figure 9.20, the first-shell fit of the EXAFS data from $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ reveals an increase in the $\langle\text{Fe-O}\rangle$ bond length for the tetrahedral site in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ compared to $\text{Li}_3\text{Fe}_5\text{O}_9$, consistent with the reduction of iron in the FeO_4 site (with $N=3.2$, Table 9.19) upon treatment with $n\text{-BuLi}$. Conversely, $\langle\text{Fe-O}\rangle$ bond lengths in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ for the octahedral site show a small decrease, indicating no significant change of the FeO_6 site upon lithiation. Both of these observations are in good agreement with the NPD and Mössbauer data discussed earlier.

Additionally, EXAFS data from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ exhibit a broad intensity feature in the R space, adjacent to the first shell which was fitted with metallic Fe-Fe bond of $2.479(7)\text{\AA}$ as shown in Figure 9.20, indicating formation of metallic iron upon lithiation of $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$.

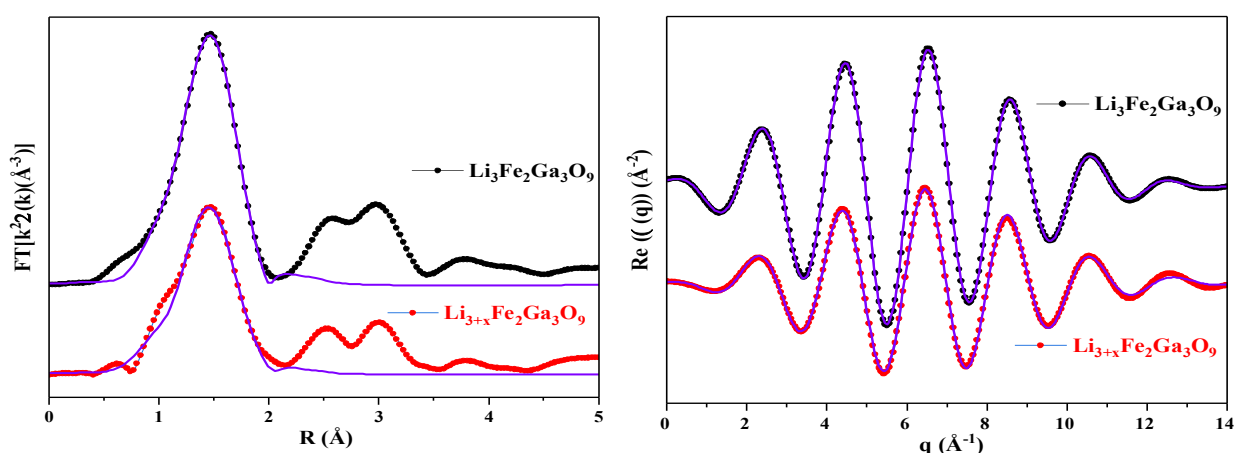


Figure 9. 21. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 9.20. Refined EXAFS parameters for $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$

Sample	Bond	N	R(Å)	Debye-Waller Factor ($10^{-3} \text{\AA}^2$)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD (Å)
$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$	Fe-O	3.2	1.899(2)	3.6(6)	0.26	2.739	1.873(3)
	Fe-O	1.2	2.028(2)	4.9(6)		2.900	1.931(4)
$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$	Fe-O	3.2	1.904(3)	2.2(4)	0.85	2.703	1.875(6)
	Fe-O	1.2	2.074(3)	4.0(3)		2.561	2.007(6)

As shown in Figure 9.21, the first-shell fit of the EXAFS data shows a modest increase in $\langle\text{Fe-O}\rangle$ bond length in the tetrahedral FeO_4 site (with $N=3.2$, Table 9.20) of $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ compared to $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ due to chemical lithiation. However, a significant increase in the $\langle\text{Fe-O}\rangle$ bond lengths is observed in the octahedral FeO_6 site (with $N=1.2$, Table 9.20) for $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ compared to $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, indicating reduction of iron in the FeO_6 site in $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ due to chemical lithiation. Both of these observations are in good agreement with the analysis of the NPD data and Mössbauer data discussed earlier.

Additionally, EXAFS data from $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ exhibit no additional peak corresponding to metallic iron, (as observed for $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$) indicating the inhibition of metallic iron formation due to gallium addition. This confirms the superiority of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ over $\text{Li}_3\text{Fe}_5\text{O}_9$ under reductive conditions.

9.5. Discussion for lithiated $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$

Structural characterization of $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases, based on SXRD data, reveals structural instability in the $x=0$ sample, leading to the formation of metallic iron under reductive conditions. The addition of gallium in samples with $x=1, 2, 3$, and 4 inhibits the formation of metallic iron, allowing reversible lithium intercalation. Analysis of the ICP-MS and iodometric titrations data confirmed lithium insertion in $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases (see Appendix-I Table 9a.15-9a.19).

Fe-XANES data collected from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ confirm the reduction of the Fe-site upon lithiation. NPD, ^{57}Fe Mössbauer, and EXAFS data collected from $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ reveal the reduction of only the FeO_4 site ($8f$), with no sign of reduction of the FeO_6 site ($4e$), indicating a preference for the FeO_4 site and a reluctance of the FeO_6 site to undergo reduction in $\text{Li}_3\text{Fe}_5\text{O}_9$ when treated with $n\text{-BuLi}$.

On the other hand, NPD, ^{57}Fe Mössbauer, and EXAFS data from $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ reveal a modest reduction of the FeO_4 site (8f) but a strong reduction in the FeO_6 site (4e). This indicates that the addition of gallium to the tetrahedral site diminishes the motivation of the tetrahedral site to undergo reduction. However, in $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, where the octahedral FeO_6 site is solely occupied by iron, allows reduction of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$.

This clear distinction in the reduction of FeO_4 and FeO_6 sites in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ is also evident in the location of inserted lithium, as shown in Figure 9.15. Out of the four present vacant lithium sites (A, B, C, and D), three of them are found to be occupied by inserted lithium cations for $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$. Additional lithiums in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ occupy channels B, C, and D, whereas in $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ they occupy channels A, B, and D. This difference in the occupation of lithium can be attributed to the different iron sites ($\text{FeO}_4/\text{FeO}_6$) undergoing reduction upon lithiation.

Results from NPD, ^{57}Fe Mössbauer, and EXAFS data are found consistent with each other, confirming that the local and average structures are largely similar. Based on such characterization results, it can be confirmed that higher gallium doping in $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ allows superior structural retention which also allows higher reversibility of the lithium intercalation reaction as observed by iodometric titration values (see Appendix-I, Table 9a.15-19).

9.6. Characterization results of the oxidised $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

9.6.1. Synchrotron x-ray diffraction (SXRD) data

SXRD data were collected from the chemically delithiated $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases henceforth referred to as $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, were indexed on the basis of a monoclinic unit cell ($C2/c$) similar to the pristine $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$. Crystallographic models based on $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ structures were refined against the SXRD data which yielded rapid convergence as shown in Appendix-I Figures 9a.11-9a.13. Collected SXRD data for $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ revealed additional broad reflections associated with the presence of LiFe_5O_8 which was added as a secondary phase during the refinement (Figure 9.22). For other $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ sample, no such impurity peaks were observed (Figure 9.22).

Figure 11.2 shows variation of lattice parameters of $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases as a function of gallium concentrations. For $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ in comparison to $\text{Li}_3\text{Fe}_5\text{O}_9$, an increase along a but decrease along b and c was observed. For all the other $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples in comparison to the corresponding $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, increase along a , b , c and β was observed. As a result, monotonic increase in volume was observed for the delithiated $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases in comparison to the pristine $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases (Figure 9.23).

Detailed structural characterization of $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ with neutron powder diffraction data will be discussed in Section 9.6.2.

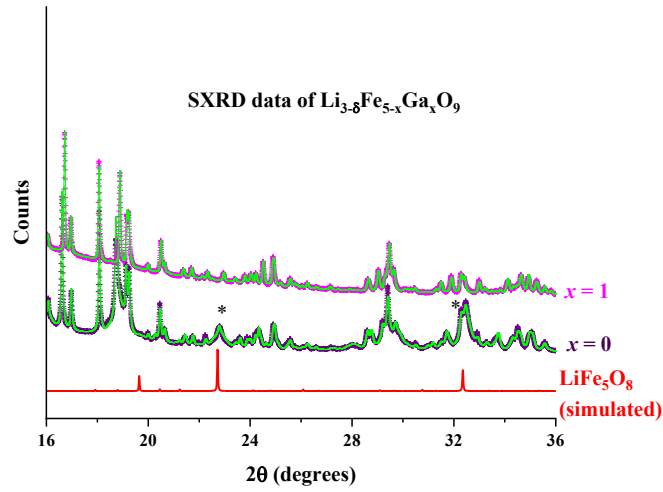


Figure 9. 22. Plot of observed, calculated (green line) SXR D data collected from $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$, for $x = 0$ and 1; * indicates reflections associated to LiFe_5O_8 in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$

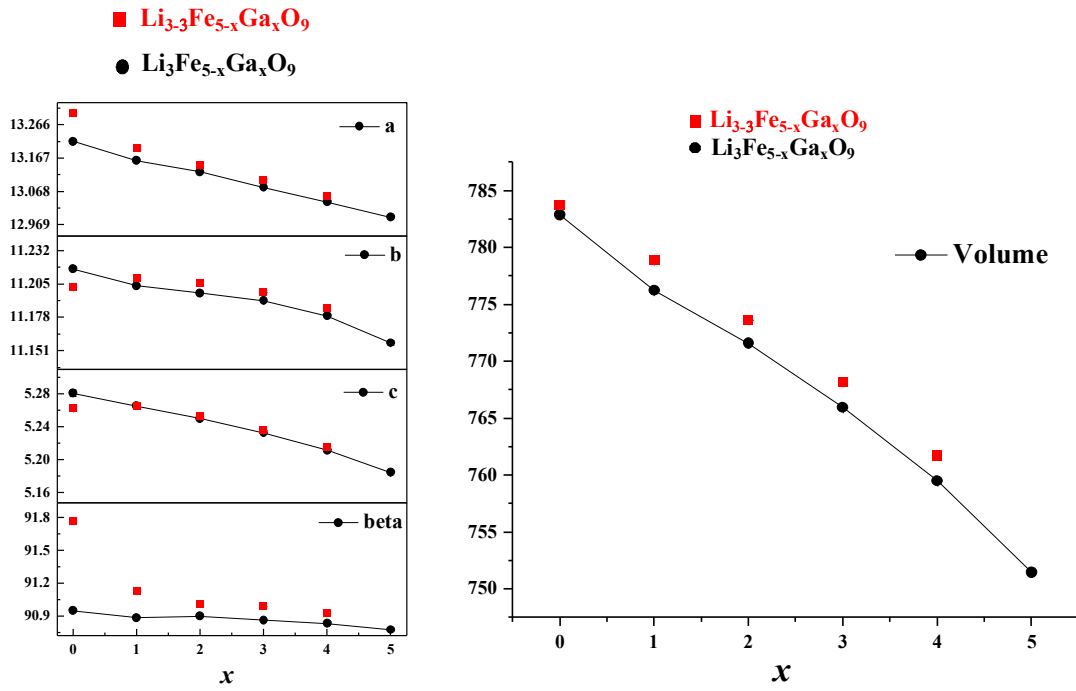


Figure 9. 23. Plot of lattice parameters as a function of compositions for $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases determined against SXR D data; Error bars are smaller than the plotted points

9.6.2. Neutron powder diffraction (NPD) data

Room temperature neutron powder diffraction data were collected from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$. Crystallographic models based on pristine $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ structure were refined to yield a convergence to the data as shown in Figures 9.24 and 9.25 with refined structural parameters in Tables 9.21 and 9.22. For both $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ the lithium occupancy parameters were refined during the structural determination and the final composition obtained as $\text{Li}_{1.56}\text{Fe}_5\text{O}_9$ and $\text{Li}_{1.964}\text{Fe}_2\text{Ga}_3\text{O}_9$ which is in good agreement with the lithium content determined from ICP-MS analysis (Appendix-I, Table 9a.20).

NPD data of $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ contained additional reflections associated with LiFe_5O_8 spinel as well as magnetic reflections from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$. LiFe_5O_8 was added as a secondary phase during the refinement process but the magnetic reflections were excluded from the analysis.

$\langle\text{Fe-O}\rangle$ bond lengths and Fe-BVS parameters were derived from the final refined structural models of $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$. These values are compared with those of other $\text{Li}_{3-8}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases in Tables 9.24 and 9.25. When contrasting $\langle\text{Fe-O}\rangle$ bond lengths and Fe-BVS between $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_5\text{O}_9$, a reduction in $\langle\text{Fe-O}\rangle$ bond lengths and an increase in the Fe-BVS parameter for Fe3 (4e) site in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ were observed. This is in line with the anticipated oxidation of iron during oxidative delithiation. Conversely, no substantial alterations in the $\langle\text{Fe-O}\rangle$ bond lengths or Fe-BVS were observed for Fe1 (8f) and Fe2 (8f) site in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$. In the case of all other $\text{Li}_{3-8}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases, a largely similar trend with decrease in $\langle\text{Fe-O}\rangle$ bond lengths and an increase in Fe-BVS parameters were evident for Fe1 (8f), Fe2 (8f), and Fe3 (4e) sites, relative to $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases, indicative of modest iron oxidation during delithiation

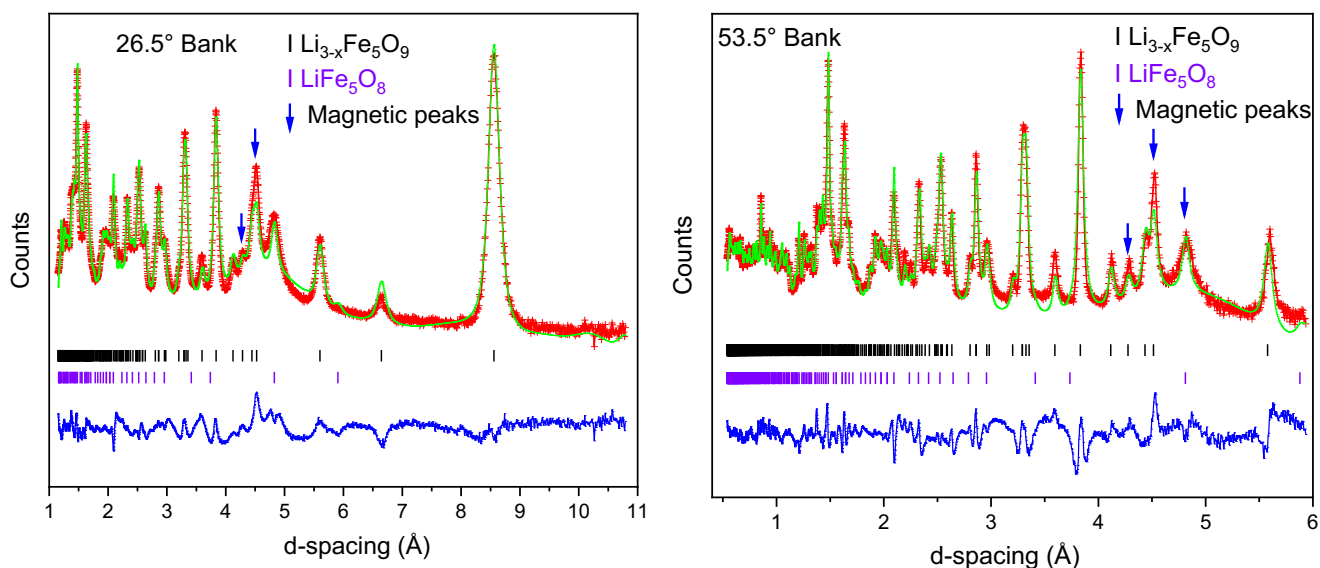


Figure 9.24. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_5\text{O}_9$ against NPD data, 26.5° Bank (left) and 53.5° Bank (right)

Table 9.21. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_5\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1	8f	0.1200(4)	0.3333(4)	0.2834(9)	1	0.44(7)
Fe2	8f	0.3590(5)	0.3302(4)	0.2183(9)	1	0.44(7)
Fe3	4e	0	0.0676(6)	$\frac{1}{4}$	1	0.44(7)
Li1	8f	0.2437(30)	0.0731(30)	0.1613(73)	0.51(5)	0.0(1)
Li2	4e	0	0.06040(45)	$\frac{1}{4}$	0.51(5)	0.0(1)
O1	8f	0.0923(6)	0.1919(7)	0.1438(14)	1	0.55(8)
O2	8f	0.3518(6)	0.1815(8)	0.3879(15)	1	0.55(8)
O3	8f	0.2227(6)	0.4051(8)	0.1380(16)	1	0.55(8)
O4	8f	0.4156(6)	0.4621(7)	0.4303(16)	1	0.55(8)
O5	4e	0	0.3855(11)	$\frac{1}{4}$	1	0.55(8)
$\text{Li}_{1.56}\text{Fe}_5\text{O}_9$ – space group $C2/c$ (#15) $a = 13.3015(16) \text{ \AA}$, $b = 11.2024(14) \text{ \AA}$, $c = 5.2623(6) \text{ \AA}$, $\beta = 91.7671 (20)^\circ$ volume = $783.770(171) \text{ \AA}^3$ Formula weight = $434.0575 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 4.42\%$, $wR_p = 6.05\%$						
Crystallographic parameters of $\text{Li}_{1-x}\text{Fe}_5\text{O}_8$ added as a secondary phase during the refinement $\text{Li}_{1-x}\text{Fe}_5\text{O}_8$ – space group $P4_332$ (#212) $a = b = c = 8.3551(7) \text{ \AA}$, volume = $583.248 (147) \text{ \AA}^3$ mass fraction weight % = 21						

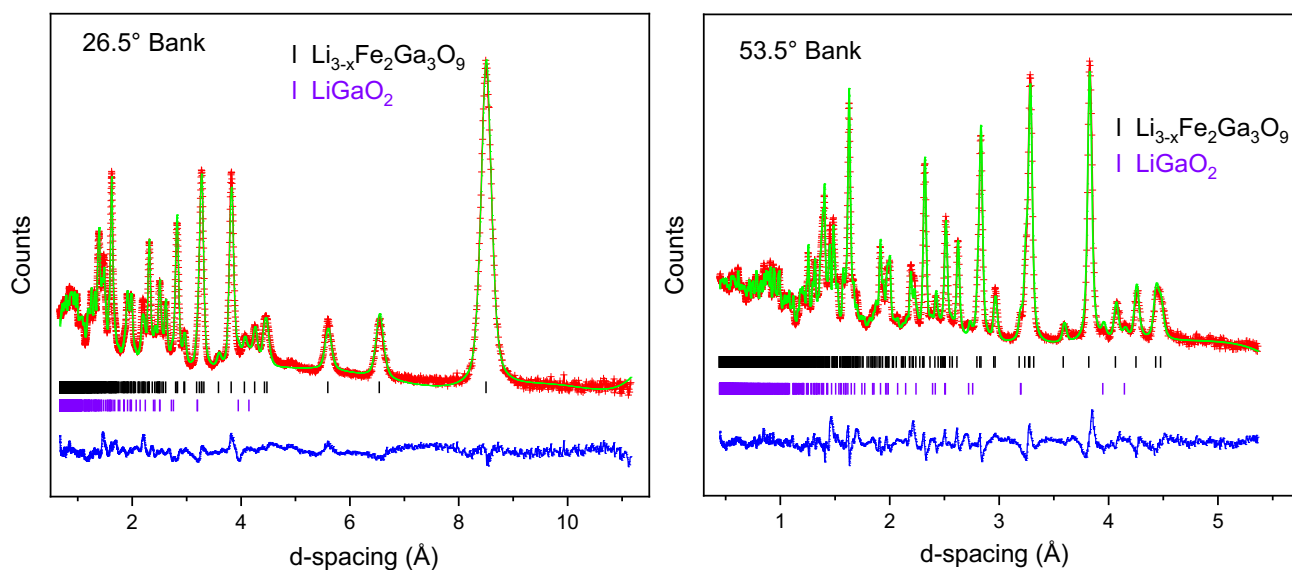


Figure 9.25. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ against NPD data, 26.5° Bank (left) and 53.5° Bank (right)

Table 9.22. Parameters from the structural refinement of $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ sample against neutron powder diffraction data

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Fe1/Ga1	8f	0.1195(2)	0.3328(2)	0.2954(4)	0.26(1)/0.74(1)	0.73(5)
Fe2/Ga2	8f	0.3556(2)	0.3356(2)	0.2121(5)	0.26(1)/0.74(1)	0.76(5)
Fe3	4e	0	0.0677(3)	$\frac{1}{4}$	1	0.36(5)
Li1	8f	0.2482(9)	0.0708(13)	0.2057(24)	0.72(1)	0.61(26)
Li2	4e	0	0.5870(29)	$\frac{1}{4}$	0.51(2)	0.61(26)
O1	8f	0.0985(2)	0.1897(3)	0.1236(6)	1	0.15(1)
O2	8f	0.02505(2)	0.1847(3)	0.3595(6)	1	0.15(1)
O3	8f	0.2282(2)	0.4089(3)	0.1484(5)	1	0.15(1)
O4	8f	0.4189(2)	0.4446(3)	0.4172(5)	1	0.15(1)
O5	4e	0	0.4199(4)	$\frac{1}{4}$	1	0.15(1)
$\text{Li}_{1.964}\text{Fe}_2\text{Ga}_3\text{O}_9$ — space group $C2/c$ (#15) $a = 13.0829(3) \text{ \AA}$, $b = 11.1849(3) \text{ \AA}$, $c = 5.2281(1) \text{ \AA}$, $\beta = 91.0028(19)^\circ$ volume = $764.929(39) \text{ \AA}^3$ Formula weight= $477.87 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: neutron, Time of flight Temperature: 298 K $R_p = 3.33 \%$, $wR_p = 4.55\%$						
Crystallographic parameters of LiGaO_2 added as a secondary phase during the refinement LiGaO_2 — space group $Pna2_1$ (#33) $a = 5.4407(6) \text{ \AA}$, $b = 6.3986(7) \text{ \AA}$, $c = 5.0158(5) \text{ \AA}$, volume = $174.617(106) \text{ \AA}^3$ weight % = 2						

Table 9.23. Table of cell parameters extracted from structural refinement against SXRD and NPD data from $\text{Li}_{3-x}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples.

	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å ³)
$\text{Li}_{3-x}\text{Fe}_5\text{O}_9$	13.3015(16)	11.2024(14)	5.2623(6)	91.7671(20)	783.770(171)
$\text{Li}_{3-x}\text{Fe}_4\text{GaO}_9$	13.1973(1)	11.2096(1)	5.2657(3)	91.1287(7)	778.855(10)
$\text{Li}_{3-x}\text{Fe}_3\text{Ga}_2\text{O}_9$	13.1447(1)	11.2058(1)	5.2529(3)	91.0080(7)	773.634(10)
$\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$	13.0829(3)	11.1849(3)	5.2281(1)	91.0028(19)	764.929(39)
$\text{Li}_{3-x}\text{FeGa}_4\text{O}_9$	13.0561(1)	11.1857(1)	5.2153(3)	90.9320(7)	761.757(25)

Table 9.24. Table of bond distance calculated from structural refinement against SXRD and NPD data from $\text{Li}_{3-x}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

<M-O>	Site	$\text{Li}_{3-x}\text{Fe}_5\text{O}_9$	$\text{Li}_{3-x}\text{Fe}_4\text{GaO}_9$	$\text{Li}_{3-x}\text{Fe}_3\text{Ga}_2\text{O}_9$	$\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$	$\text{Li}_{3-x}\text{FeGa}_4\text{O}_9$
		Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)	Bond distance (Å)
Fe1-O	8f	1.856(8)	1.855(5)	1.832(5)	1.844(4)	1.865(4)
Ga1-O	8f					
Fe2-O	8f	1.916(8)	1.896(3)	1.885(3)	1.859(5)	1.877(3)
Ga2-O	8f					
Fe3-O	4e	1.944(5)	2.002(4)	2.004(4)	1.992(4)	1.932(3)
Ga3-O	4e					

Table 9.25. Table of bond-valence-sum calculated from structural refinement against SXRD and NPD data from $\text{Li}_{3-x}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

<M-O>	site	$\text{Li}_{3-x}\text{Fe}_5\text{O}_9$	$\text{Li}_{3-x}\text{Fe}_4\text{GaO}_9$	$\text{Li}_{3-x}\text{Fe}_3\text{Ga}_2\text{O}_9$	$\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$	$\text{Li}_{3-x}\text{FeGa}_4\text{O}_9$
		BVS	BVS	BVS	BVS	BVS
Fe1-O	8f	3.283	3.084	3.279	3.1765	
Ga1-O	8f		2.852	3.031	2.9353	2.807
Fe2-O	8f	2.686	2.777	2.852	3.0565	
Ga2-O	8f		2.568	2.637	2.8261	2.914
Fe3-O	4e	3.743	3.115	3.096	3.202	3.758
Ga3-O	4e					

9.6.3. X-ray absorption spectroscopy

9.6.3.1. Fe-XANES data

To investigate the change in oxidation state of iron in $\text{Li}_{3-x}\text{Fe}_5\text{Ga}_x\text{O}_9$ after oxidative lithium extraction, Fe K-edge XANES data was collected from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ along with Fe_2O_3 and SrFeO_3 . XANES data from Fe_2O_3 and SrFeO_3 were used as references for Fe (III) and Fe (IV) K-edges respectively. The normalized data are presented below.

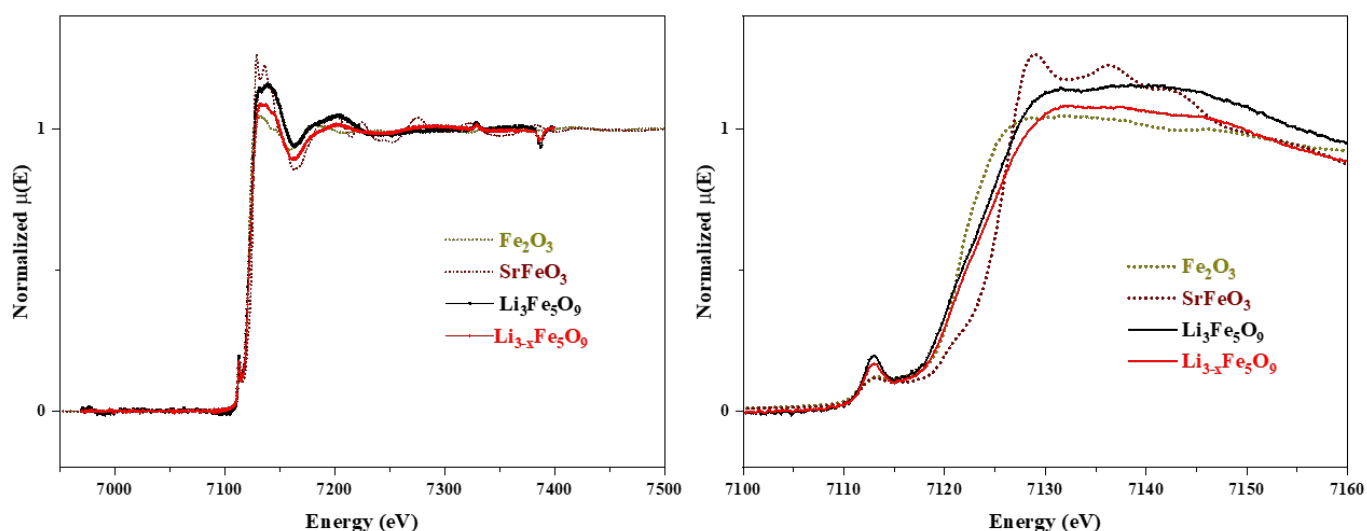


Figure 9.26. XANES data of $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ with references (dotted lines); normalization (left), enlarged comparison (right)

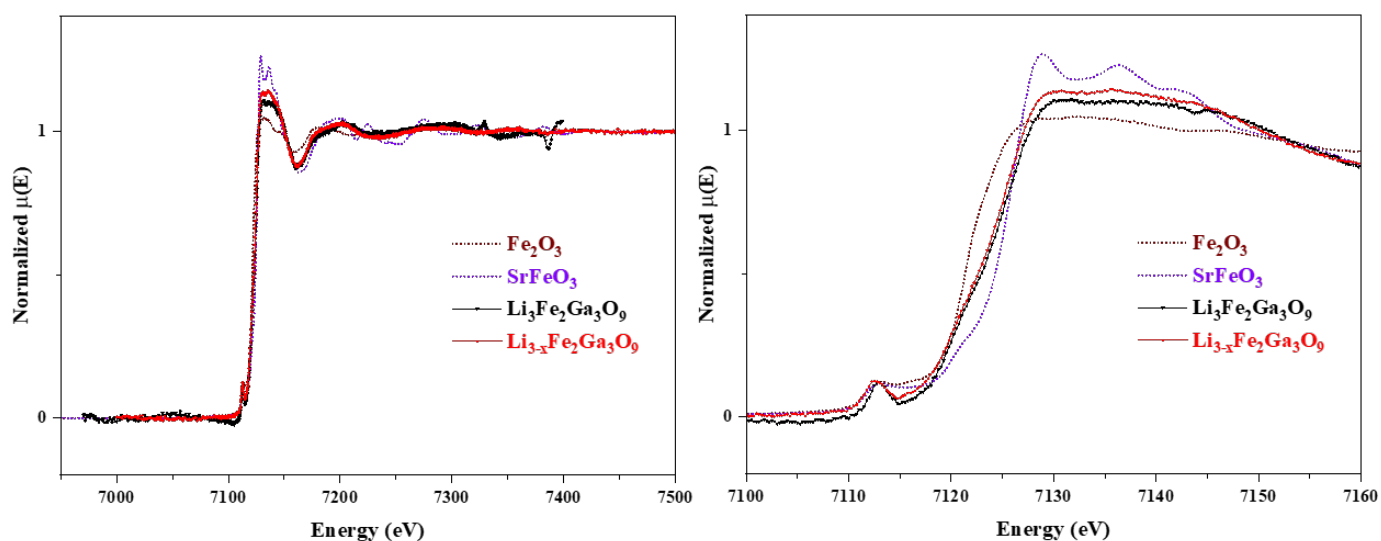


Figure 9.27. XANES data of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ with references (dotted lines); normalization (left), enlarged comparison (right)

As shown in Figures 9.26 and 9.27, the XANES data from $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ (both pristine and reduced) reveal a pre-edge feature at an energy of approximately 7112 eV, followed by a sharp K-edge ($E \sim 7125$ eV). A close inspection of the data discloses a ~ 0.6 eV energy shift to higher energy in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ compared to $\text{Li}_3\text{Fe}_5\text{O}_9$, indicating a slight oxidation of the iron site from Fe^{3+} to $\text{Fe}^{3.x+}$.

A similar analysis of the Fe-XANES data for $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ is presented in Figure 9.27. The comparison between $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ reveals no significant shift of the K-edge to higher energy. A mere ~ 0.3 eV difference in the Fe K-edge energy between $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ is observed, indicating minimal oxidation of the iron site due to the chemical delithiation reaction.

9.6.3.2. EXAFS data

High-resolution X-ray absorption spectroscopy (XAS) data, distinct from the datasets presented in Figures 9.26 and 9.27, were collected for $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$. These datasets served as extended X-ray absorption fine structure (EXAFS) data to examine the local structural modifications within the FeO_4 and FeO_6 sites induced by lithium insertion. The XAS data, above the absorption edge, underwent conversion into various oscillations specific to the absorber atom and were subsequently analyzed as EXAFS data.

The first shell of the EXAFS data, encompassing both the FeO_4 tetrahedra and FeO_6 octahedra, derived from $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$, was carefully fitted by refining the crystallographic models obtained post the structural refinement against NPD data.

As described in Section 9.4.4.1, due to three different iron sites in present in $\text{Li}_3\text{Fe}_5\text{O}_9$, the first shell of the EXAFS data in R space was fit with $3.2 \times \text{Fe-O (Td)}$ and $1.2 \times \text{Fe-O (Oh)}$ bonds. The same approach was maintained for $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$. The fits in R and

q space with the fitting parameters for $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ are given in Figures 9.28, 9.29 and Tables 9.28, 9.29 below.

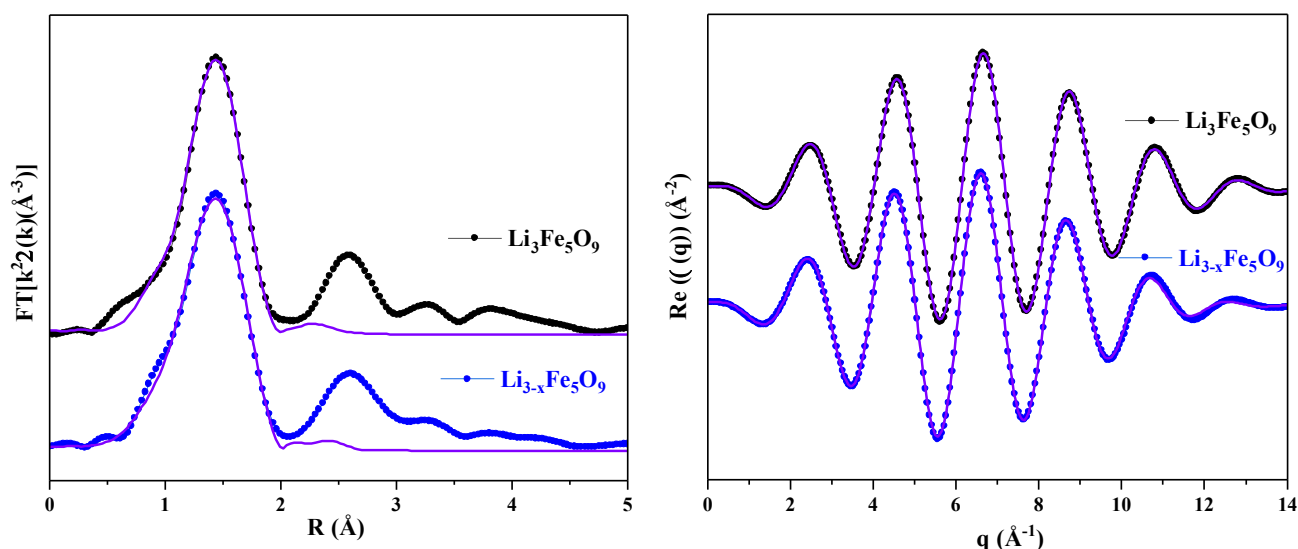


Figure 9. 28. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 9.28. Refined EXAFS parameters for $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$

Sample	Bond	N	$R(\text{\AA})$	Debye-Waller Factor ($10^{-3} \text{\AA}^2$)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD ($\text{\AA}$)
$\text{Li}_3\text{Fe}_5\text{O}_9$	Fe-O	3.2	1.870(2)	4.2(4)	0.31	2.963	1.876(6)
	Fe-O	1.2	2.003(2)	2.5(9)		3.102	2.014(4)
$\text{Li}_{3-x}\text{Fe}_5\text{O}_9$	Fe-O	3.2	1.90(2)	14.8(8)	0.89	2.732	1.886(6)
	Fe-O	1.2	1.915(4)	4.47(2)		3.935	1.944(5)

As shown in Figure 9.28, the fitting of the first shell of the EXAFS data from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ reveals a significantly smaller octahedral $\langle\text{Fe-O}\rangle$ bond compared to the corresponding $\langle\text{Fe-O}\rangle$ bond in $\text{Li}_3\text{Fe}_5\text{O}_9$ which indicates the oxidation of the FeO_6 unit (4e site) in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ upon chemical delithiation. Conversely, no significant change in $\langle\text{Fe-O}\rangle$ is observed for the FeO_4 site in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ compared to $\text{Li}_3\text{Fe}_5\text{O}_9$, suggesting minimal oxidation of the FeO_4 unit (8f

site) during delithiation. These observations are also consistent with the NPD analysis, as presented in Table 9.24.

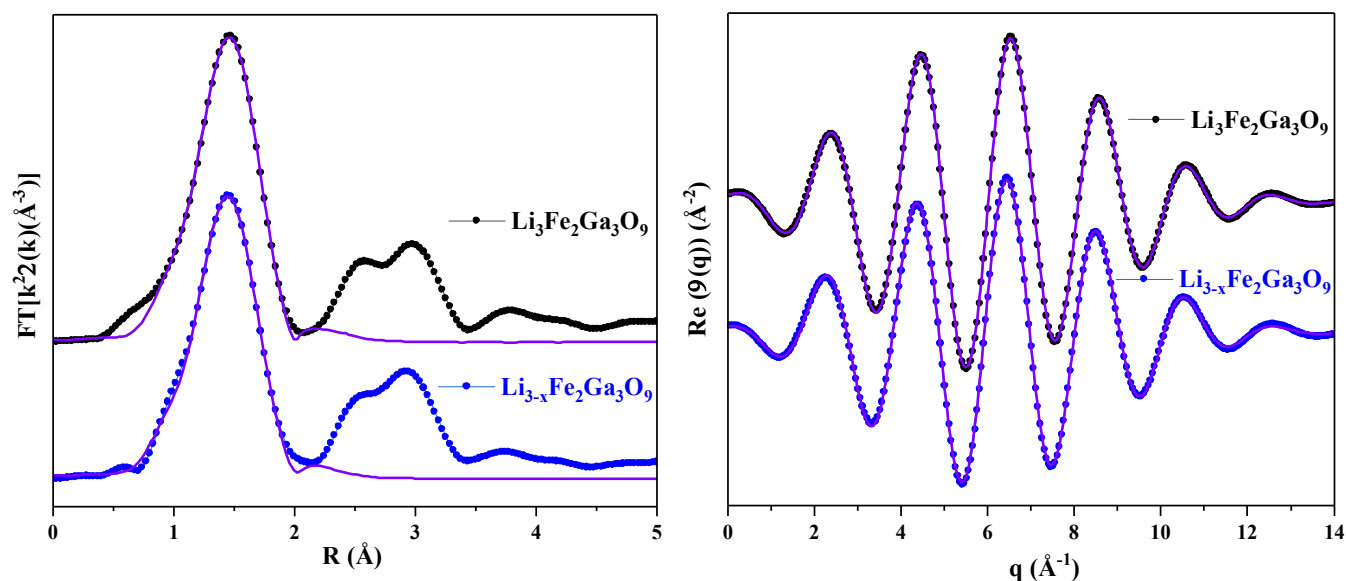


Figure 9.29. EXAFS data and fit (purple line), Fourier transforms of the k^2 weighted EXAFS oscillations for $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ (left); corresponding back Fourier transformed EXAFS oscillations in the q -space (right)

Table 9.29. Refined EXAFS parameters for $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$

Sample	Bond	N	R(Å)	Debye-Waller Factor (10^{-3} Å^2)	EXAFS agreement factor (%)	Bond-Valence Sum	Average bond length from NPD (Å)
$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$	Fe-O	3.2	1.863(2)	3.6(6)	0.26	3.0198	1.873(5)
	Fe-O	1.2	1.985(2)	4.9(6)		3.2574	1.989(3)
$\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$	Fe-O	3.2	1.866(4)	1.8(6)	0.57	2.9954	1.851(4)
	Fe-O	1.2	1.962(4)	3.4(6)		3.4663	1.992(4)

Figure 9.29 displays the first shell fit of the EXAFS data from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$, with the fitting parameters outlined in Table 9.29. The tetrahedral FeO_4 site ($N=3.2$, Table 9.29) exhibits a similar $\langle\text{Fe-O}\rangle$ bond length in both $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, indicating minimal oxidation of iron in the FeO_4 site during delithiation. However, a decrease in $\langle\text{Fe-O}\rangle$ from 1.985(2) Å to 1.962(4) Å is observed for the octahedral FeO_6 site ($N=1.2$, Table 9.29), suggesting oxidation of iron in the FeO_6 site upon chemical delithiation. This iron oxidation in the octahedral site of $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ is not as pronounced as observed in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$.

Additionally, a slight difference in the $\langle \text{Fe-O} \rangle$ bond lengths determined by EXAFS and NPD is noted. This difference may be attributed to the presence of Fe/Ga disorder within the $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ structure. It is noteworthy that while NPD identifies changes in the average Fe-O/Ga-O bond lengths, EXAFS specifically detects alterations in pure Fe-O bond lengths.

9.6.4. Oxygen K-edge X-ray absorption spectroscopy

O K-edge XAS data were collected from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ in fluorescence yield (FY) mode. The normalized data are presented below.

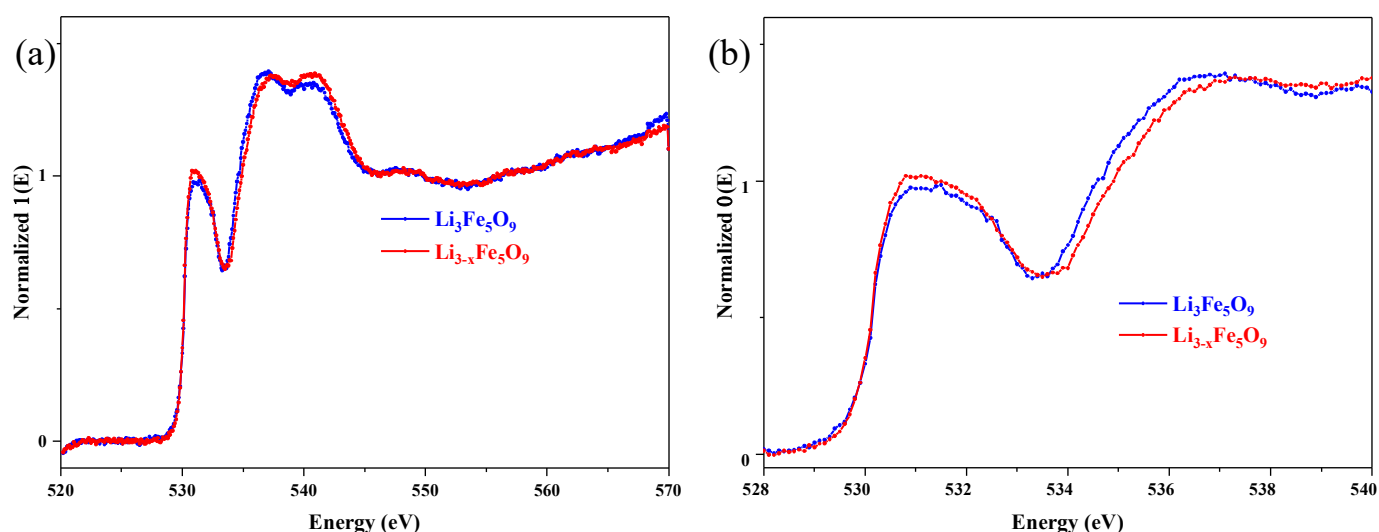


Figure 9.30. Plot of O K-edge XAS data collected from $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ in fluorescence yield mode (a,b), Normalization: (a), enlarged comparison (b)

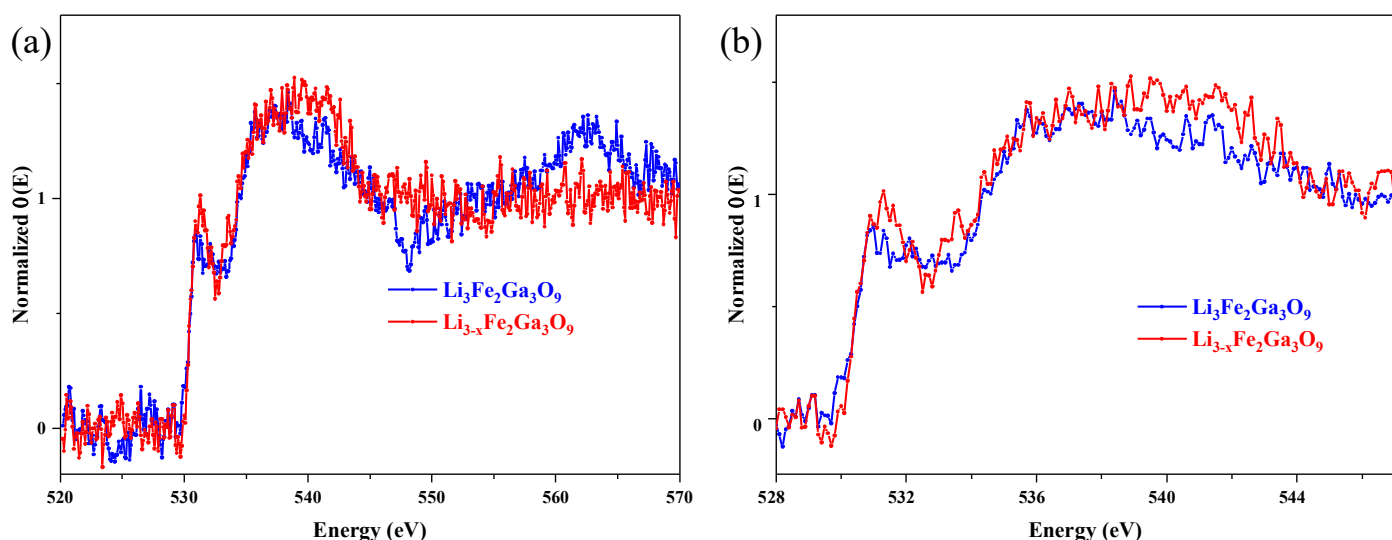


Figure 9.31. Plot of O K-edge XAS data collected from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ in fluorescence yield mode (a,b), Normalization: (a), enlarged comparison (b)

Figures 9.30 and 9.31 display the O K-edge XAS data collected from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$. A distinct sharp feature at 531 eV is attributed to the excitation of the Oxygen 1s electron to the $\text{Fe}(3d)\text{-O}(2p)$ hybridized band⁸³, while broad features above 534 eV indicate the excitation of the Oxygen 1s electron to the $\text{Fe}(4s,4p)\text{-O}(2p)$ hybridized band⁸³.

Comparing XAS data from pristine ($\text{Li}_3\text{Fe}_5\text{O}_9$) and delithated ($\text{Li}_{3-x}\text{Fe}_5\text{O}_9$) materials [(a,b) Figure 9.30], no shift in K-edge energy is observed for the sharp feature at 531 eV. However, a slight increase in intensity is noted. For the broad feature in the O K-edge spectra [(b) in Figure 9.30], there is a noticeable shift towards higher energy in the oxidized material compared to the pristine $\text{Li}_3\text{Fe}_5\text{O}_9$ sample.

Despite the lower resolution in the XAS data from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$, a similar trend of enhanced intensity at 531 eV and a shift of the broad feature to higher energies is evident as shown in Figure 9.31.

The intensity enhancement at 531 eV and the shift of the broad feature to higher energies in O K-edge XAS data are consistent with oxygen oxidation in the delithiated materials ($\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$), aligning with recent reports on the oxidation of other cathode materials^{89,156–159}.

9.6.5. Resonance in-elastic X-ray scattering (RIXS) data

To further investigate the participation of oxygen redox, RIXS line scan data were collected from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ at an excitation energy of 531.75 eV, from 10 different points of the sample to avoid any beam damage. The final data was averaged from the 10 scans which are presented below in Figure 9.32.

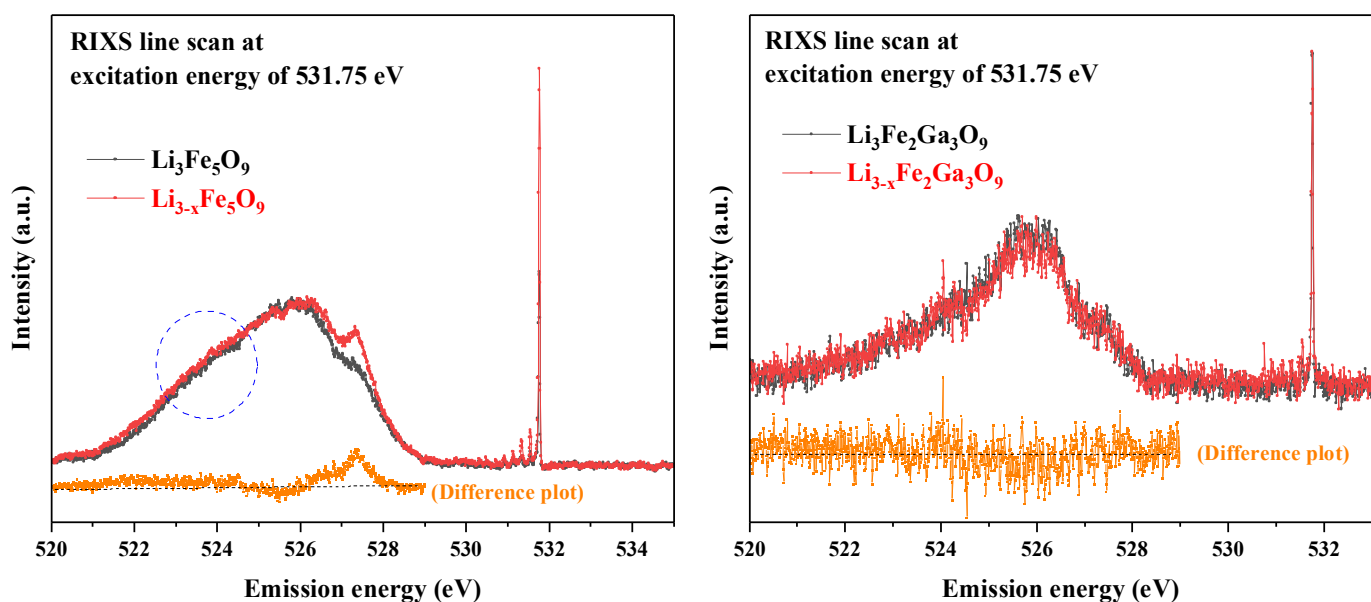


Figure 9.32. RIXS line scan data from $\text{Li}_3\text{Fe}_5\text{O}_9$ (black line) and $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ (red line) [left], $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ (black line) and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ (red line) [right]

Figure 9.32 presents RIXS line scan data at an excitation energy of 531.75 eV from $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, $\text{Li}_3\text{Fe}_5\text{O}_9$, $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$, and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, revealing a broad intensity feature in the emission energy range of 522-528 eV. The intensity feature at an energy loss of 523.75 eV is considered a hallmark of oxygen oxidation, originating from intraband excitons of $\pi_u \rightarrow \sigma_u^*$ during the emission process⁹⁴(Section 1.9).

When comparing the RIXS line scan data between pristine $\text{Li}_3\text{Fe}_5\text{O}_9$ and delithiated $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$, a modest increase in intensity for $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ at an emission energy of 524 eV (dotted blue circle, Figure 9.32) suggests oxygen oxidation in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$. In contrast, RIXS line scan data from $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ show no clear distinction, making it challenging to conclusively identify the participation of oxygen oxidation during chemical delithiation of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$.

9.7. Electrochemical cycling

To study the electrochemical performance of $\text{Li}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, cyclic voltammetry (CV) profile and charge-discharge capacity data were collected.

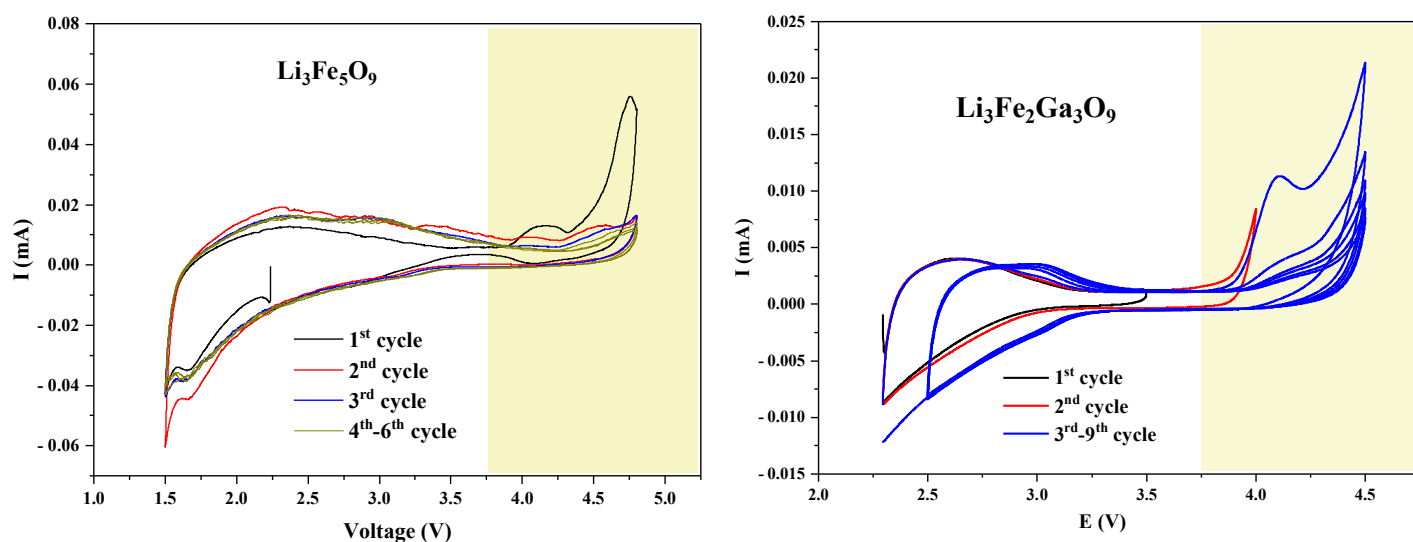


Figure 9.33. Cyclic voltammogram profile from $\text{Li}_3\text{Fe}_5\text{O}_9$ (left) and $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ (right). Highlighted region indicates the voltage range of irreversible oxidation

Figure 9.33 (left) shows the cyclic voltammetry (CV) data obtained from $\text{Li}_3\text{Fe}_5\text{O}_9$ within the voltage range of 1.5-4.8 V, revealing two distinct processes. The first process exhibits reversible cycling, featuring a reduction peak at 1.5 V (sharp) and an oxidation peak at 2.25 V (broad), attributed to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. Conversely, the second process, observed at voltages higher than 3.75 V, only displays an oxidation feature without a corresponding reduction peak, indicating an irreversible oxidation process which saturates in the subsequent cycles.

A similar characteristic is evident in the CV data obtained from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ within the voltage range of 2.25-4.5 V, with the irreversible oxidation process highlighted in yellow in Figure 9.33 (right).

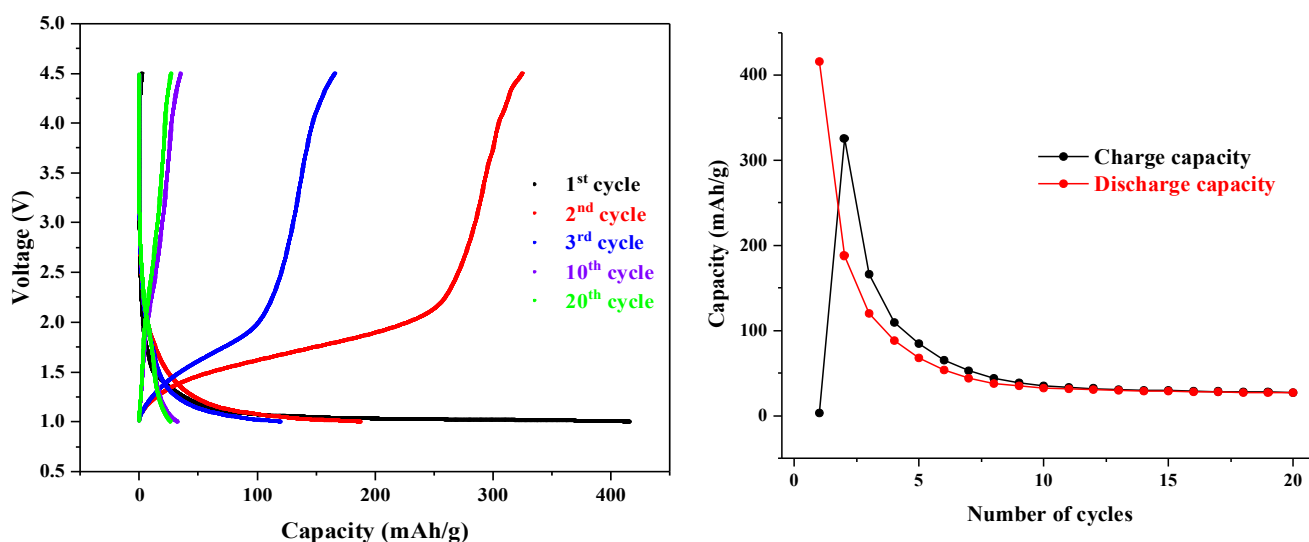


Figure 9. 34. Charge-discharge capacity profile of $\text{Li}_3\text{Fe}_5\text{O}_9$ in the voltage range of 1V-4.5V; Left: Voltage vs capacity plot, Right: Capacity vs number of cycles,

In Figure 9.34, the charge-discharge capacity profile of $\text{Li}_3\text{Fe}_5\text{O}_9$ within the voltage range of 1-4.5 V is presented. In the first cycle, a notable discharge capacity of 420 mAh/g is observed, equivalent to inserting 6.96 extra lithium ions per formula unit. This exceeds the allowed limit by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, indicating additional processes during discharge at 1 V. Structural characterization through SXRD and NPD data uncovered the presence of a LiFe_5O_8 impurity (20%) in $\text{Li}_3\text{Fe}_5\text{O}_9$ and the concurrent reduction of both $\text{Li}_3\text{Fe}_5\text{O}_9$ and LiFe_5O_8 under reductive conditions. EXAFS data further confirmed the presence of metallic iron in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$ (Section 9.4.4.2), explaining the additional ~ 2 lithium ions insertion in $\text{Li}_3\text{Fe}_5\text{O}_9$ during discharge at 1 V.

Remarkably, at the end of the second charge cycle at 4.5 V (red line, Figure 9.34), approximately 5 lithium ions are reversibly extracted, indicating the potential cycling of 5 Li^+ ions in $\text{Li}_3\text{Fe}_5\text{O}_9$ owing to $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox. Despite observing a degree of reversible lithiation and delithiation in the initial cycles, closer examination reveals that in each cycle, the amount of lithium extracted is consistently less than the lithium inserted. This non-recovery of lithium ions in each cycle accumulates to a point where lithium insertion becomes minimal, resulting in a rapid capacity drop to 19 mAh/g within 20 cycles.

This irreversible electrochemical lithiation of $\text{Li}_3\text{Fe}_5\text{O}_9$ aligns with the structural changes discussed in Section 9.5 and the iodometric titration values presented in Appendix-I Table 9a.20. Notably, no distinct oxidation feature associated with combined Fe-O redox (similar to substituted LiFeO_2 materials, Chapters 5 and 8) at voltages greater than 4.25 V is observed, explained by the electrochemical window not being high enough, as seen for chemical delithiation with NO_2BF_4 .

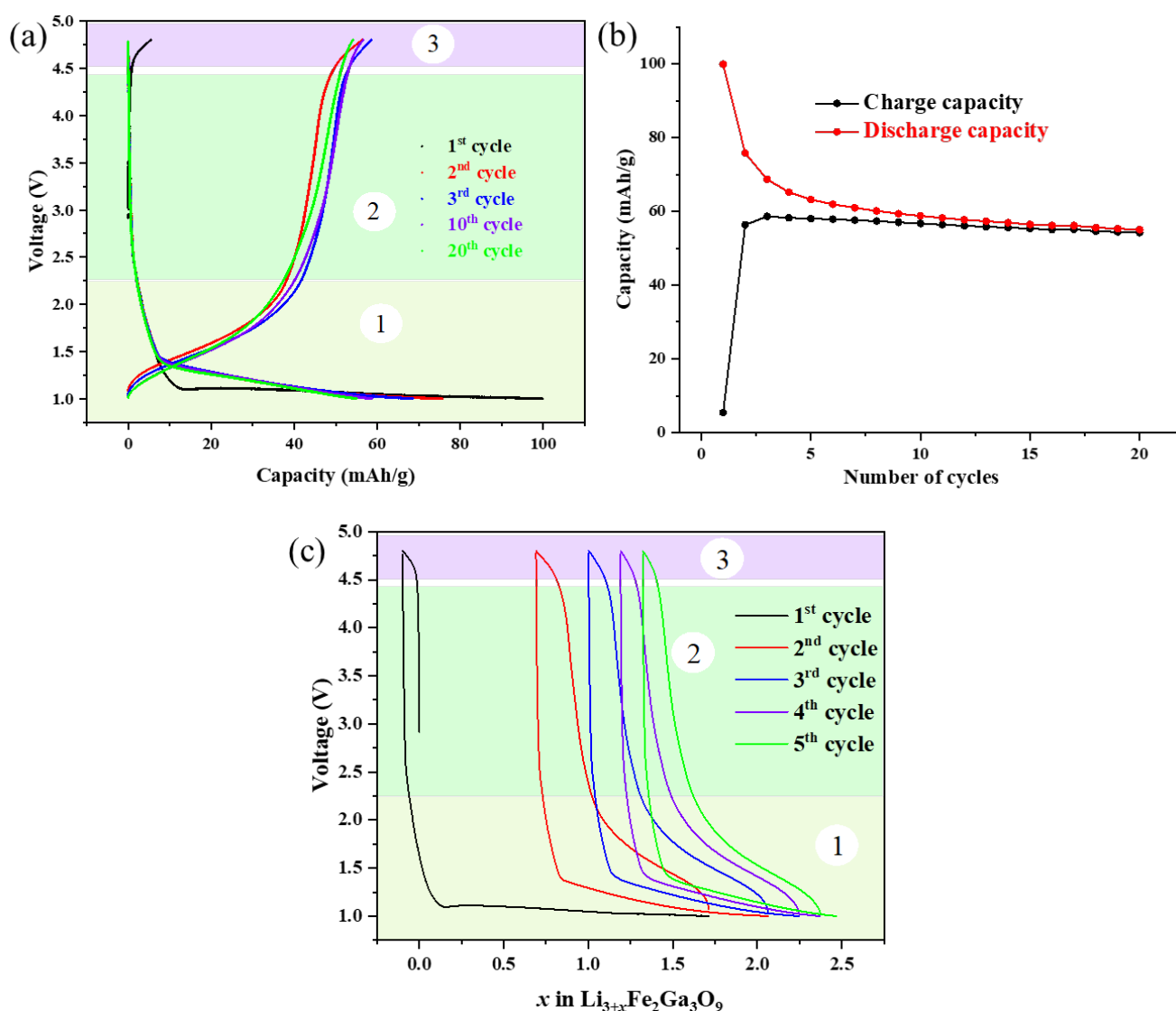


Figure 9. 35. Charge-discharge capacity profile of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ sample; (a) Voltage vs capacity plot, (b) Capacity vs number of cycles, (c) voltage vs number of lithium being inserted (x), Process1: charge-discharge profile region with voltage window of 1-2.25 V, Process2: mostly redox inactive region with the voltage window of 2.25-4.5 V Process3: charge region with the voltage window of 4.5-4.8 V

Figure 9.35 presents the charge-discharge profile of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ within the voltage range of 1-4.8 V. In the initial discharge cycle, a capacity of 100 mAh/g, equivalent to the insertion of 1.81 Li^+ , is observed, consistent with the ICP-MS and NPD data discussed earlier for $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$. In subsequent cycles, a reduction in capacity to 60 mAh/g is noted, maintaining steadily over 20 cycles. This capacity corresponds to the cycling of 1.08 lithium ions, suggesting that while $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ allows the insertion of two lithium ions, only half of them cycle reversibly in an electrochemical manner. Although the observed capacity is not as high as in $\text{Li}_3\text{Fe}_5\text{O}_9$, it remains remarkably stable, with one lithium being cycled, as depicted in Figure 9.35 (right).

The charge-discharge capacity profile of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ reveals three distinct processes:

Process 1 (1V-2.25 V): Partial reversible lithium insertion and extraction are observed in this voltage range. In the first discharge cycle, $\sim 1.81 \text{ Li}^+$ is inserted at 1 V, but upon charging to 2.25 V, only $\sim 0.8 \text{ Li}^+$ is extracted, indicating only partial recovery of inserted lithium. Subsequent cycles show a decline in the amount of lithium inserted during the discharge process [for e.g., from 1.81 to 1.38 to 1.23 Li^+ in first three discharge cycles] reaching approximately one lithium insertion in each cycle. In the charge process from 1-2.25 V, a steady $\sim 0.8 \text{ Li}^+$ extraction is observed in each cycle. This process can be attributed to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple in $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$.

Process 2 (2.25-4.5 V): In this voltage range, mostly a redox-inactive region is observed. However, close inspection reveals around 0.1 Li^+ extraction in each cycle during the charge process from 2.5 to 4.5 V, with no corresponding reduction feature.

Process 3 (Higher than 4.5 V): In the voltage range higher than 4.5 V, a minor oxidation feature is observed, corresponding to the extraction of $\sim 0.1 \text{ Li}^+$ per formula unit. This process

is also electrochemically irreversible, as the corresponding reduction is non-existent, attributed to the combined Fe-O redox in $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$.

In summary, one discharge process (2.5-1.0 V) and three charge processes (1.0-2.5 V, 2.5-4.5 V, and 4.5-4.8 V) contribute jointly to the stable capacity of ~ 60 mAh/g in $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$, explained as 1 Li^+ insertion in the discharge process at 1 V and cumulative extraction of 1 Li^+ in the three charge steps of Processes 1, 2, and 3.

9.8. Discussion of the oxidised $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples

The structural characterization of $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples against SXRD and NPD data demonstrates that there is no observable change in the structure for $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples ($4 \geq x \geq 0$) after chemical de-lithiation with NO_2BF_4 . NPD and ICP-MS analyses confirm the deficiency of lithium in the oxidized sample, and additional data from ICP-MS and titration support the reversible chemical lithium re-insertion through treatment with LiI (Appendix-I Tables 9.21-9.22).

The analysis of Fe XANES data indicates a slight oxidation of iron in $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ but minimal oxidation of iron in $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$. EXAFS data further reveals preferential oxidation of Fe^{3+} (4e) sites over other iron sites in both $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ and $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$. These results indicate that iron (III) in the octahedral site is more likely to be oxidized to iron (IV) than iron (III) in the tetrahedral site. O K-edge XAS and RIXS data additionally indicate the participation of oxygen redox combined with $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox in these phases upon treatment with NO_2BF_4 .

The electrochemical features observed in the data from $\text{Li}_3\text{Fe}_5\text{O}_9$ categorize it as a conversion-type cathode material, which is not reversible electrochemically. Although an initial high capacity of ~ 420 mAh/g is observed, equivalent to the insertion of ~ 7 $\text{Li}^+/\text{f.u.}$, the capacity drops to 19 mAh/g within 20 cycles after the structural change.

In contrast, electrochemical data from $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ reveals a stable capacity of 60 mAh/g, indicating the cycling of one Li^+ per formula unit. Despite the complex electrochemical features involving $\text{Fe}^{2+}/\text{Fe}^{3+}$ as well as combined $\text{Fe}^{3+}/\text{Fe}^{4+}$ -O redox, the capacity retention underscores the superiority of $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$ over $\text{Li}_3\text{Fe}_5\text{O}_9$, confirming the effectiveness of gallium doping in stabilizing Fe-based cathode materials.

Analysis of EXAFS, Mössbauer, and NPD data confirms that in $\text{Li}_{3+x}\text{Fe}_5\text{O}_9$, tetrahedral Fe (III) is reduced to Fe (II), whereas octahedral Fe (III) remains unaffected. Conversely, in $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$, tetrahedral Fe (III) is largely unaffected, and octahedral Fe (III) is reduced to Fe (II). Combining this information with the electrochemical features, the higher reversibility and superior electrochemical performance in $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ can be attributed to the reduction of octahedral Fe (III) to Fe (II), making it more reversible electrochemically.

The recurring presence of combined iron-oxygen redox at high voltages ($E > 4$ V) emerges as a common characteristic in iron-based oxide cathode materials. Notably, this feature is identified as chemically reversible but electrochemically irreversible, reflecting the poor conductivity of these samples. To match the level of chemical delithiation and enhance reversibility, electrochemical measurements conducted at slower rates (C/50, C/100, etc) can be employed. This approach could mitigate the challenges associated with poor conductivity and facilitate a more controlled and reversible electrochemical response in iron-based oxide cathode materials.

9.9. Conclusion

In this chapter, the synthesis and characterization of $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases, as well as the impact of gallium substitution under both reductive and oxidative conditions, both chemically and electrochemically have been discussed. The unique structural architecture of $A_3\text{Fe}_5\text{O}_9$ phases, wherein iron resides in both FeO_4 and FeO_6 environments, provided a distinctive opportunity to investigate the involvement of these tetrahedral and octahedral sites in response to oxidative and reductive reagent.

Our findings revealed that the introduction of gallium in $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases leads to a preferential occupation of gallium in the tetrahedral $8f$ sites of the structure. This distinct distribution of iron and gallium within the structure significantly influences the nature and extent of the observed electrochemical and chemical features. Substitution of gallium in the tetrahedral iron site of $A_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ phases is found effective stabilising the structure which allows reversible electrochemical cycling as demonstrated for $\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$. Additionally, a preference for iron cations in either a tetrahedral environment (FeO_4) or in an octahedral environment (FeO_6) to undergo reduction or oxidation is discussed in this chapter.

Chapter 10 – Conclusion

The work presented in this thesis primarily focuses on the investigation of a series of metastable iron-based oxide materials, and their evaluation as potential cathode materials for lithium-ion batteries. Prior research on iron-based cathode materials has highlighted the challenges associated with Fe(III) cathodes under reductive and oxidative conditions.^{14,27,47,55,71,72,74,76,179,185} When subjected to electrochemical cycling, structural decomposition due to cation migration, and oxygen loss due to the complex Fe-O redox couple is reported. Both these factors contribute to the capacity fading.

In an effort to gain deeper insight into the complex behaviour of iron cations during cycling and to enhance the structural stability under oxidative and reductive conditions, a range of substituted iron-based compounds—comprising both previously reported and novel materials—were synthesized. These compounds underwent lithiation and delithiation processes (discharge/charge) in both chemical and electrochemical contexts and were characterised at various points of lithium intercalation/deintercalation. Based on the analyses of these characterization results, several significant conclusions can be drawn.

(1). Cation substitution for structural stability:

In Chapters 4-9 of this thesis, the decomposition of LiFeO_2 and $\text{Li}_3\text{Fe}_5\text{O}_9$ during both chemical and electrochemical cycling is observed, which matches with the instability of iron-based cathodes according to the previous reports.^{14,27,47,55,71,72,74,76,179,185} Effective stabilization of LiFeO_2 and $\text{Li}_3\text{Fe}_5\text{O}_9$ structures under oxidative and reductive conditions is achieved through the substitution of iron cations by Al, Si, Ga, and Ge cations in the case of LiFeO_2 , and through the substitution of iron cations by Ga cations in the case of $\text{Li}_3\text{Fe}_5\text{O}_9$. The characterization results presented in this thesis demonstrate successful reversibility of lithium intercalation and de-intercalation in these substituted phases. Additionally, the required degree

of cation substitution to inhibit structural decomposition of iron cations in these phases is also discussed.

(2). Influence of topochemical cation exchange on the redox potential of iron:

During the preparation of metastable Li-precursor phases ($\text{LiFe}_{1-x}\text{M}_x\text{O}_2$, $M = \text{Al, Ga, Si, Ge}$) detailed in Chapters 3-8, the corresponding Na-parent phases ($\text{NaFe}_{1-x}\text{M}_x\text{O}_2$) were subjected to topochemical cation exchange reactions. Comparative analysis of the $\langle\text{Fe-O}\rangle$ bond lengths between the Na-parent phases and the corresponding Li-exchanged phases indicates an elongation of the $\langle\text{Fe-O}\rangle$ bond length in the Li-exchanged phase resulting from the cation exchange reaction.

Electrochemical cycling data from these Li-exchanged samples, in the first encounter to low voltage (reductive conditions) reveals a reduction from Fe^{3+} to Fe^{2+} . However, during the subsequent charge process at higher voltage (oxidative conditions), a complete re-oxidation from Fe^{2+} to Fe^{3+} is generally not observed, suggesting a preference for maintaining Fe(II). In later cycles, the change in the oxidation state of iron is observed as $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{2.x+}$. This preference aligns with the earlier-discussed enlargement of $\langle\text{Fe-O}\rangle$ bond lengths as a result of topochemical Li for Na cation exchange, which would be expected to favour Fe(II) over Fe(III).

In the specific cases of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, the stabilization of Fe(II) is so strong, that even at an average iron oxidation state lower than +3, the anion redox processes are active. Consequently, it can be inferred that in the cases of $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, due to topochemical cation exchange accompanied by the elongation of the $\langle\text{Fe-O}\rangle$ bond, the redox potentials of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Fe-O redox are significantly influenced, leading to the extraction of electron from a state associated with “anion redox” before a state associated with $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox.

(3). Influence of cation substitution on the redox potential of iron:

The substitution of iron cations by Al/Si/Ga/Ge cations, within the LiFeO_2 system further influences the redox potential of iron. For instance, in $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple operates within the voltage range of 2.0-3.0 V, while in $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, the same redox couple operates within the voltage range of 1.8-2.5 V. This difference in $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential between $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ is attributed to the influence of the different cation orderings of the substituents on the average $\langle\text{Fe-O}\rangle$ bond lengths within the $\text{LiFe}_{1-x}\text{M}_x\text{O}_2$ phases. A similar impact on the Fe-redox potential due to cation substitution is reported for $\text{LiFe}_{2-x}\text{In}_x\text{SbO}_6$ ⁷⁵ and $\text{Li}_3\text{Fe}_{3-x}\text{M}_x\text{Te}_2\text{O}_{12}$ ($M = \text{Al}, \text{In}$)¹⁸⁶, which is consistent with the proposed hypothesis.

The preference for maintaining Fe(II) during the electrochemical cycling of $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ is also consistent with the elongation of the $\langle\text{Fe-O}\rangle$ bond occurring after lithium exchange. However, both $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ display a fully reversible $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox behaviour despite an elongation of $\langle\text{Fe-O}\rangle$ bond lengths when compared to their respective Na-precursor phases. This behaviour during the electrochemical cycling for $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, and $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ is again attributed to the unique cation orderings present in these structures, influencing the redox potential of iron. Thus, the difference in the substitution patterns of the cations emerges as a significant controlling factor in modulating the redox potential of iron within these materials.

(4). Instability of the $\gamma\text{-NaFeO}_2$ structure type on lithiation/delithiation:

Characterisation results from delithiated $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{O}_4$ reveal a structural transformation during delithiation, from a $\gamma\text{-NaFeO}_2$ type structure a $\beta\text{-NaFeO}_2$ type structure in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$. On reinsertion of lithium, by treating with LiI , the $\beta\text{-NaFeO}_2$ type structure is retained.

A similar structural change from the γ -NaFeO₂ type structure in Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄ to the β -NaFeO₂ type structure in Li_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄ is evident during lithium insertion. On re-extraction of lithium, by treating with I₂, the β -NaFeO₂ type structure is retained.

In both Li_{1.5-x}Fe_{0.5}Si_{0.5}O₄ and Li_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄, a structural transition from the γ -NaFeO₂ structure type to the β -NaFeO₂ structure type is observed during delithiation and lithiation, respectively. The β -NaFeO₂ structure type is retained during the subsequent cycling of lithium in Li_{1.5}Fe_{0.5}Si_{0.5}AlO₄ and Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄. Consequently, it can be concluded that, although the pristine Li-phases adopt the γ -NaFeO₂ type structure after lithium exchange, on lithation/delithiation it transforms to the β -NaFeO₂ type structure which is energetically more favourable than the γ -NaFeO₂ structure type. However, it is worth pointing out that, the potential change from the β -NaFeO₂ structure type to the original γ -NaFeO₂ structure type, through a complete lithium insertion/extraction matching the initial compositions (e.g., Li_{1.5}Fe_{0.5}Si_{0.5}O₄ and Li_{1.5}FeGe_{0.5}Ga_{0.5}O₄) remains uncertain, as only partial lithium reinsertion (with LiI) or re-extraction (with I₂) is observed.

(5). Reduction of Fe^{III}O₄ in Li₃Fe₅O₉:

In the structure of Li₃Fe₅O₉, iron cations are located in both tetrahedral (Fe^{III}O₄) and octahedral environments (Fe^{III}O₆), which allows us to study the redox chemistry of iron in two different geometries (Chapter 9). Characterization results from lithiated Li_{3+x}Fe₅O₉ reveal that, upon lithiation, Fe³⁺ in the tetrahedral site (Fe^{III}O₄) undergoes reduction to Fe²⁺, while Fe³⁺ in the octahedral site (Fe^{III}O₆) remains unchanged. This indicates that Fe³⁺ in a tetrahedral oxygen environment (Fe^{III}O₄) is more prone to reduction than Fe³⁺ in an octahedral oxygen environment (Fe^{III}O₆). This observation contradicts the expected enhanced stability of Fe(II) in FeO₆ environments in comparison to FeO₄ environments. For example, in the structure of Fe₃O₄ Fe(II) resides in octahedral sites (electronic configuration: $t_{2g}^4 e_g^2$), instead of tetrahedral sites (electronic configuration: $e^3 t^3$), owing to the higher crystal field stabilization energy

(CFSE) in the octahedral site¹⁸⁷. The deviation from this expected trend, i.e., reduction of $\text{Fe}^{\text{III}}\text{O}_4$ not $\text{Fe}^{\text{III}}\text{O}_6$ in $\text{Li}_3\text{Fe}_5\text{O}_9$ on lithiation, can again be attributed to the change in $\langle\text{Fe-O}\rangle$ bond length as a result of topochemical cation exchange from the corresponding Na-precursor phase. A comparison of the $\langle\text{Fe-O}\rangle$ bond lengths between $\text{Na}_3\text{Fe}_5\text{O}_9$ and $\text{Li}_3\text{Fe}_5\text{O}_9$ reveals a significant elongation of the $\langle\text{Fe-O}\rangle$ bond associated to the FeO_4 coordination in $\text{Li}_3\text{Fe}_5\text{O}_9$, while the $\langle\text{Fe-O}\rangle$ bond associated to the FeO_6 coordination remains nearly unchanged. This elongation of the $\langle\text{Fe-O}\rangle$ bond in the FeO_4 coordination in $\text{Li}_3\text{Fe}_5\text{O}_9$ favours the presence of $\text{Fe}(\text{II})$, which supports this deviation.

(6). Oxidation of $\text{Fe}^{\text{III}}\text{O}_6$ in $\text{Li}_3\text{Fe}_5\text{O}_9$:

Characterization of delithiated $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ reveals that, on delithiation, Fe^{3+} in FeO_6 environment undergo oxidation to Fe^{4+} , while Fe^{3+} in FeO_4 environment remain unchanged (Chapter 9). This observation aligns well with the stabilization of $\text{Fe}(\text{IV})$ in an octahedral environment (electronic configuration: $t_{2g}^4e_g^2$), attributed to higher crystal field stabilization energy (CFSE), in contrast to $\text{Fe}(\text{IV})$ in a tetrahedral environment (electronic configuration: e^2t^2) with lower CFSE. Perovskite materials^{188–191} containing Fe^{4+} in FeO_6 environments are reported, which is consistent with this observed trend. Based on such observations, it can be concluded that structures containing Fe^{3+} in FeO_6 environments are more prone to oxidation to Fe^{4+} . Therefore, cathode materials containing FeO_6 will have a higher chance of utilizing $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox than materials containing FeO_4 .

(7). Comparison of electrochemical and chemical lithiation/delithiation:

Comparison of the extent of electrochemical and chemical lithiation/delithiation for the materials described in this thesis reveals both methods demonstrate a 0.5 $\text{Li}^+/\text{f.u.}$ insertion/extraction attributed to $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox. Conversely, a 0.5 $\text{Li}^+/\text{f.u.}$ extraction/insertion related to Fe-O redox is only observed via the chemical method, while the electrochemical process shows a 0.05 $\text{Li}^+/\text{f.u.}$ extraction in each cycle, indicating a gradual approach to the

extraction of 0.5 Li⁺ in ~10 cycles. Based on these observations, it can be concluded that, although substitution of iron by Al/Si/Ga/Ge cations in the LiFeO₂ and Li₃Fe₅O₉ structure allows chemically reversible lithium extraction and insertion, the electrochemical behaviour (specially the oxidation process) still suffers from the poor transport kinetics of these phases. The chemical delithiation through treatment with NO₂BF₄ and lithium re-insertion via treatment with LiI, requires approximately 7 days and 3 days respectively. Maintaining similar timescales during electrochemical cycling is implausible. Consequently, only $\sim \frac{1}{10}$ th of the lithium extraction is achieved in each cycle during the electrochemical cycling when compared to the extent of lithium extraction via chemical methods. This disparity between chemical and electrochemical delithiation aligns with the proposed hypothesis of poor transport characteristics inherent in these phases.

(8). Mechanism of the oxygen redox:

The participation of oxygen redox during the delithiation processes of LiFe_{0.5}Al_{0.5}O₂ and Li_{1.5}Fe_{0.5}Ge_{0.5}GaO₄, is supported by the characteristic RIXS signals corresponding to the excitons of $\pi_u \rightarrow \sigma_u^*$ during the emission process⁹⁴ (Chapters 5 and 8). However, the exact nature of the oxidized oxygen species generated upon delithiation, whether peroxide, superoxide, or molecular oxygen, remains uncertain. For systems like Sr₃Fe₂O₇⁵⁹, CaFeO₃^{60,61}, CaCu₃Fe₄O₁₂⁶², and Ca₂FeMnO₆⁶³, the concept of ligand hole is introduced to compensate for the oxidation of iron centre. A similar hypothesis can be proposed for the materials described in this thesis, with the oxidation process to be associated with the formation of metal-ligand hole as $d^5L \rightarrow d^5L^+ + e^-$.

Appendix -I

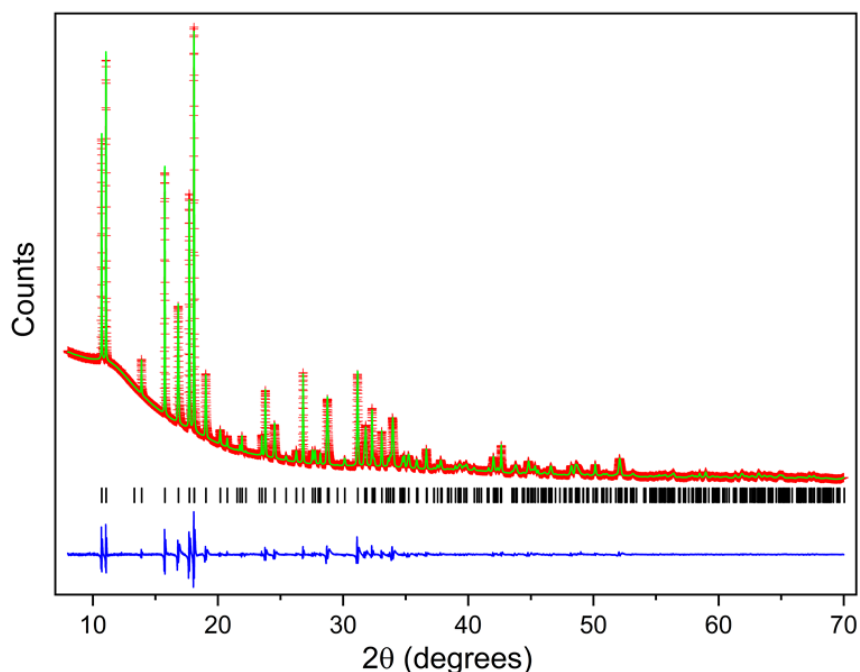


Figure 3a. 1. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data.

Table 3a.1. Parameters from the structural refinement of $\text{NaFe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data collected at room temperature

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4261(5)	0.1221(10)	0.4833(12)	1	1.01(6)
Fe/Al	$4a$	0.0662(2)	0.1263(4)	0	0.875/0.125	0.58(2)
O(1)	$4a$	0.0399(9)	0.0877(8)	0.3378(6)	1	1.4(1)
O(2)	$4a$	0.3818(7)	0.1621(7)	0.9234(7)	1	1.4(1)
$\text{NaFe}_{0.875}\text{Al}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.6485(1) \text{ \AA}$, $b = 7.1327(1) \text{ \AA}$, $c = 5.3688(1) \text{ \AA}$ volume = $216.30(1) \text{ \AA}^3$ Formula weight = $107.2251 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.75 \%$, $wR_p = 3.35 \%$, $R_{\text{Bragg}} = 1.015$						

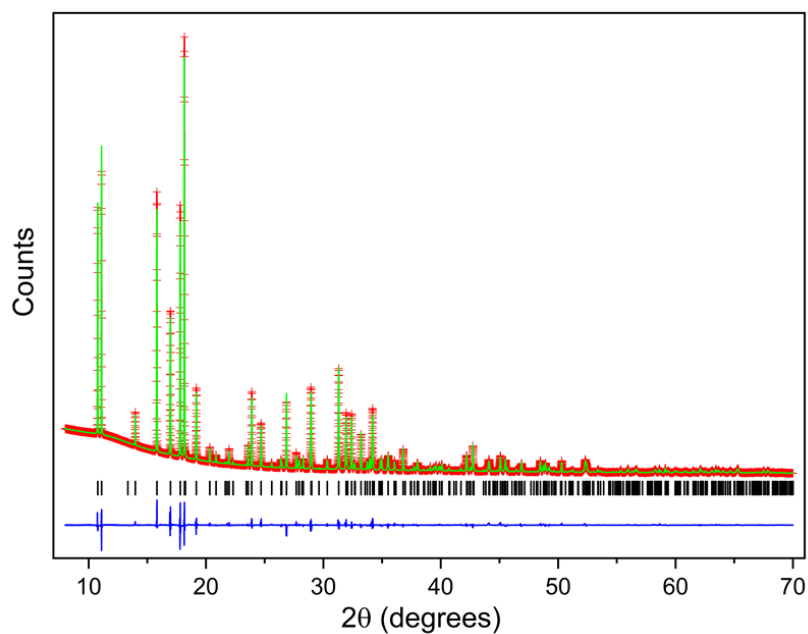


Figure 3a. 2. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.75}\text{Al}_{0.25}\text{O}_2$ against SXRD data

Table 3a.2. Parameters from the structural refinement of $\text{NaFe}_{0.75}\text{Al}_{0.25}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4282(1)	0.1233(2)	0.4834(4)	1	1.36(2)
Fe/Al	$4a$	0.0663(7)	0.1261(1)	0	0.75/0.25	0.52(1)
O(1)	$4a$	0.0441(3)	0.0789(2)	0.3391(2)	1	0.96(3)
O(2)	$4a$	0.3829(2)	0.1684(2)	0.9223(2)	1	0.96(3)
$\text{NaFe}_{0.75}\text{Al}_{0.25}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.6051(1) \text{ \AA}$, $b = 7.1216(1) \text{ \AA}$, $c = 5.3433(1) \text{ \AA}$ volume = $213.29(1) \text{ \AA}^3$ Formula weight = $103.6172 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.56 \%$, $wR_p = 2.91 \%$, $R_{\text{Bragg}} = 1.84$						

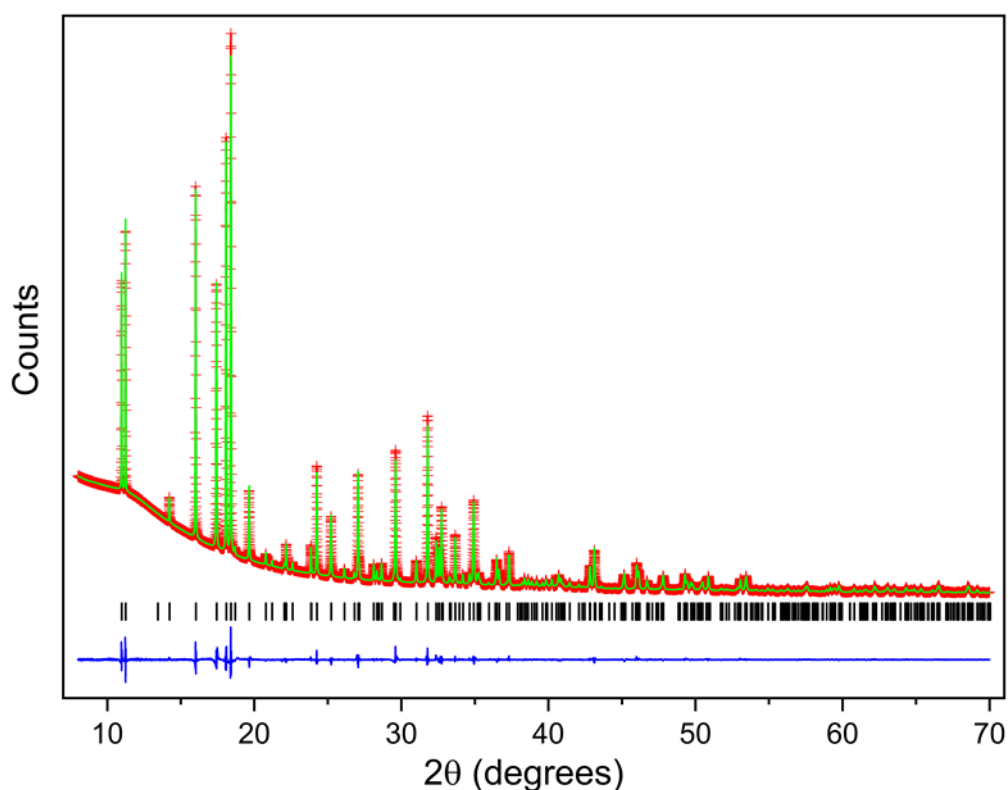


Figure 3a. 3. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.25}\text{Al}_{0.75}\text{O}_2$ against SXRD data.

Table 3a.3. Parameters from the structural refinement of $\text{NaFe}_{0.25}\text{Al}_{0.75}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4319(1)	0.1230(1)	0.4830(1)	1	1.15(2)
Fe/Al	$4a$	0.0622(1)	0.1256(1)	0	0.25/0.75	0.54(1)
O(1)	$4a$	0.0346(1)	0.0787(2)	0.3324(2)	1	0.82(3)
O(2)	$4a$	0.3778(2)	0.1726(2)	0.9303(2)	1	0.82(3)
$\text{NaFe}_{0.25}\text{Al}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4572(1) \text{ \AA}$, $b = 7.0677(1) \text{ \AA}$, $c = 5.2590(1) \text{ \AA}$ volume = $202.84(1) \text{ \AA}^3$ Formula weight = $89.1857 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.02 \%$, $wR_p = 1.48 \%$, $R_{\text{Bragg}} = 1.01$						

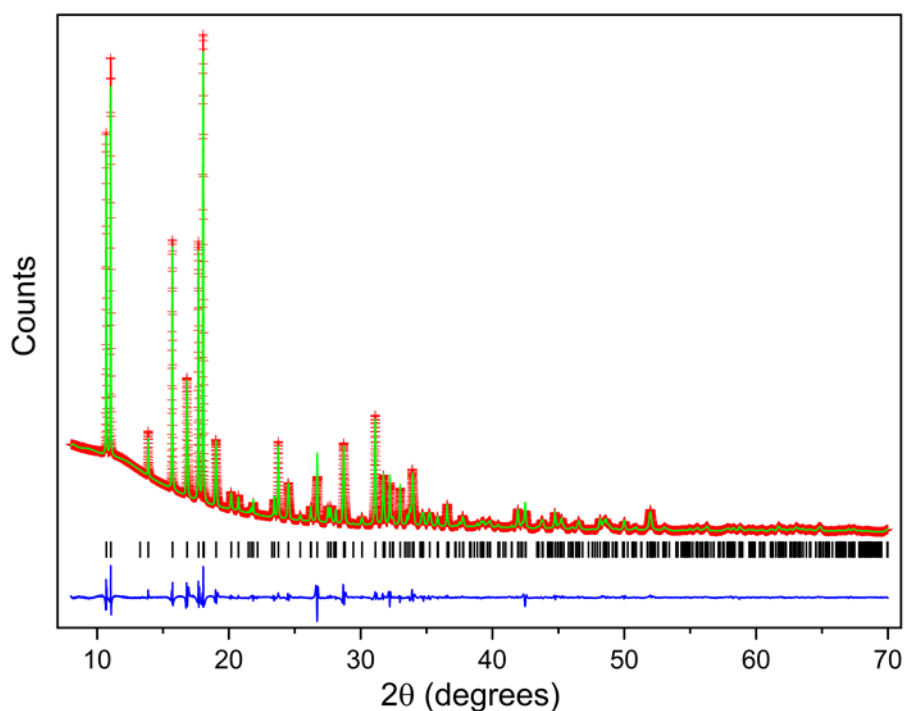


Figure 3a. 4. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ against SXRD data

Table 3a.4. Parameters from the structural refinement of $\text{NaFe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	4a	0.4277(3)	0.1184(5)	0.4865(9)	1	1.09(4)
Fe/Ga	4a	0.0674(1)	0.1248(2)	0	0.9/0.1	0.70(1)
O(1)	4a	0.0471(7)	0.0811(5)	0.3395(4)	1	1.05(6)
O(2)	4a	0.3852(5)	0.1688(5)	0.9198(5)	1	1.05(6)
$\text{NaFe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.6504(1) \text{ \AA}$, $b = 7.1615(1) \text{ \AA}$, $c = 5.3761(1) \text{ \AA}$ volume = $217.55(1) \text{ \AA}^3$ Formula weight = $112.2208 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.98 \%$, $wR_p = 3.33 \%$, $R_{\text{Bragg}} = 1.01$						

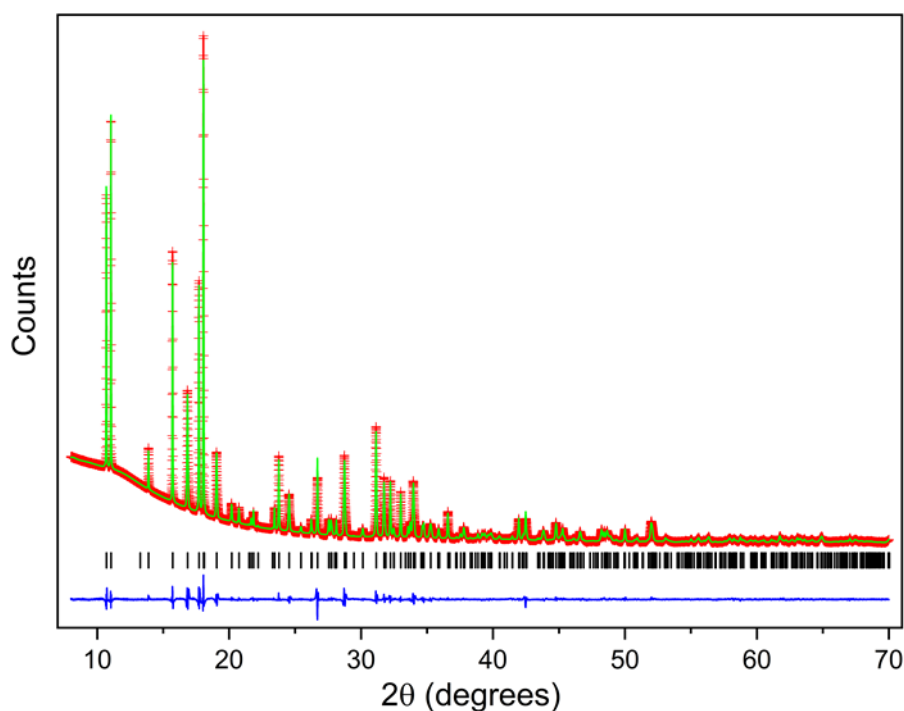


Figure 3a. 5. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ against SXRD data.

Table 3a.5. Parameters from the structural refinement of $\text{NaFe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4278(2)	0.1213(4)	0.4849(6)	1	0.91(3)
Fe/Ga	$4a$	0.0668(1)	0.1261(1)	0	0.8/0.2	0.40(1)
O(1)	$4a$	0.0452(5)	0.0846(5)	0.3404(3)	1	0.80(4)
O(2)	$4a$	0.3842(3)	0.1667(3)	0.9198(3)	1	0.80(4)
$\text{NaFe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.6431(1) \text{ \AA}$, $b = 7.1623(1) \text{ \AA}$, $c = 5.3682(1) \text{ \AA}$ volume = $216.97(1) \text{ \AA}^3$ Formula weight = $113.6086 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.39 \%$, $wR_p = 2.35 \%$, $R_{\text{Bragg}} = 1.01$						

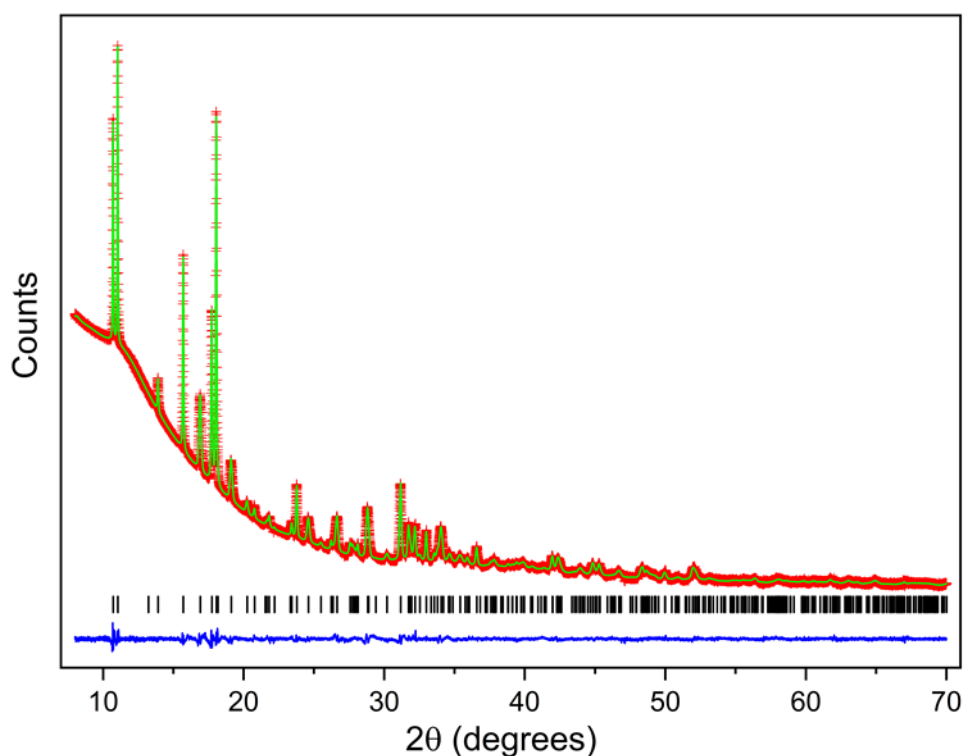


Figure 3a. 6. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ against SXRD data.

Table 3a.6. Parameters from the structural refinement of $\text{NaFe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ against SXRD data collected at room temperature

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4293(3)	0.1258(8)	0.4798(1)	1	0.48(5)
Fe/Ga	$4a$	0.0657(1)	0.1267(3)	0	0.7/0.3	0.58(1)
O(1)	$4a$	0.0413(6)	0.0845(6)	0.3337(4)	1	0.91(6)
O(2)	$4a$	0.3853(5)	0.1586(5)	0.9196(5)	1	0.91(6)
$\text{NaFe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.6221(1) \text{ \AA}$, $b = 7.1775(1) \text{ \AA}$, $c = 5.3616(1) \text{ \AA}$ volume = $216.36(1) \text{ \AA}^3$ Formula weight = $114.9964 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.02 \%$, $wR_p = 1.07 \%$, $R_{\text{Bragg}} = 1.01$						

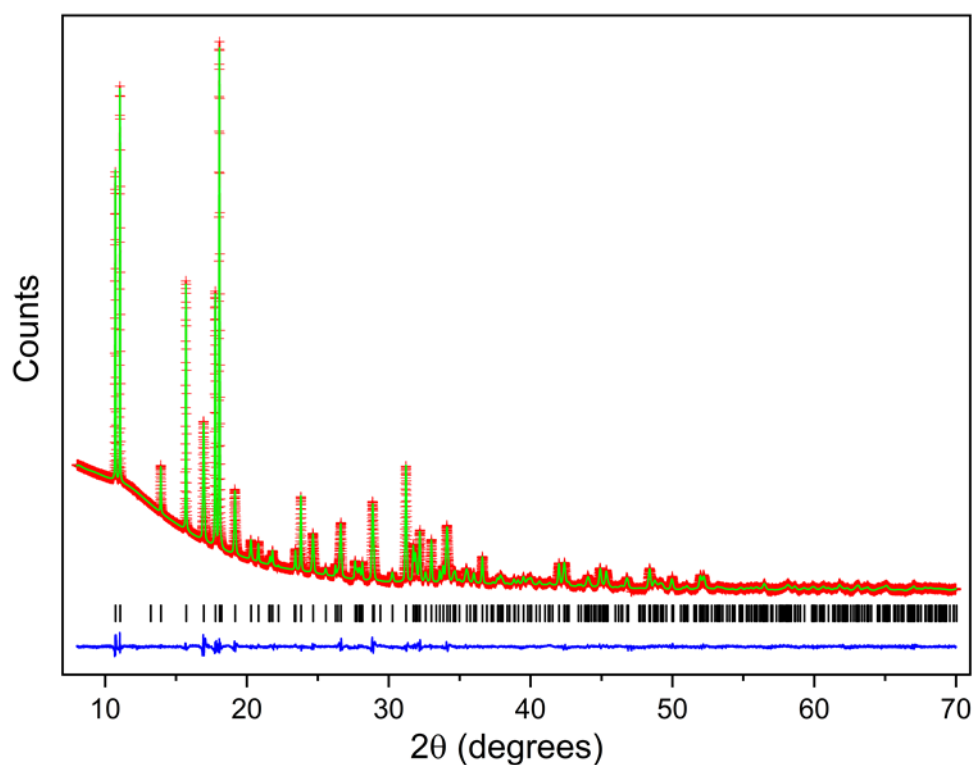


Figure 3a. 7. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ against SXRD data.

Table 3a.7. Parameters from the structural refinement of $\text{NaFe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4290(2)	0.1220(5)	0.4821(6)	1	0.78(3)
Fe/Ga	$4a$	0.0653(1)	0.1259(2)	0	0.6/0.4	0.47(1)
O(1)	$4a$	0.0361(4)	0.0861(4)	0.3398(3)	1	0.66(4)
O(2)	$4a$	0.3868(3)	0.1616(3)	0.9197(3)	1	0.66(4)
$\text{NaFe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.6067(1) \text{ \AA}$, $b = 7.1831(1) \text{ \AA}$, $c = 5.3502(1) \text{ \AA}$ volume = $215.47(1) \text{ \AA}^3$ Formula weight = $116.3842 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.06 \%$, $wR_p = 1.53 \%$, $R_{\text{Bragg}} = 1.02$						

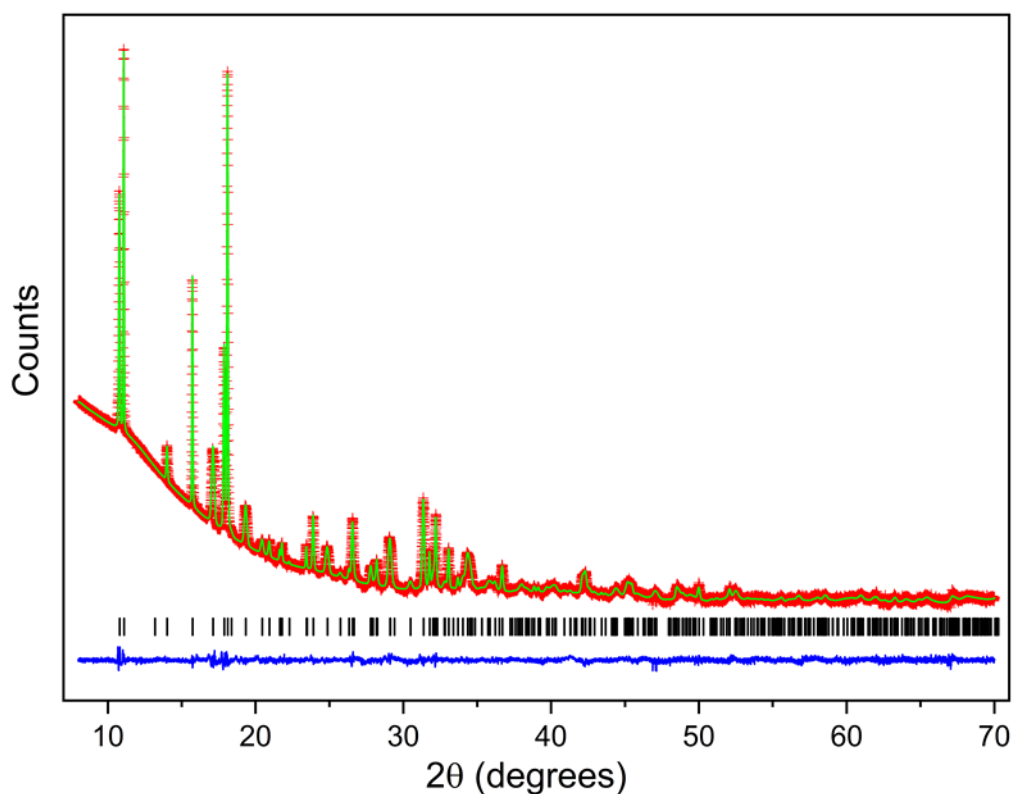


Figure 3a. 8. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data.

Table 3a.8. Parameters from the structural refinement of $\text{NaFe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	$4a$	0.4326(4)	0.1224(4)	0.4882(9)	1	0.68(5)
Fe/Ga	$4a$	0.0637(1)	0.1275(2)	0	0.25/0.75	0.31(1)
O(1)	$4a$	0.0384(7)	0.0846(6)	0.3381(5)	1	0.28(7)
O(2)	$4a$	0.3845(6)	0.1609(5)	0.9204(6)	1	0.28(7)
$\text{NaFe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.5518(1) \text{ \AA}$, $b = 7.1976(1) \text{ \AA}$, $c = 5.3205(1) \text{ \AA}$ volume = $212.61(1) \text{ \AA}^3$ Formula weight = $121.2415 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.025 \%$, $wR_p = 1.41 \%$, $R_{\text{Bragg}} = 1.02$						

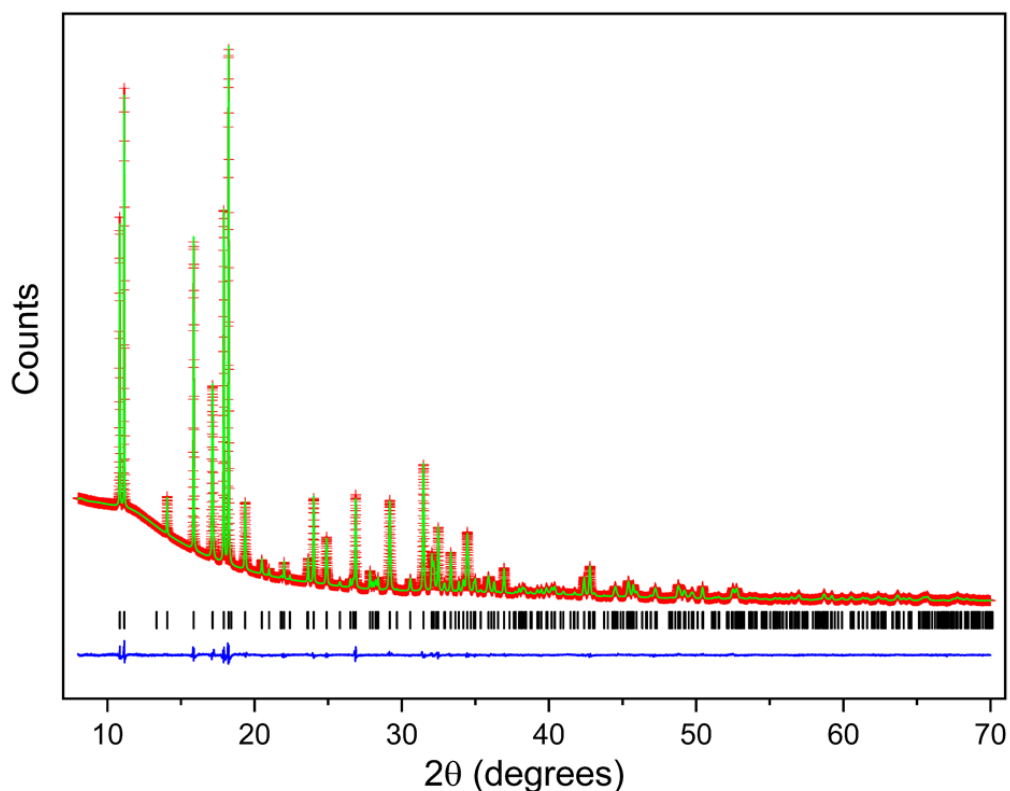


Figure 3a. 9. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data.

Table 3a.9. Parameters from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	4a	0.4299(1)	0.1233(2)	0.4841(3)	1	1.21(2)
Fe/Al/Ga	4a	0.0640(1)	0.1263(1)	0	0.5/0.375/0.125	0.63(1)
O(1)	4a	0.0361(2)	0.0836(2)	0.3374(2)	1	0.82(2)
O(2)	4a	0.3822(2)	0.1690(1)	0.9268(2)	1	0.82(2)
$\text{NaFe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.5474(1) \text{ \AA}$, $b = 7.1189(1) \text{ \AA}$, $c = 5.3118(1) \text{ \AA}$ volume = $209.773(3) \text{ \AA}^3$ Formula weight = $101.7452 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.83 \%$, $wR_p = 1.25 \%$, $R_{\text{Bragg}} = 0.41$						

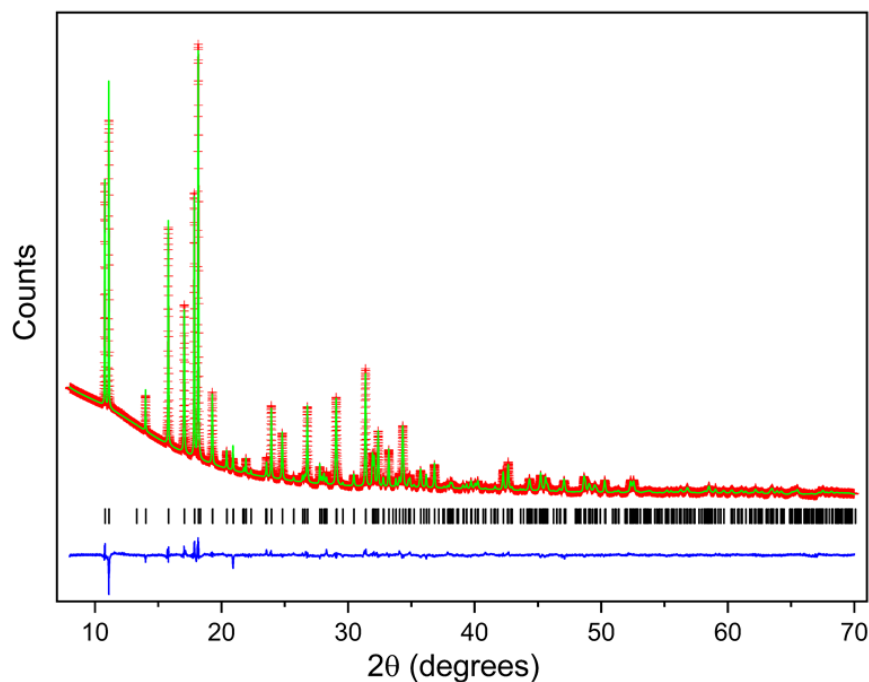


Figure 3a. 10. Observed, calculated and difference plots from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXRD data.

Table 3a.10. Parameters from the structural refinement of $\text{NaFe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Na	4a	0.4253(2)	0.1220(5)	0.5126(1)	1	0.33(3)
Fe/Al/Ga	4a	0.0635(1)	0.1236(2)	0	0.5/0.25/0.25	0.50(1)
O(1)	4a	0.0424(5)	0.0902(5)	0.6531(4)	1	2.57(5)
O(2)	4a	0.3839(4)	0.1601(4)	0.9368(5)	1	2.57(5)
$\text{NaFe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.5694(1) \text{ \AA}$, $b = 7.1370(1) \text{ \AA}$, $c = 5.3236(1) \text{ \AA}$ volume = $211.610(3) \text{ \AA}^3$ Formula weight = $107.0875 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.32 \%$, $wR_p = 2.01 \%$, $R_{\text{Bragg}} = 1.70$						

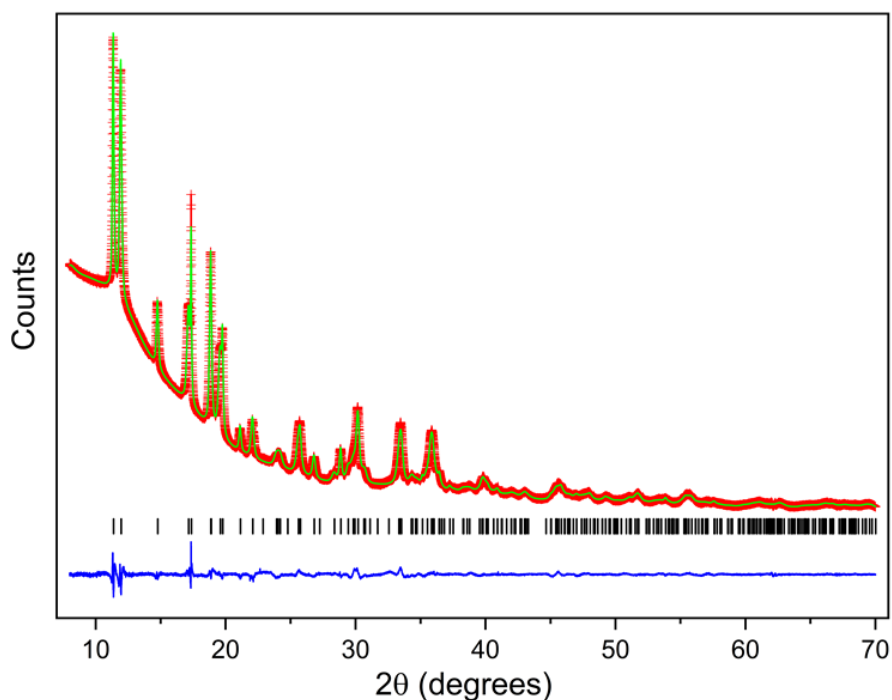


Figure 3a. 11. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data.

Table 3a.11. Parameters from the structural refinement of $\text{LiFe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.4240	0.1211	0.4820	1	0.5
Fe/Al	$4a$	0.0853(1)	0.1259(1)	0	0.875/0.125	0.36(1)
O(1)	$4a$	0.0740(3)	0.1317(5)	0.3733(2)	1	0.56(1)
O(2)	$4a$	0.4260(4)	0.1468(5)	0.8951(2)	1	0.56(1)
$\text{LiFe}_{0.875}\text{Al}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4679(1) \text{ \AA}$, $b = 6.3937(1) \text{ \AA}$, $c = 5.0306(1) \text{ \AA}$ volume = $175.87(1) \text{ \AA}^3$ Formula weight = 91.1751 mol^{-1} , $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.52 \%$, $wR_p = 2.32 \%$, $R_{\text{Bragg}} = 1.01$						

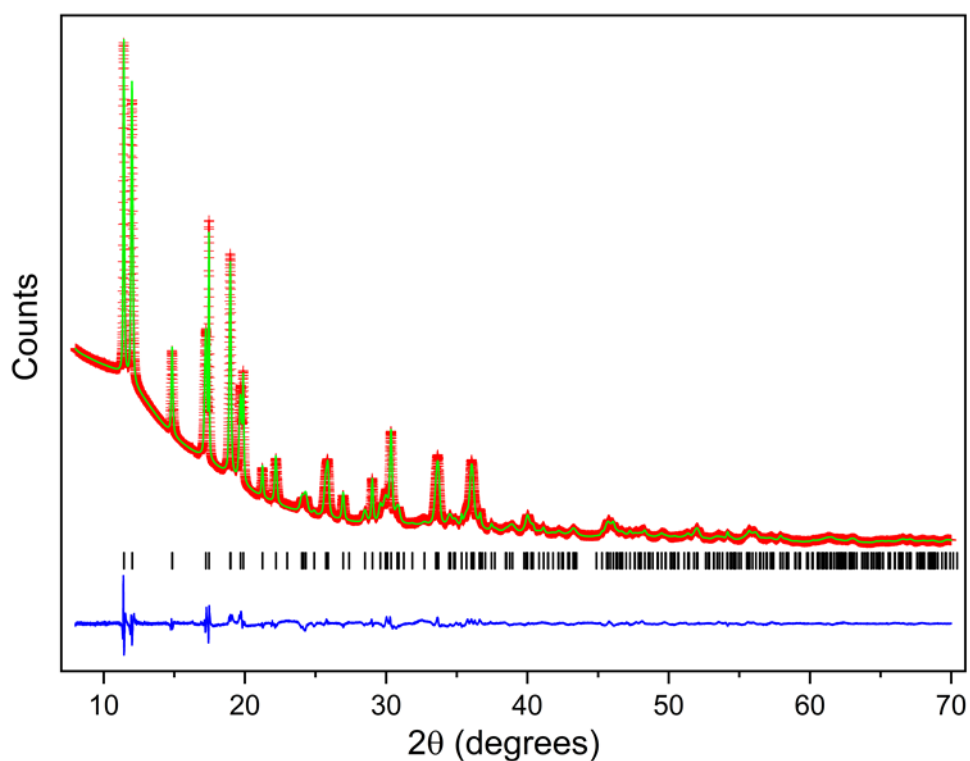


Figure 3a.12. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.75}\text{Al}_{0.25}\text{O}_2$ against SXRD data.

Table 3a.12. Parameters from the structural refinement of $\text{LiFe}_{0.75}\text{Al}_{0.25}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.4240	0.1211	0.4820	1	0.5
Fe/Al	$4a$	0.0849(1)	0.1312(1)	0	0.75/0.25	0.49(1)
O(1)	$4a$	0.0694(3)	0.1003(5)	0.3774(2)	1	0.59(1)
O(2)	$4a$	0.4253(4)	0.1211(4)	0.9001(2)	1	0.59(1)
$\text{LiFe}_{0.75}\text{Al}_{0.25}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4481(1) \text{ \AA}$, $b = 6.4004(1) \text{ \AA}$, $c = 5.0211(1) \text{ \AA}$ volume = $175.09(1) \text{ \AA}^3$ Formula weight = $87.5672 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.39 \%$, $wR_p = 2.03 \%$, $R_{\text{Bragg}} = 1.06$						

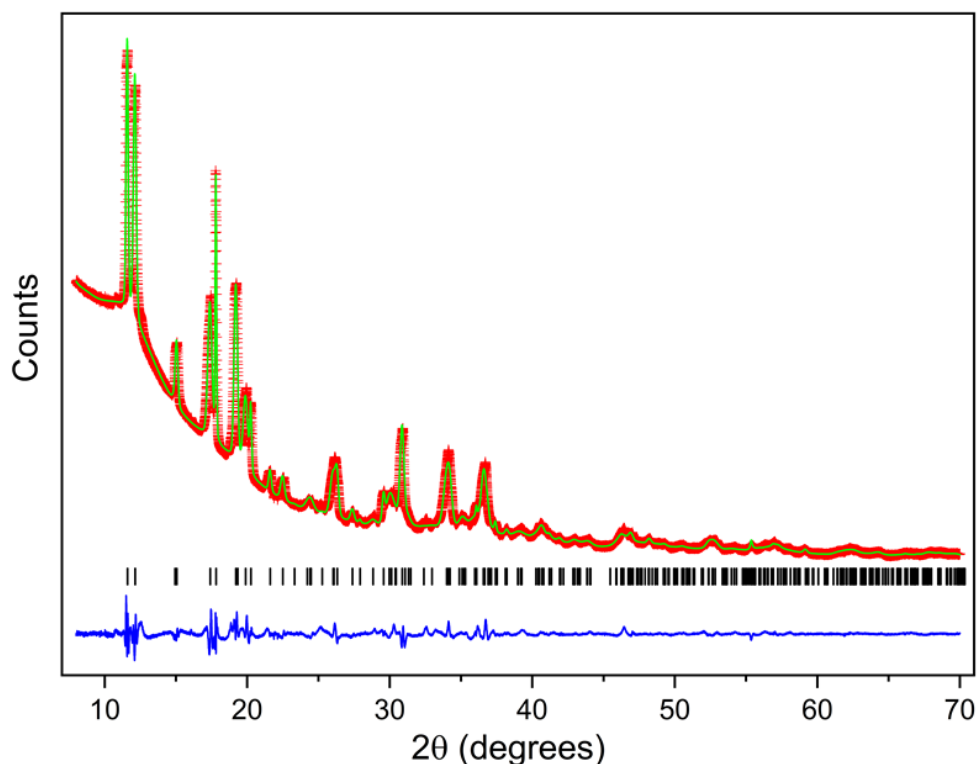


Figure 3a. 13. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.25}\text{Al}_{0.75}\text{O}_2$ against SXRD data.

Table SX. Parameters from the structural refinement of $\text{LiFe}_{0.25}\text{Al}_{0.75}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.4240	0.1211	0.4820	1	0.5
Fe/Al	$4a$	0.0775(1)	0.1261(1)	0	0.25/0.75	1.24(3)
O(1)	$4a$	0.0642(5)	0.0925(5)	0.3701(3)	1	0.87(1)
O(2)	$4a$	0.4044(6)	0.1231(5)	0.9004(2)	1	0.87(1)
$\text{LiFe}_{0.25}\text{Al}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.3387(2) \text{ \AA}$, $b = 6.3643(3) \text{ \AA}$, $c = 4.9568(2) \text{ \AA}$ volume = $168.42(1) \text{ \AA}^3$ Formula weight = $73.1357 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.48 \%$, $wR_p = 2.18 \%$, $R_{\text{Bragg}} = 1.03$						

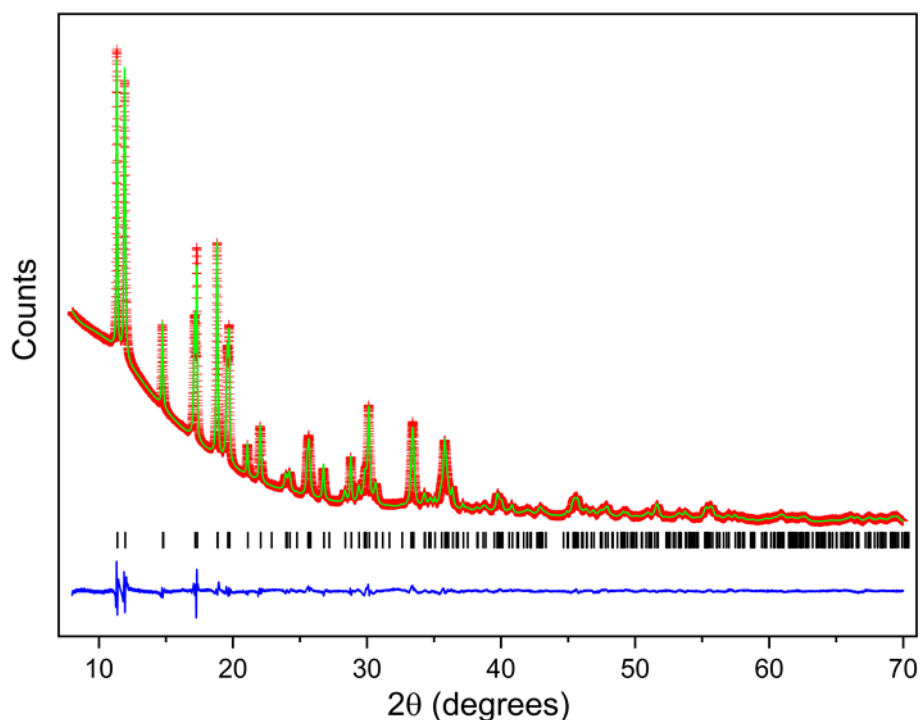


Figure 3a. 14. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ against SXRD data.

Table 3a.14. Parameters from the structural refinement of $\text{LiFe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.422(1)	0.144(1)	0.509(3)	1	1.09(4)
Fe/Ga	$4a$	0.0843(1)	0.1281(1)	0	0.9/0.1	0.68(1)
O(1)	$4a$	0.0715(4)	0.1029(7)	0.3757(3)	1	0.83(6)
O(2)	$4a$	0.4254(1)	0.1206(6)	0.8897(3)	1	0.83(6)
$\text{LiFe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4874(1) \text{ \AA}$, $b = 6.4135(1) \text{ \AA}$, $c = 5.0521(1) \text{ \AA}$ volume = $177.80(1) \text{ \AA}^3$ Formula weight = $96.1708 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.12 \%$, $wR_p = 1.56 \%$, $R_{\text{Bragg}} = 1.01$						

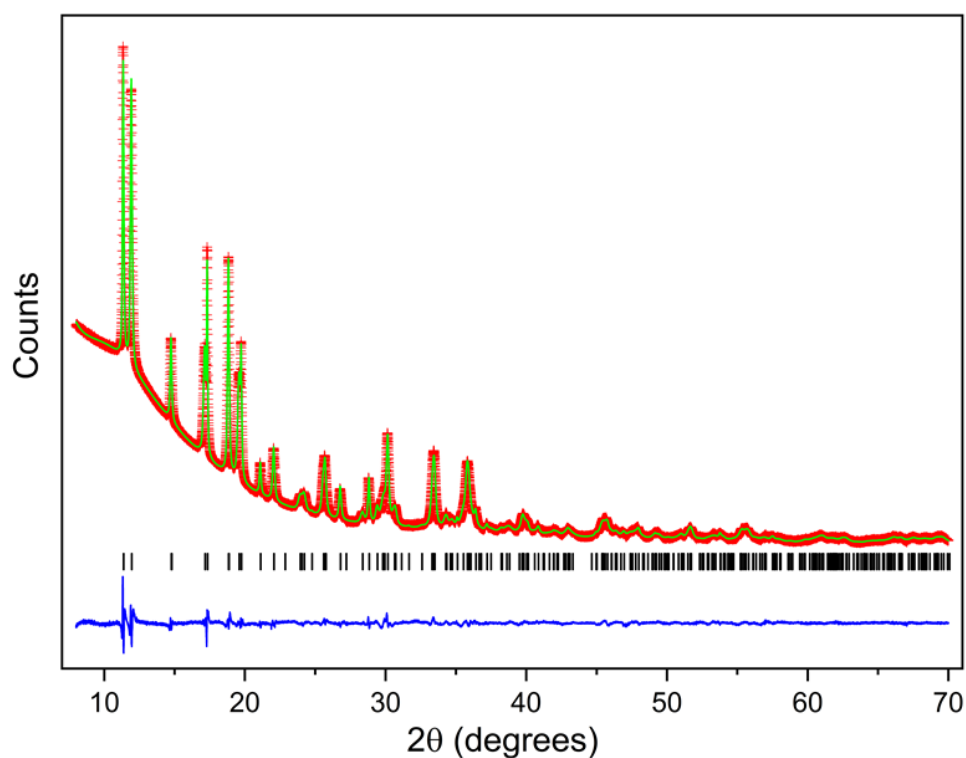


Figure 3a. 15. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ against SXRD data.

Table 3a.15. Parameters from the structural refinement of $\text{LiFe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.422(1)	0.144(1)	0.509(3)	1	1.09(4)
Fe/Ga	$4a$	0.0845(1)	0.1278(1)	0	0.8/0.2	0.53(1)
O(1)	$4a$	0.0658(4)	0.0983(7)	0.3762(3)	1	0.87(6)
O(2)	$4a$	0.4294(1)	0.1182(6)	0.8919 (3)	1	0.87(6)
$\text{LiFe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4836(1) \text{ \AA}$, $b = 6.4205(1) \text{ \AA}$, $c = 5.0501(1) \text{ \AA}$ volume = $177.80(1) \text{ \AA}^3$ Formula weight = $97.5586 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.12 \%$, $wR_p = 1.56 \%$, $R_{\text{Bragg}} = 1.01$						

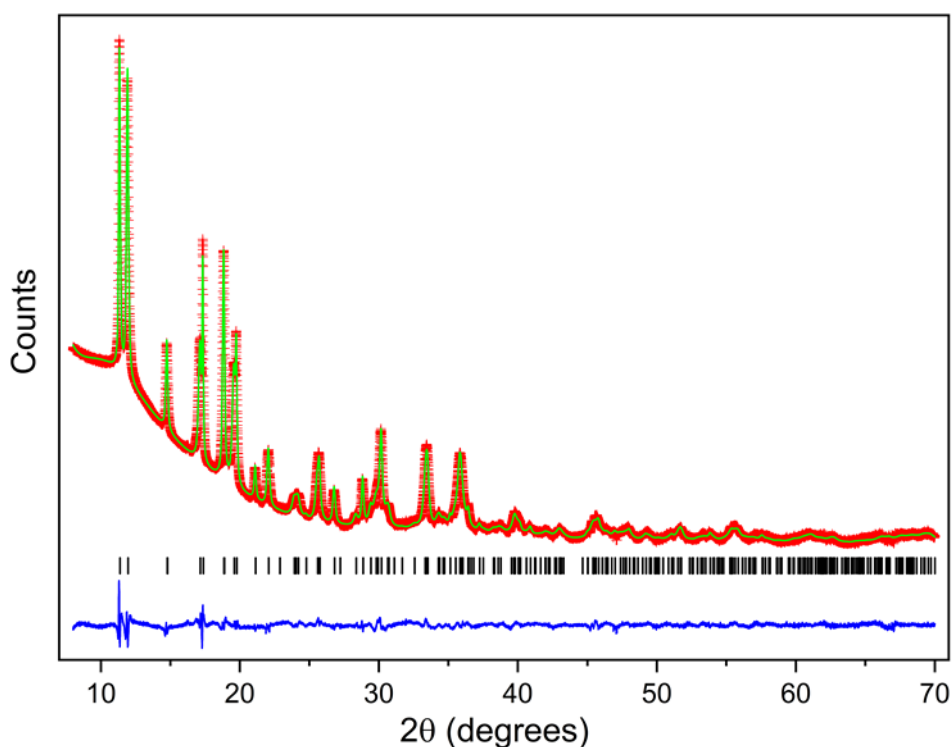


Figure 3a. 16. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ against SXRD data.

Table 3a.16. Parameters from the structural refinement of $\text{LiFe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.422(1)	0.144(1)	0.509(3)	1	1.09(4)
Fe/Ga	$4a$	0.0840(1)	0.1286(1)	0	0.7/0.3	0.28(1)
O(1)	$4a$	0.0668(6)	0.0927(7)	0.3771(3)	1	0.67(6)
O(2)	$4a$	0.4266(7)	0.1104(6)	0.8894(3)	1	0.67(6)
$\text{LiFe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4772(2) \text{ \AA}$, $b = 6.4253(2) \text{ \AA}$, $c = 5.0472(2) \text{ \AA}$ volume = $177.63(1) \text{ \AA}^3$ Formula weight = $98.9464 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.38 \%$, $wR_p = 1.83 \%$, $R_{\text{Bragg}} = 1.01$						

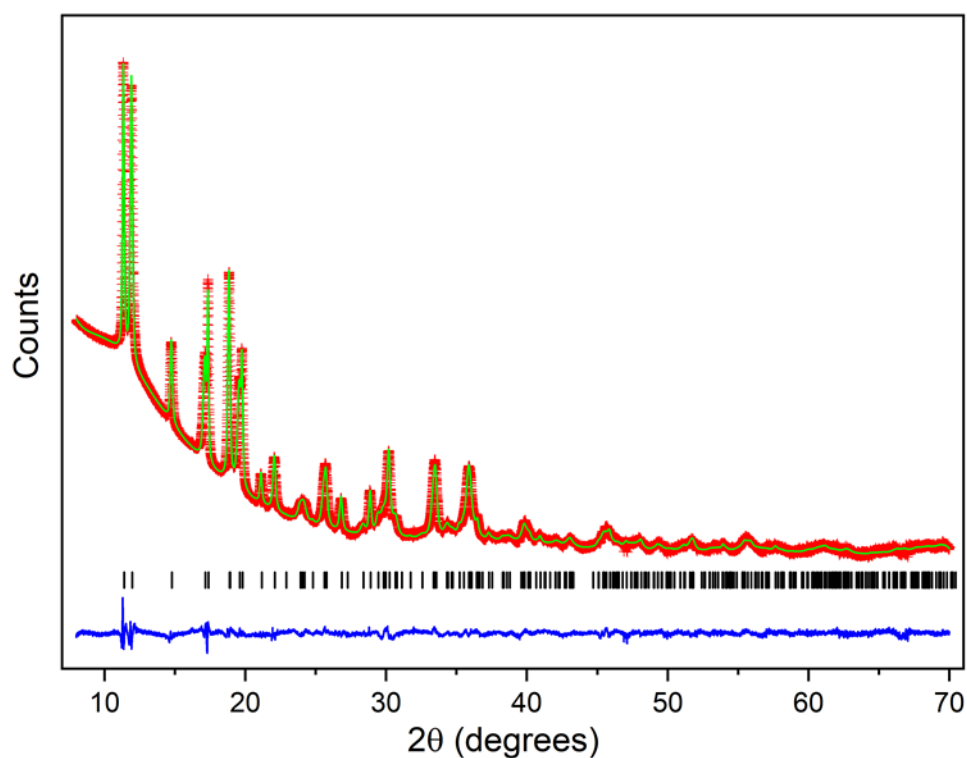


Figure 3a. 17. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ against SXRD data.

Table 3a.17. Parameters from the structural refinement of $\text{LiFe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.422(1)	0.144(1)	0.509(3)	1	1.09(4)
Fe/Ga	$4a$	0.0846(1)	0.1288(1)	0	0.6/0.4	0.34(1)
O(1)	$4a$	0.0631(6)	0.0917(8)	0.3787(3)	1	0.48(6)
O(2)	$4a$	0.4303(7)	0.1111(6)	0.8892(3)	1	0.48(6)
$\text{LiFe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4685(2) \text{ \AA}$, $b = 6.4259(3) \text{ \AA}$, $c = 5.0431(2) \text{ \AA}$ volume = $177.21(1) \text{ \AA}^3$ Formula weight = $100.3342 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.18 \%$, $wR_p = 1.58 \%$, $R_{\text{Bragg}} = 1.01$						

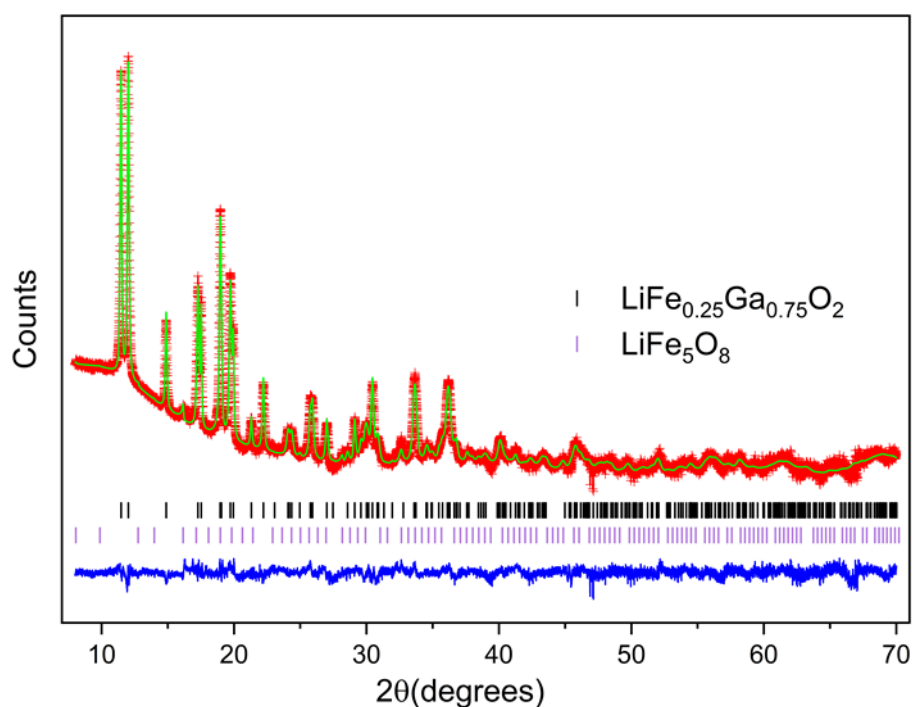


Figure 3a. 18. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data.

Table 3a.18. Parameters from the structural refinement of $\text{LiFe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.422(1)	0.144(1)	0.509(3)	1	1.09(4)
Fe/Ga	$4a$	0.0804(2)	0.1304(1)	0	0.25/0.75	0.34(1)
O(1)	$4a$	0.0707(10)	0.0976(13)	0.3786(6)	1	0.47(6)
O(2)	$4a$	0.3847(9)	0.1121(9)	0.8850(7)	1	0.47(6)
$\text{LiFe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4298(1) \text{ \AA}$, $b = 6.3886(1) \text{ \AA}$, $c = 5.0220(1) \text{ \AA}$ volume = $174.21(1) \text{ \AA}^3$ Formula weight = $105.1915 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K NB – contains 2.25 weight percent LiFe_5O_8 $R_p = 1.65 \%$, $wR_p = 2.21 \%$, $R_{\text{Bragg}} = 1.01$						

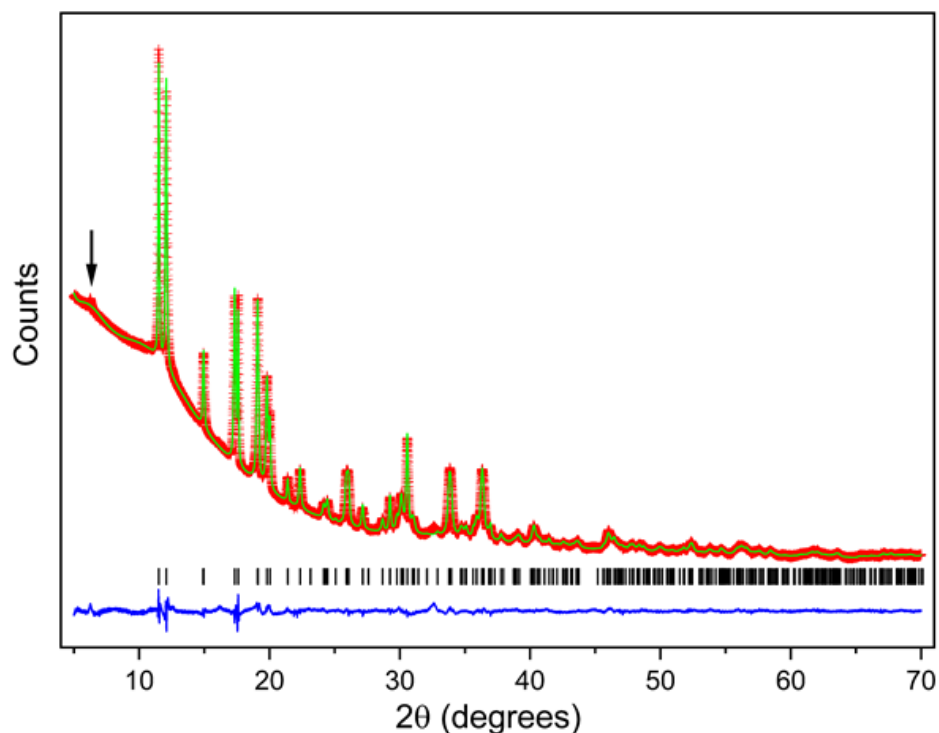


Figure 3a. 19. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data. Black arrow indicates unidentified impurity

Table 3a.19. Parameters from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.4228(11)	0.1554(11)	0.4913(49)	1	0.22(14)
Fe/Al/Ga	4a	0.0831(1)	0.1298(1)	0	0.5/0.375/0.125	0.29(1)
O(1)	4a	0.0684(5)	0.1019(7)	0.3747(5)	1	1.53(4)
O(2)	4a	0.4123(5)	0.1284(7)	0.8980(5)	1	1.53(4)
$\text{LiFe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4049(1) \text{ \AA}$, $b = 6.3661(1) \text{ \AA}$, $c = 4.9868(1) \text{ \AA}$ volume = $171.593(10) \text{ \AA}^3$ Formula weight = $85.6962 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.01 \%$, $wR_p = 1.48 \%$, $R_{\text{Bragg}} = 0.72$						

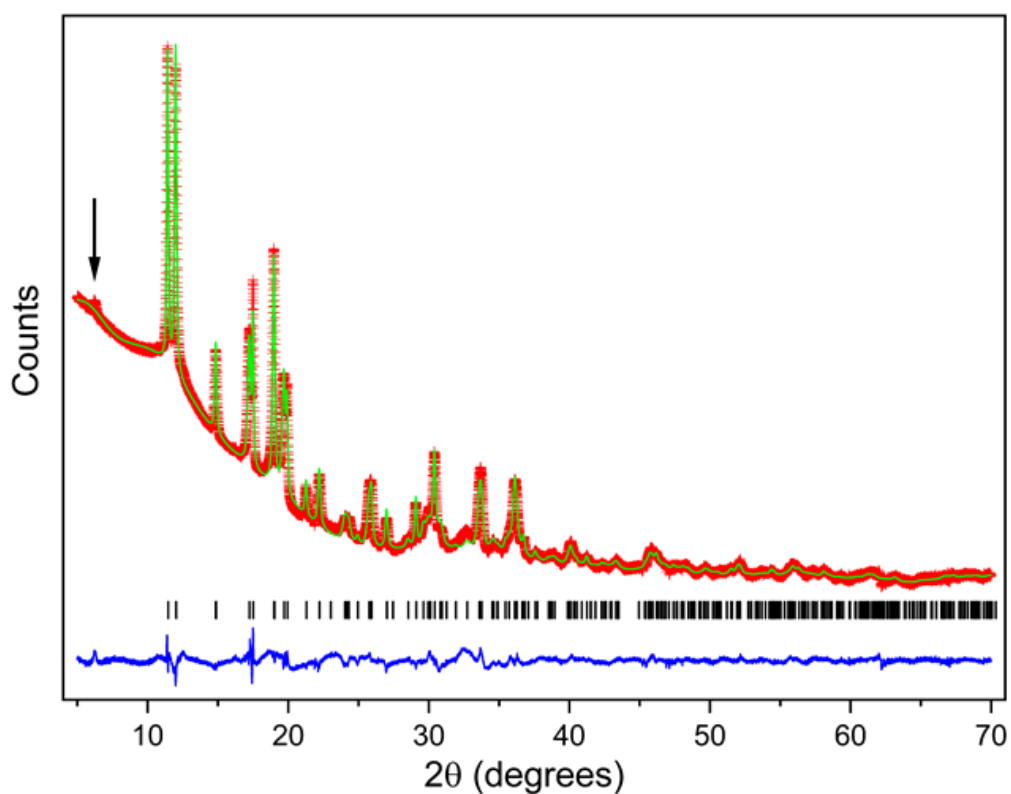


Figure 3a. 20. Observed, calculated and difference plots from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXRD data. Black arrow indicates unidentified impurity

Table 3a.20. Parameters from the structural refinement of $\text{LiFe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.4702(17)	0.1840(16)	0.5085(80)	1	0.1
Fe/Al/Ga	4a	0.0790(2)	0.1343(2)	0	0.5/0.125/0.375	0.69(2)
O(1)	4a	0.0855(8)	0.0961(9)	0.3794(7)	1	0.1
O(2)	4a	0.4018(8)	0.1058(8)	0.8962(7)	1	0.1
$\text{LiFe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4309(2) \text{ \AA}$, $b = 6.3980(3) \text{ \AA}$, $c = 5.0132(2) \text{ \AA}$ volume = $174.198(15) \text{ \AA}^3$ Formula weight = $96.381 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.58 \%$, $wR_p = 2.20 \%$, $R_{\text{Bragg}} = 1.19$						

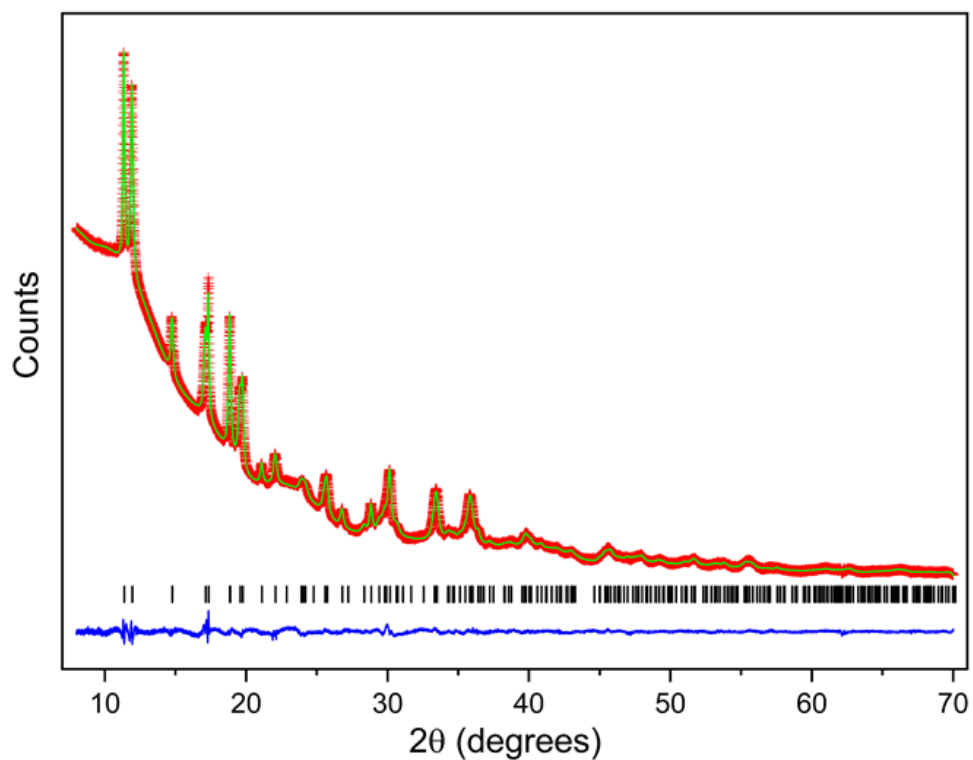


Figure 4a. 1. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data

Table 4a.1. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.4318(16)	0.1307(80)	0.5018(15)	1	0.1
Fe/Al	$4a$	0.0832(1)	0.1263(7)	0	0.875/0.125	0.37(1)
O(1)	$4a$	0.0694(7)	0.1199(27)	0.3649(12)	1	0.1
O(2)	$4a$	0.4244(8)	0.1322(25)	0.8936(13)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4804(3) \text{ \AA}$, $b = 6.4295(3) \text{ \AA}$, $c = 5.0483(3) \text{ \AA}$ volume = $177.886(15) \text{ \AA}^3$ Formula weight = $96.381 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.76 \%$, $wR_p = 1.03 \%$, $R_{\text{Bragg}} = 0.41$						

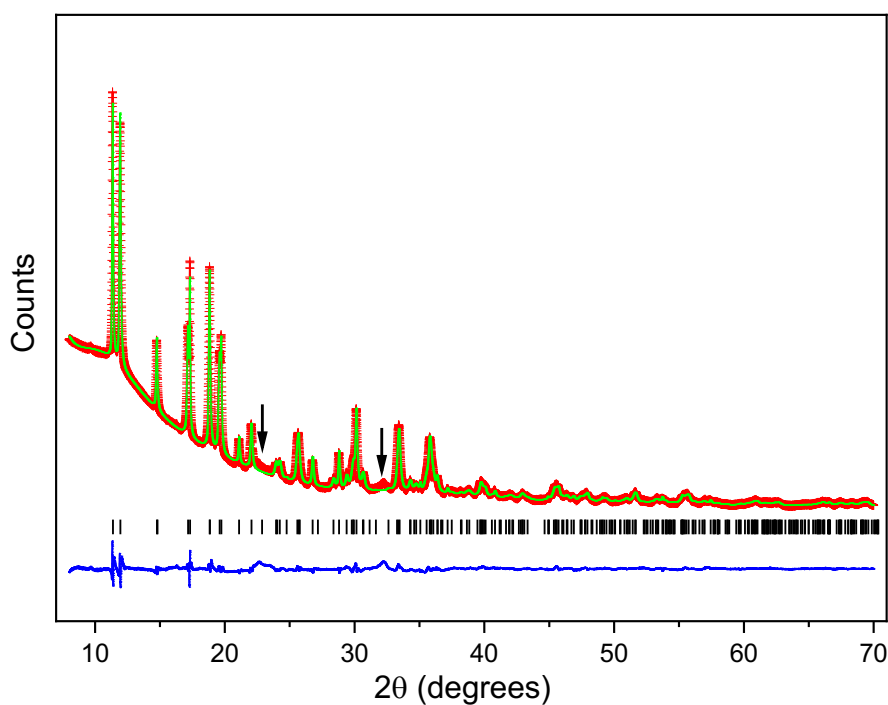


Figure 4a. 2. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ against SXRD data

Table 4a.2. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.418(1)	0.141(2)	0.500(18)	1	0.1
Fe/Ga	4a	0.0849(1)	0.1283(2)	0	0.9/0.1	0.42(1)
O(1)	4a	0.0685(7)	0.1008(9)	0.3779(14)	1	0.1
O(2)	4a	0.4279(7)	0.1157(9)	0.8905(15)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.9}\text{Ga}_{0.1}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4901(2) \text{ \AA}$, $b = 6.4147(2) \text{ \AA}$, $c = 5.0547(1) \text{ \AA}$ volume = $178.019(11) \text{ \AA}^3$ Formula weight = $96.174 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.48 \%$, $wR_p = 2.18 \%$, $R_{\text{Bragg}} = 0.74$						

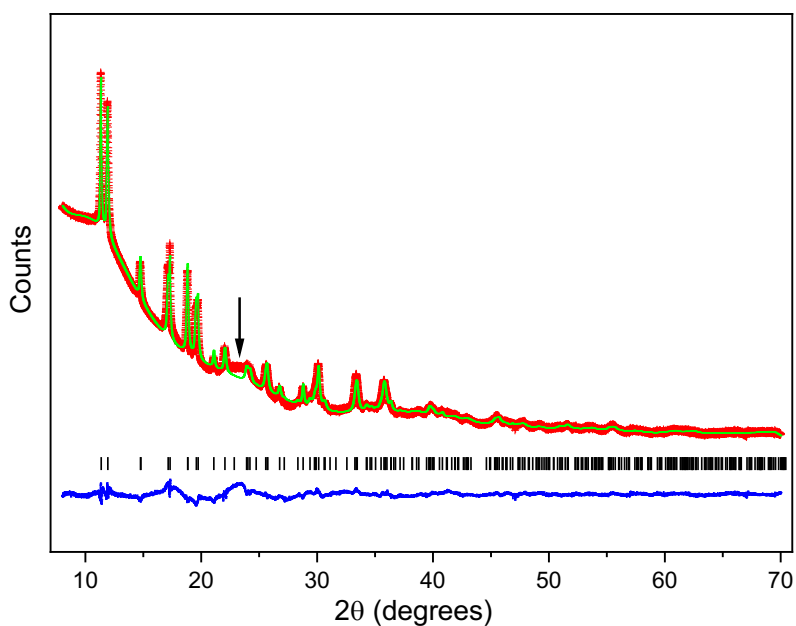


Figure 4a. 3. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ against SXRD data, arrow indicates broad intensity feature associated with metallic iron

Table 4a.3. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.413(3)	0.179(3)	0.519(7)	1	0.1
Fe/Ga	4a	0.0754(3)	0.1302(3)	0	0.8/0.2	0.82(4)
O(1)	4a	0.0687(18)	0.1349(29)	0.3723(10)	1	0.1
O(2)	4a	0.4054(18)	0.1151(29)	0.8956(11)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.8}\text{Ga}_{0.2}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4921(7) \text{ \AA}$, $b = 6.4244(8) \text{ \AA}$, $c = 5.0556(7) \text{ \AA}$ volume = $178.385(42) \text{ \AA}^3$ Formula weight = $97.5615 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.59 \%$, $wR_p = 2.22 \%$, $R_{\text{Bragg}} = 1.48$						

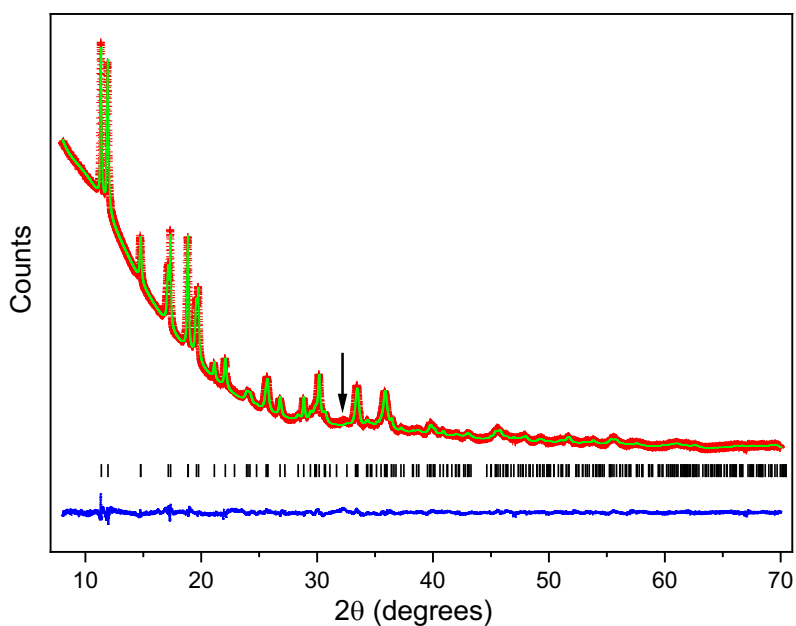


Figure 4a. 4. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ against SXRD data

Table 4a.4. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.426(2)	0.159(2)	0.501(2)	1	0.1
Fe/Ga	4a	0.0841(1)	0.1309(2)	0	0.7/0.3	0.32(1)
O(1)	4a	0.0671(9)	0.0962(9)	0.3785(15)	1	0.1
O(2)	4a	0.4257(9)	0.1105(8)	0.8886(15)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4804(2) \text{ \AA}$, $b = 6.4267(3) \text{ \AA}$, $c = 5.0489(2) \text{ \AA}$ volume = $177.829(13) \text{ \AA}^3$ Formula weight = $98.9487 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.82 \%$, $wR_p = 1.09 \%$, $R_{\text{Bragg}} = 0.42$						

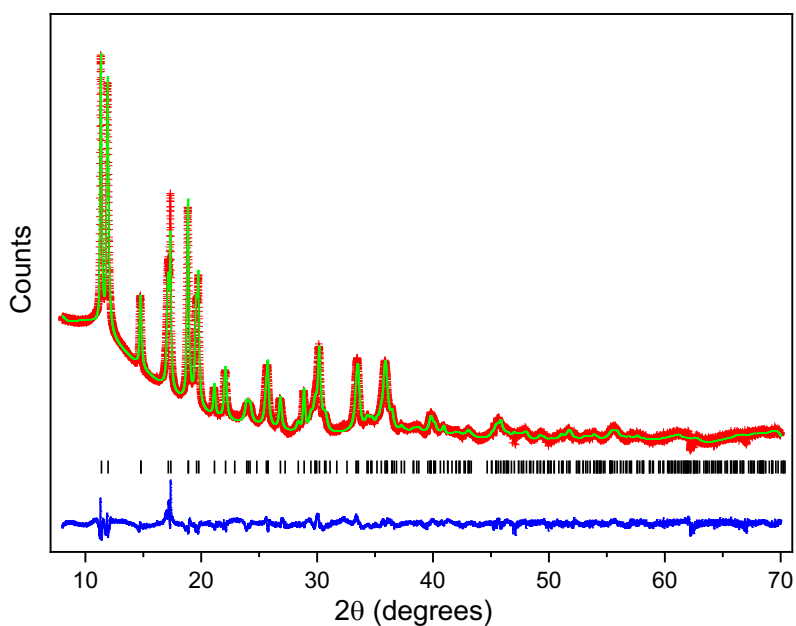


Figure 4a. 5. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ against SXRD data

Table 4a.5. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.421(2)	0.131(9)	0.503(23)	1	0.1
Fe/Ga	4a	0.0820(2)	0.1282(8)	0	0.6/0.4	0.69(2)
O(1)	4a	0.0666(9)	0.1194(40)	0.3829(17)	1	0.1
O(2)	4a	0.4299(10)	0.1221(41)	0.8898(19)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4746(3) \text{ \AA}$, $b = 6.4254(4) \text{ \AA}$, $c = 5.0422(3) \text{ \AA}$ volume = $177.372(22) \text{ \AA}^3$ Formula weight = $100.336 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.67\%$, $wR_p = 2.25 \%$, $R_{\text{Bragg}} = 1.15$						

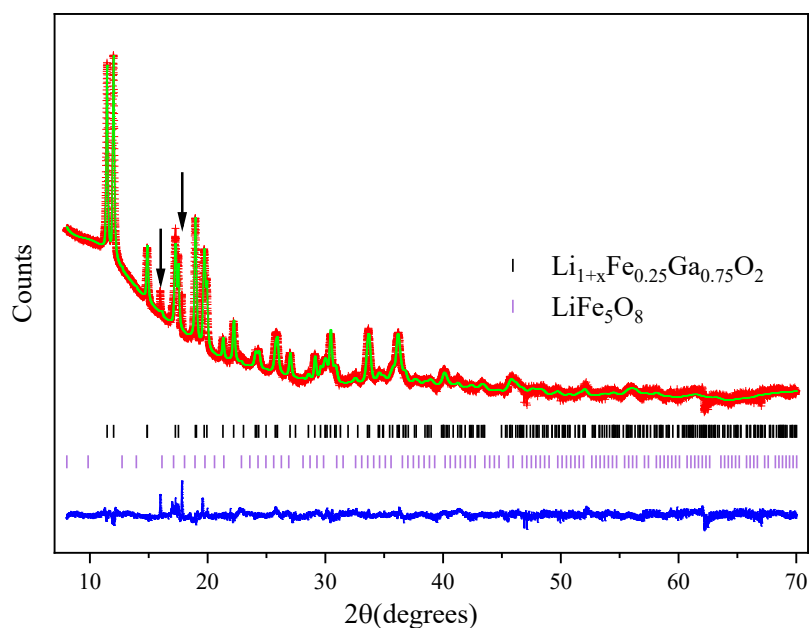


Figure 4a. 6. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data

Table 4a.6. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.463(2)	0.137(6)	0.532(4)	1	0.1
Fe/Ga	4a	0.0811(2)	0.1277(3)	0	0.25/0.75	0.1
O(1)	4a	0.0799(14)	0.01043(22)	0.3712(8)	1	0.1
O(2)	4a	0.4032(16)	0.1243(22)	0.8803(8)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4288(2) \text{ \AA}$, $b = 6.3916(4) \text{ \AA}$, $c = 5.0198(3) \text{ \AA}$ volume = $174.184(18) \text{ \AA}^3$ Formula weight = $105.1915 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K 7.78% LiFe_5O_8 impurity $R_p = 1.37\%$, $wR_p = 1.97\%$, $R_{\text{Bragg}} = 0.85$						

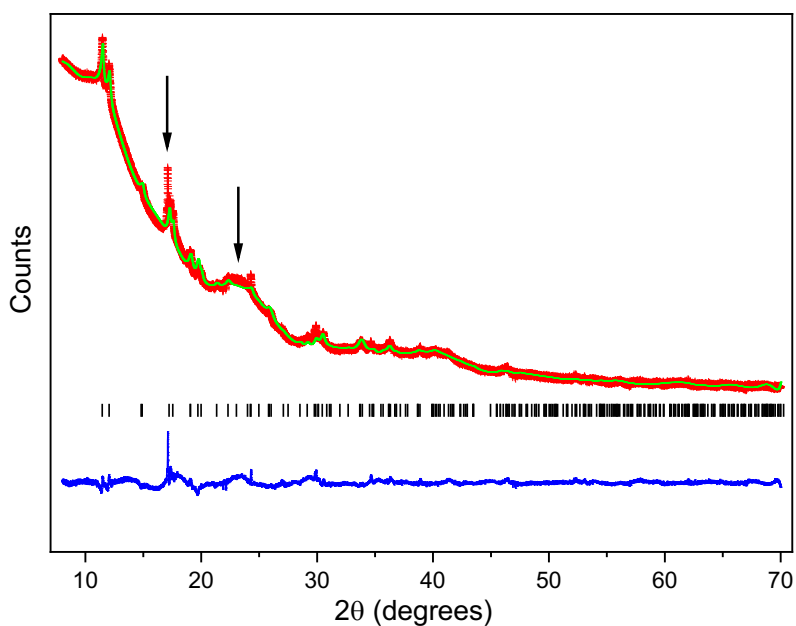


Figure 4a. 7. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data

Table 4a.7. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.435(9)	0.165(5)	0.684(9)	1	0.1
Fe/Ga	4a	0.0735(11)	0.1114(8)	0	0.5/0.375/0.125	0.94(17)
O(1)	4a	0.0845(29)	0.1307(39)	0.3795(18)	1	0.1
O(2)	4a	0.4283(32)	0.1167(30)	0.9367(21)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4255(12) \text{ \AA}$, $b = 6.4218(15) \text{ \AA}$, $c = 4.9934(15) \text{ \AA}$ volume = $173.983(78) \text{ \AA}^3$ Formula weight = $85.69625 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.23\%$, $wR_p = 1.70\%$, $R_{\text{Bragg}} = 1.09$						

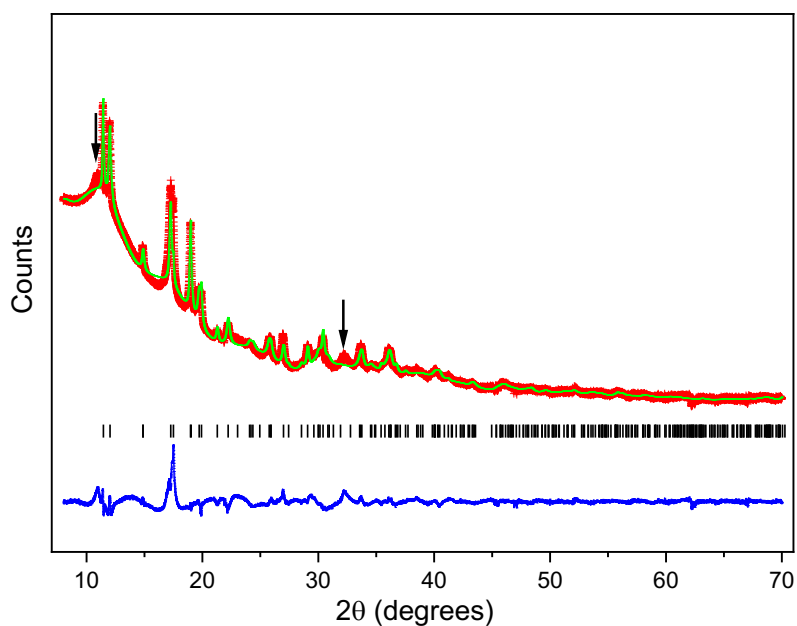
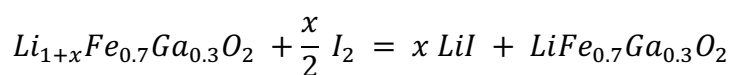


Figure 4a. 8. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXR data

Table 4a.8. Parameters from the structural refinement of $\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXR data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.448(6)	0.147(8)	0.603(5)	1	0.1
Fe/Al/Ga	4a	0.0906(5)	0.1264(5)	0	0.5/0.25/0.25	0.1
O(1)	4a	0.1495(13)	0.1238(33)	0.4321(17)	1	0.1
O(2)	4a	0.4059(24)	0.1250(37)	0.8761(13)	1	0.1
$\text{Li}_{1+x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4366(6) \text{ \AA}$, $b = 6.3886(11) \text{ \AA}$, $c = 5.0156(6) \text{ \AA}$ volume = $174.207(44) \text{ \AA}^3$ Formula weight = $91.03875 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.92\%$, $wR_p = 2.89\%$, $R_{\text{Bragg}} = 1.77$						

Table 4a.9. Titrations table for $\text{Li}_{1+x}\text{Fe}_{1-x}\text{Ga}_x\text{O}_2$ samples



$\text{Li}_{1+x}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_2$ taken (mg)	$\text{I}_2(\text{mg})$	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
13.9	36.0	20	19.2	0.57
15.4	35.3	20	17.5	0.58
18.6	25.8	20	9.7	0.53

Concentration of thiosulphate = 0.0107 (M)

$\text{Li}_{1+x}\text{Fe}_{0.6}\text{Ga}_{0.4}\text{O}_2$ taken (mg)	$\text{I}_2(\text{mg})$	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
17.3	33.4	20	17.25	0.44
19.3	35.7	20	16.4	0.55
21.4	37.2	20	18.9	0.41

Concentration of thiosulphate = 0.0109 (M)

$\text{Li}_{1+x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ taken (mg)	$\text{I}_2(\text{mg})$	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
14.1	31.7	20	17.0	0.47
17.2	32.3	20	15.0	0.55
18.9	28.6	20	12.8	0.47

Concentration of thiosulphate = 0.0109 (M)

$\text{Li}_{1+x}\text{Fe}_{0.5}\text{Al}_{0.125}\text{Ga}_{0.375}\text{O}_2$ taken (mg)	I_2 (g)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
0.0154	0.0215	20	10.1	0.40
0.0161	0.0254	20	12.8	0.39
0.0204	0.0332	20	17.1	0.38

Concentration of thiosulphate solution= 0.010 (M)

5a.1. XRD analysis of annealed T-Li_{1-x}FeO₂

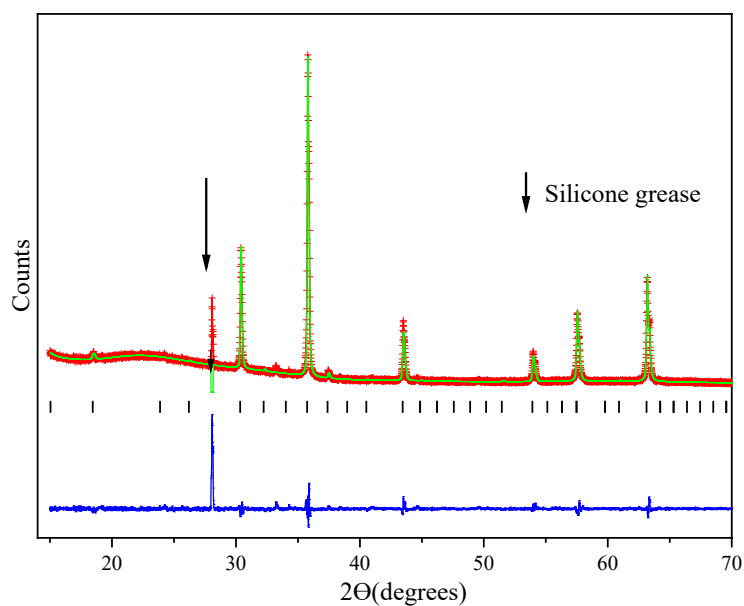


Figure 5a. 1. Observed, calculated and difference plots from the structural refinement of de-lithiated LiFeO₂ sample against XRD data, Confirms LiFe₅O₈ spinel formation

Table 5a.1. Parameters from the structural refinement of T-Li_{1-x}FeO₂ against XRD data

Atom	site	<i>x</i>	<i>y</i>	<i>z</i>	Fraction	B _{eq} (Å ²)
Fe1	12 <i>d</i>	0.125	0.3674(4)	0.8837(4)	0.58(1)	0.35(1)
Fe2	8 <i>c</i>	0.9987(5)	0.9987(5)	0.9987(5)	0.77(1)	0.35(1)
O1	8 <i>c</i>	0.3853(4)	0.3853(4)	0.3853(4)	1	0.78(2)
O2	24 <i>e</i>	0.1166(5)	0.1285(5)	0.3839(2)	1	0.78(2)
Li1	4 <i>b</i>	0.625	0.625	0.625	1	0.1
LiFe ₅ O ₈ – space group <i>P</i> 4 ₃ 32 (#33) $a=8.3260$ (5) Å, volume =577.168(63) Å ³ Radiation source: X-ray, $\lambda = 1.54059$ Å Temperature: 298 K $R_p = 3.83$ %, $wR_p = 5.22$ %, $R_{Bragg} = 1.43$						

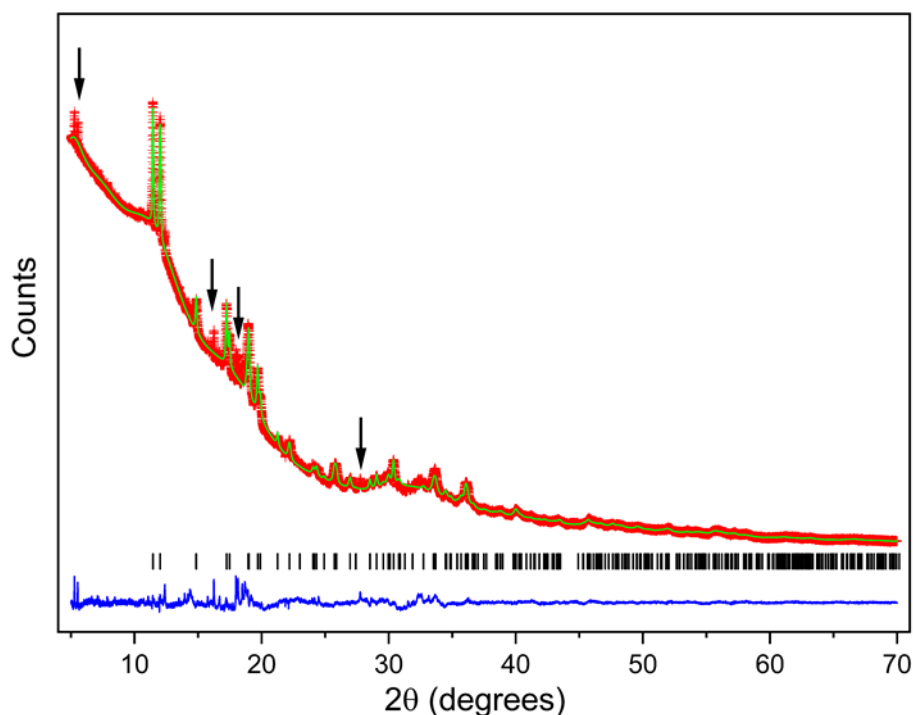


Figure 5a. 2. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data. Black arrows indicate reflections associated with unindexed impurity phase

Table 5a.2. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.477(3)	0.102(4)	0.502(25)	1	0.1
Fe/Al	$4a$	0.0876(4)	0.1196(4)	0	0.875/0.125	0.42(5)
O(1)	$4a$	0.0990(15)	0.1466(15)	0.3935(18)	1	0.1
O(2)	$4a$	0.4414(18)	0.1716(14)	0.9179(24)	1	0.1
$\text{Li}_{1-x}\text{Fe}_{0.875}\text{Al}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4417(8) \text{ \AA}$, $b = 6.3951(11) \text{ \AA}$, $c = 5.0228(8) \text{ \AA}$ volume = $174.799(50) \text{ \AA}^3$ Formula weight = $96.381 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.03 \%$, $wR_p = 1.58 \%$, $R_{\text{Bragg}} = 0.77$						

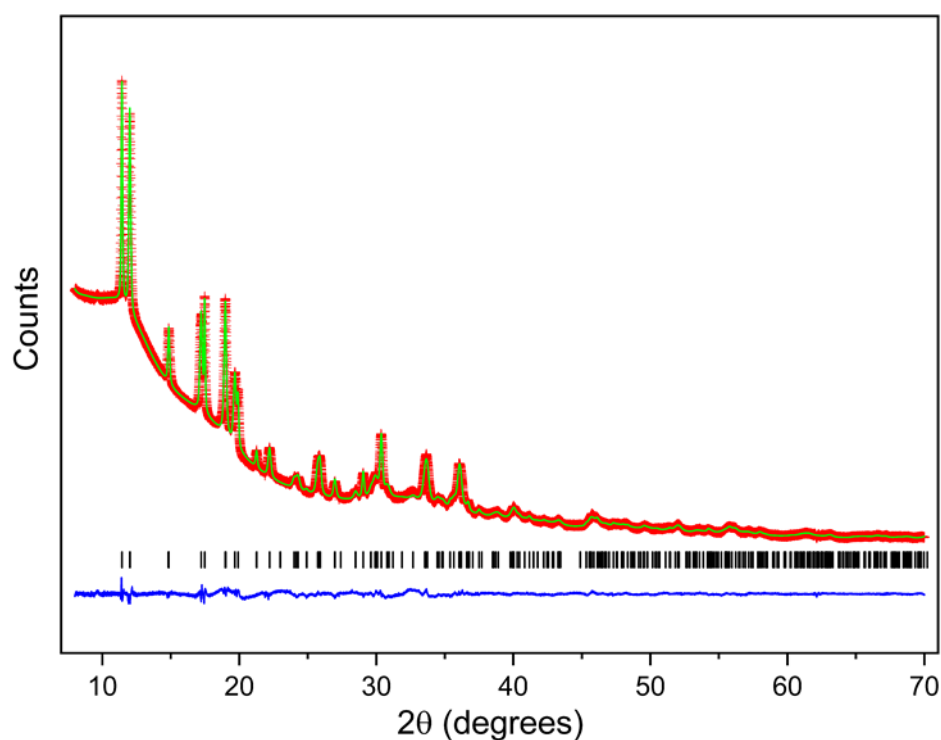


Figure 5a.3. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.75}\text{Al}_{0.25}\text{O}_2$ against SXRD data.

Table 5a.3. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.75}\text{Al}_{0.25}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.4618(11)	0.1655(13)	0.500(9)	1	0.1
Fe/Al	$4a$	0.0821(2)	0.1302(1)	0	0.75/0.25	0.57(2)
O(1)	$4a$	0.0821(6)	0.0971(6)	0.3795(7)	1	0.1
O(2)	$4a$	0.4123(7)	0.1169(6)	0.8952(7)	1	0.1
$\text{Li}_{1-x}\text{Fe}_{0.75}\text{Al}_{0.25}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4421(1) \text{ \AA}$, $b = 6.4082(2) \text{ \AA}$, $c = 5.0172(1) \text{ \AA}$ volume = $174.972(6) \text{ \AA}^3$ Formula weight = $87.5705 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.92 \%$, $wR_p = 1.28 \%$, $R_{\text{Bragg}} = 0.53$						

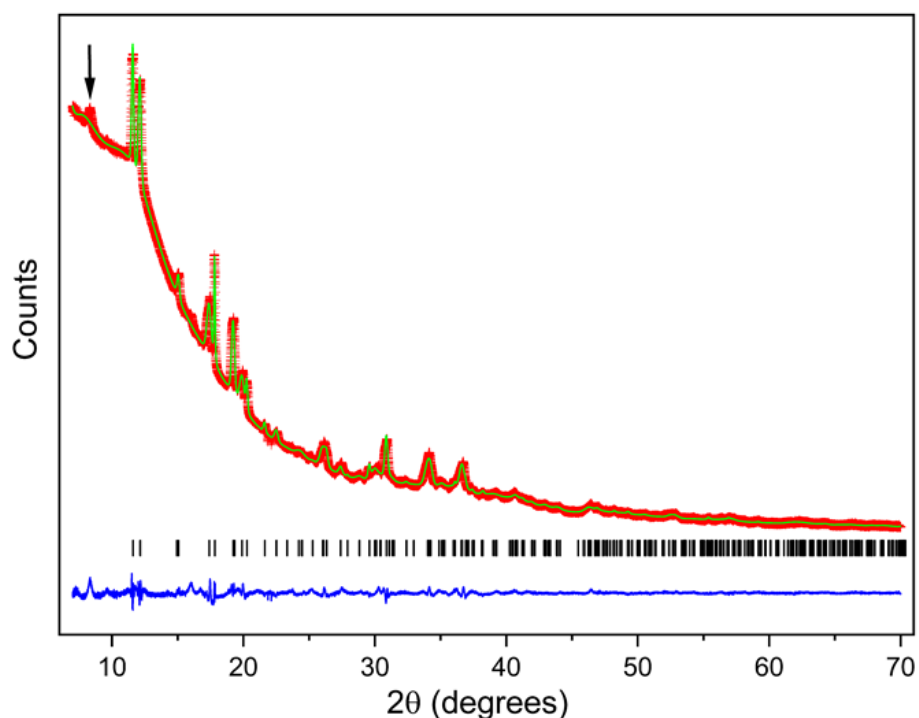


Figure 5a. 4. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.25}\text{Al}_{0.75}\text{O}_2$ against SXRD data. Black arrow indicates reflection associated to unidentified impurity phase

Table 5a.4. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.25}\text{Al}_{0.75}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	$4a$	0.3864(15)	0.1029(32)	0.4695(26)	1	0.1
Fe/Al	$4a$	0.0846(3)	0.1278(5)	0	0.25/0.75	1.04(3)
O(1)	$4a$	0.0501(6)	0.1172(10)	0.3662(5)	1	0.1
O(2)	$4a$	0.4149(8)	0.1617(9)	0.8913(6)	1	0.1
$\text{Li}_{1-x}\text{Fe}_{0.25}\text{Al}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.3375(2) \text{ \AA}$, $b = 6.3654(4) \text{ \AA}$, $c = 4.9528(2) \text{ \AA}$ volume = $168.275(17) \text{ \AA}^3$ Formula weight = $73.13775 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.82 \%$, $wR_p = 1.14 \%$, $R_{\text{Bragg}} = 0.49$						

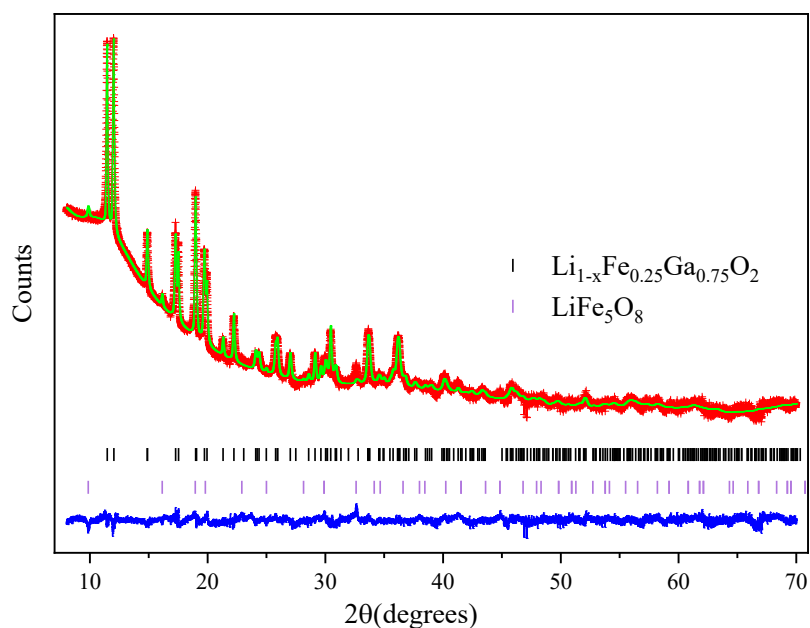


Figure 5a. 5. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data. Black arrow indicates reflection associated to the unidentified impurity phase

Table 5a.5. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.460(2)	0.459(3)	0.502(30)	1	0.1
Fe/Ga	4a	0.0819(3)	0.1303(3)	0	0.25/0.75	0.08(2)
O(1)	4a	0.0763(14)	0.1023(17)	0.3847(19)	1	0.1
O(2)	4a	0.4066(16)	0.1065(15)	0.8913(20)	1	0.1
$\text{Li}_{1-x}\text{Fe}_{0.25}\text{Ga}_{0.75}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4264(5) \text{ \AA}$, $b = 6.3851(6) \text{ \AA}$, $c = 5.0156(5) \text{ \AA}$ volume = $173.784(30) \text{ \AA}^3$ Formula weight = $105.1915 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.82\%$, $wR_p = 1.33\%$, $R_{\text{Bragg}} = 0.67$						

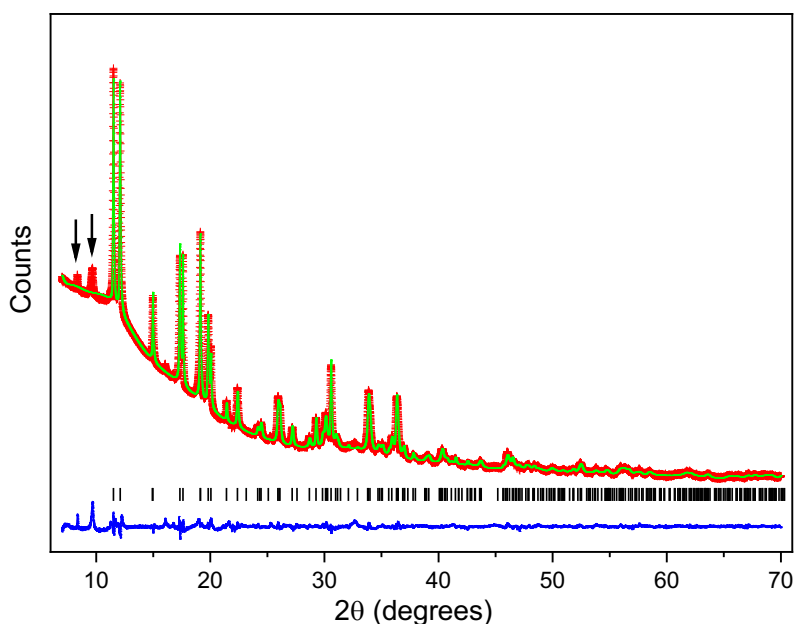


Figure 5a. 6. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.25}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data. Black arrows indicate reflections associated to the unidentified impurity phase

Table 5a.6. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ against SXRD data collected at room temperature.

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.471(1)	0.151(1)	0.531(2)	1	0.1
Fe/Al/Ga	4a	0.0791(1)	0.1288(2)	0	0.5/0.375/0.125	0.22(1)
O(1)	4a	0.0778(5)	0.1011(8)	0.3798(4)	1	0.1
O(2)	4a	0.3978(5)	0.1300(8)	0.8954(4)	1	0.1
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.375}\text{Ga}_{0.125}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4042(1) \text{ \AA}$, $b = 6.3696(1) \text{ \AA}$, $c = 4.9792(1) \text{ \AA}$ volume = $171.402(7) \text{ \AA}^3$ Formula weight = $85.69625 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.11\%$, $wR_p = 1.56\%$, $R_{\text{Bragg}} = 0.59$						

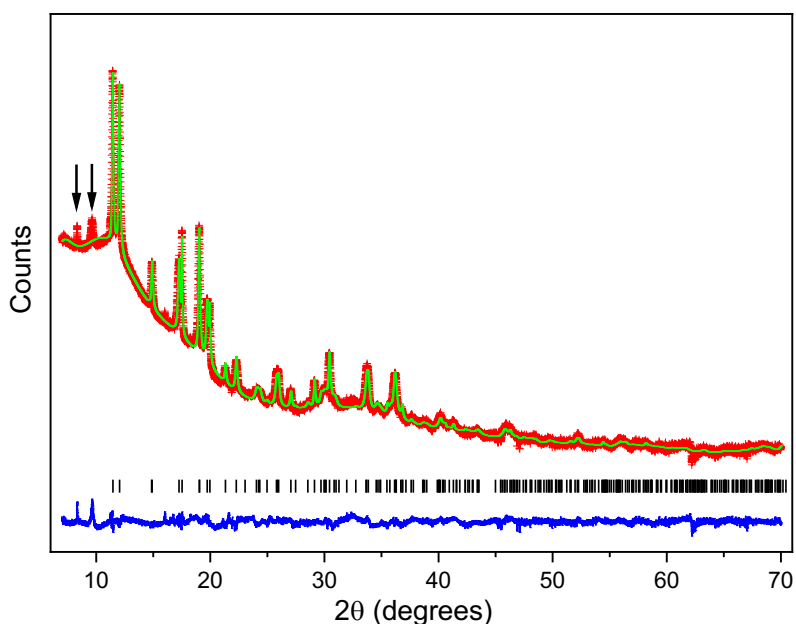


Figure 5a. 7. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.25}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXRD data. Black arrows indicate reflections associated to the unidentified impurity phase

Table 5a.7. Parameters from the structural refinement of $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ against SXRD data collected at room temperature

Atom	site	x	y	z	Fraction	$B_{\text{eq}} (\text{\AA}^2)$
Li	4a	0.401(2)	0.075(3)	0.489(10)	1	0.1
Fe/Al/Ga	4a	0.0776(3)	0.1225(3)	0	0.5/0.25/0.25	0.44(3)
O(1)	4a	0.0774(12)	0.1473(14)	0.3792(10)	1	0.1
O(2)	4a	0.3913(12)	0.1516(14)	0.8990(12)	1	0.1
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.25}\text{Ga}_{0.25}\text{O}_2$ – space group $Pna2_1$ (#33) $a = 5.4275(4) \text{ \AA}$, $b = 6.3972(5) \text{ \AA}$, $c = 5.0017(3) \text{ \AA}$ volume = $173.666(24) \text{ \AA}^3$ Formula weight = $91.03875 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.26\%$, $wR_p = 1.69\%$, $R_{\text{Bragg}} = 0.54$						

Table 5a.8. Table of ICP-MS data of $\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$ system

Sample	Elements		
	Li	Fe	Al
$\text{LiFe}_{0.5}\text{Al}_{0.5}\text{O}_2$	1.01	0.5	0.61
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (sample I)	0.64	0.5	0.57
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (sample II)	0.81	0.5	0.66
Sample II + LiI	0.88	0.5	0.66

$$\text{Li}_{0.64}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2 + y \text{LiI} = \frac{y}{2} \text{I}_2 + \text{Li}_{0.68+y}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$$

Table 5a.9. Titrations table for reversibility check of $\text{Li}_{0.64}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ (oxidised material, value of lithium content taken from ICPMS data)

$\text{Li}_{0.64}\text{Fe}_{0.5}\text{Al}_{0.5}\text{O}_2$ taken (mg)	LiI (mg)	Thiosulphate solution consumed (mL)	Reversibly lithium intercalated (y)
44.7	175	8.1	0.15
53.0	175	8.4	0.13

*Concentration of thiosulphate solution used = 0.01094(M)

Table 5a.10. Table of ICP-MS data for $\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ system

Sample	Elements		
	Li	Fe	Ga
$\text{LiFe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	0.99	0.5	0.60
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$	0.57	0.5	0.42
$\text{Li}_{1-x}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2 + \text{LiI}$	0.75	0.5	0.42

$$\text{Li}_{0.57}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2 + y \text{LiI} = \frac{y}{2} \text{I}_2 + \text{Li}_{0.57+y}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$$

Table 5a.11 Titration table for reversibility check of $\text{Li}_{0.57}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ (oxidised material)

$\text{Li}_{0.57}\text{Fe}_{0.5}\text{Ga}_{0.5}\text{O}_2$ taken (mg)	LiI (mg)	Thiosulphate solution consumed (mL)	Reversibly lithium intercalated (y)
36.3	175	4.7	0.138
36.6	175	5.1	0.149

*Concentration of thiosulphate solution used = 0.01072(M)

Table 6a.16. Titration table for the determination of lithium deficiency in $\text{Na}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$

Composition	Sample taken (g)	KI taken (g)	Thiosulphate consumed (mL)	x	Final composition
$\text{Na}_{2-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	0.0158	~0.3	5.7	0.631	$\text{Na}_{1.375}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$
	0.0198	~0.3	7	0.619	
$\text{N}_{2-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	0.0208	~0.3	4.6	0.544	$\text{N}_{1.485}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$
	0.0209	~0.3	4.2	0.497	
	0.0501	~0.6	10.2	0.504	
$\text{Na}_{2-x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$	0.0199	~0.3	5.5	0.653	$\text{Na}_{1.36}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$
	0.0205	~0.3	5.4	0.624	
	0.0279	~0.3	7.5	0.636	

Concentration of thiosulphate solution used =0.0101 (M)

Table 6a.17. Titration table for the determination of lithium deficiency in $\text{Li}_{1.5}\text{Fe}_{2-x-y}\text{M}_x^{\text{III}}\text{N}_y^{\text{IV}}\text{O}_4$

Composition	Sample taken (g)	KI taken (g)	Thiosulphate consumed (mL)	x	Final composition
$\text{Li}_{2-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	0.0206	~0.3	6.95	0.487	$\text{Li}_{1.508}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$
	0.0207	~0.3	7.25	0.504	
	0.0232	~0.3	7.8	0.485	
$\text{Li}_{2-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	0.0189	~0.3	5.1	0.570	$\text{Li}_{1.429}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$
	0.0193	~0.3	5.4	0.590	
	0.03	~0.3	7.8	0.551	
$\text{Li}_{2-x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$	0.02	~0.3	5.7	0.581	$\text{Li}_{1.413}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$
	0.0204	~0.3	5.9	0.589	
	0.0228	~0.3	6.6	0.589	

[Concentration of thiosulphate solution used =0.0101 (M)]

Table 7a.1 Table of ICP-MS data

Sample	Elements			
	Na	Fe	Ge	Ga
Na _{1.5} FeGe _{0.5} Ga _{0.5} O ₄	1.36	1	0.37	0.39
Na _{1.5+x} FeGe _{0.5} Ga _{0.5} O ₄	2.53	1	0.33	0.36

Table 7a.2. Titrations table for Na_{1+x}FeGe_{0.5}Ga_{0.5}O₄

Na _{1.5+x} FeGe _{0.5} Ga _{0.5} O ₄ taken (g)	I ₂ (g)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Na- intercalated (x)
0.0193	0.0297	20	7.1	1.28
0.0199	0.0243	20	9.5	1.25
0.0200	0.0276	20	10.2	1.42

Table 7a.3. Titrations table for Li_{1.5+x}Fe_{0.5}Si_{0.5}AlO₄

Li _{1.5+x} Fe _{0.5} Si _{0.5} AlO ₄ taken (g)	I ₂ (g)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
0.0184	0.0257	20	11.6	0.587
0.0202	0.0287	20	13.4	0.558
0.0223	0.0294	20	13.5	0.533

Conc. of thiosulphate = 0.0106 (M)

Table 7a.4 Titrations table for Li_{1.5+x}Fe_{0.5}Ge_{0.5}GaO₄

Li _{1.5+x} Fe _{0.5} Ge _{0.5} GaO ₄ taken (g)	I ₂ (g)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
0.0194	0.0363	20	20.1	0.66
0.0213	0.0400	20	22.4	0.63
0.0214	0.0567	20	34	0.65

Conc. of thiosulphate = 0.0106 (M)

Table 7a.5. Titrations table for Li_{1.5+x}FeGe_{0.5}Ga_{0.5}O₄

Li _{1.5+x} FeGe _{0.5} Ga _{0.5} O ₄ taken (g)	I ₂ (g)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
0.0202	0.0566	20	30.5	1.11
0.0204	0.0458	20	23.5	1.02
0.0245	0.0521	20	25.3	1.11

Conc. of thiosulphate = 0.0106 (M)

Table 7a.6. Table of ICP-MS data

Sample	Elements			
	Li	Fe	Ga	Ge
$\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$	1.30	1	0.37	0.32
$\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$	2.42	1	0.32	0.26

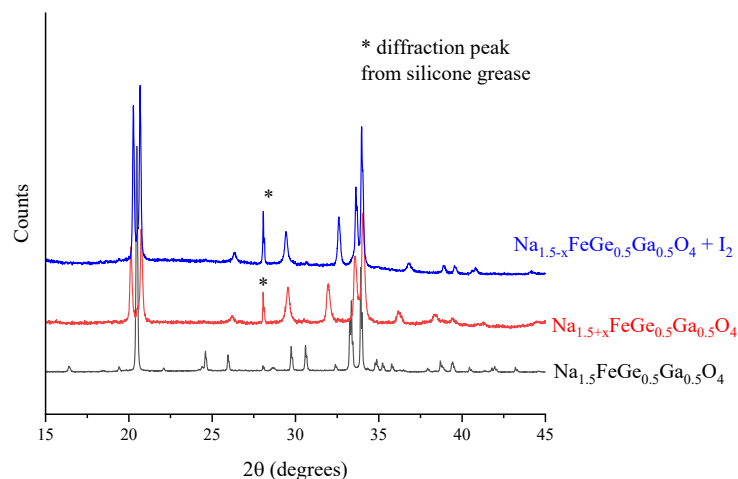


Figure 7a. 1. Plot of XRD data from $\text{Na}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, $\text{Na}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ and $\text{Na}_{1.5-x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4 + \text{I}_2$

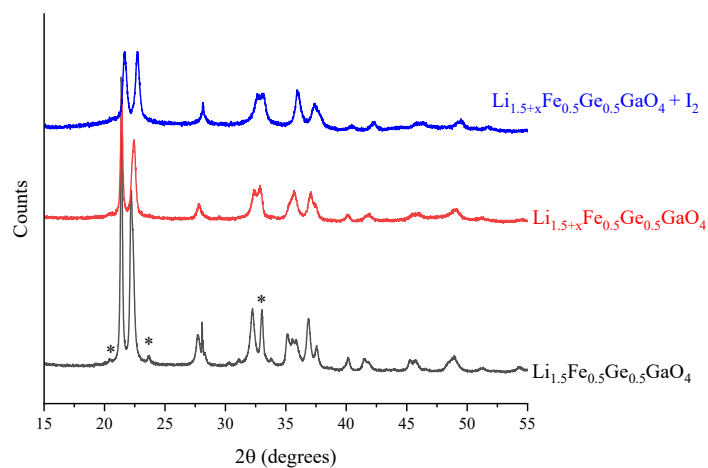


Figure 7a. 2. Plot of XRD data from $\text{Li}_{1.5}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$, $\text{Li}_{1.5+x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4$ and $\text{Li}_{1.5-x}\text{FeGe}_{0.5}\text{Ga}_{0.5}\text{O}_4 + \text{I}_2$, * indicate reflections which can only be indexed using the unit cell parameters from the structure described in space group Pc

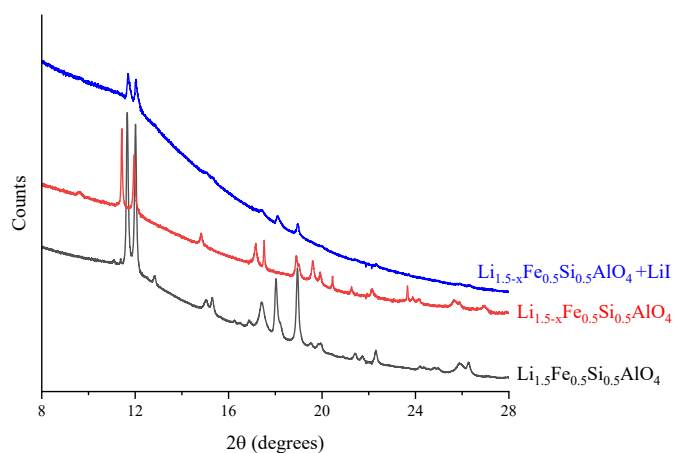


Figure 8a. 1. Plot of SXRD data from $\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$, $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ and $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4 + \text{LiI}$

Table 8a.1 Table of ICPMS data

Sample	Elements			
	Li	Fe	Ga	Ge
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	1.46	0.5	0.91	0.36
$\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	1.09	0.5	0.90	0.37
$\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4 + \text{LiI}$	1.40	0.5	0.89	0.36

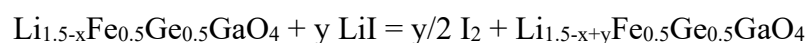


Table 8a.2 Titration table for reversibility check of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$; $x = 0.5$ (as per the ICP-MS value)

$\text{LiFe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ taken (g)	LiI (mg)	Thiosulphate solution consumed (mL)	Reversibly lithium intercalated (y)
0.0325	~175	6.7	0.44
0.0351	~175	5.5	0.34

* Concentration of thiosulphate solution = 0.0106 (M)

Table 8a.3. Iodometric titration table for the reversibility check of $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$

$\text{LiFe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ taken (g)	LiI (mg)	Thiosulphate solution consumed (mL)	Reversibly lithium intercalated (y)
0.040	~175	8.5	0.35
0.047	~175	9.2	0.32
0.056	~175	11.5	0.33

Assuming in $\text{Li}_{1.5-x}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ sample, $x = 0.5$

Table 8a.4. Table of lithium ions inserted/extracted with the corresponding $\text{Li}_x\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$ composition and oxidation state of iron determined from the plot of voltage vs number of lithium being cycled (Figure 8.14, d)

Cycles	step	Lithium inserted (total)	Lithium insertion leading to decomposition	Lithium extracted	Composition	Oxidation state of iron	Oxygen redox
0					$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	3	Y
1	Process1/ discharge (4.8-1.0 V)	0.54	0.04		$\text{Li}_2\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2	
1	Process1/ charge (1.0-4.5 V)			0.19	$\text{Li}_{1.79}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.38	
1	Process2/ charge (4.5-4.8 V)			0.05	$\text{Li}_{1.74}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.38	Y
2	Process1/ discharge (4.8-1.0 V)	0.25	0.06		$\text{Li}_{1.99}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2	
2	Process1/ charge (1.0-4.5 V)			0.18	$\text{Li}_{1.79}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.36	
2	Process2/ charge (4.5-4.8 V)			0.05	$\text{Li}_{1.74}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.36	Y
3	Process1/ discharge (4.8-1.0 V)	0.21	0.04		$\text{Li}_{1.95}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2	
3	Process1/ charge (1.0-4.5 V)			0.16	$\text{Li}_{1.78}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.33	
3	Process2/ charge (4.5-4.8 V)			0.04	$\text{Li}_{1.74}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.33	Y
4	Process1/ discharge (4.8-1.0 V)	0.20	0.04		$\text{Li}_{1.90}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2	
4	Process1/ charge (1.0-4.5 V)			0.15	$\text{Li}_{1.75}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.30	
4	Process2/ charge (4.5-4.8 V)			0.035	$\text{Li}_{1.71}\text{Fe}_{0.5}\text{Si}_{0.5}\text{AlO}_4$	2.30	Y

Table 8a.5. Table of lithium inserted/extracted in the discharge/charge cycle with the corresponding $\text{Li}_x\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$ composition and oxidation state of iron, determined from the plot of voltage vs number of lithium being cycled (Figure 8.17, c)

Cycles	step	Lithium inserted	Lithium insertion leading to decomposition	Lithium extracted	Composition	Oxidation state of iron	Oxygen redox
0					$\text{Li}_{1.5}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	3	
1	Process3/ charge (4.5-4.8 V)			0.05	$\text{Li}_{1.45}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	3	Y
1	Process1/ discharge (4.8-1.0 V)	0.83	0.33		$\text{Li}_{1.95}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2	
2	Process1/ charge (1.0-3.5 V)			0.34	$\text{Li}_{1.54}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2.814	
2	Process3/ charge (4.5-4.8 V)			0.08	$\text{Li}_{1.46}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2.814	Y
2	Process1/ discharge (4.8-1.0 V)	0.48	0.13		$\text{Li}_{1.88}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2	
3	Process1/ charge (1.0-3.5 V)			0.32	$\text{Li}_{1.49}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2.83	
3	Process3/ charge (4.5-4.8 V)			0.05	$\text{Li}_{1.44}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2.83	Y
3	Process1/ discharge (4.8-1.0 V)	0.41	0.11		$\text{Li}_{1.82}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2	
4	Process1/ charge (1.0-3.5 V)			0.35	$\text{Li}_{1.38}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2.96	
4	Process3/ charge (4.5-4.8 V)			0.06	$\text{Li}_{1.32}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2.96	Y
4	Process1/ discharge (4.8-1.0 V)	0.39	0.096		$\text{Li}_{1.71}\text{Fe}_{0.5}\text{Ge}_{0.5}\text{GaO}_4$	2	

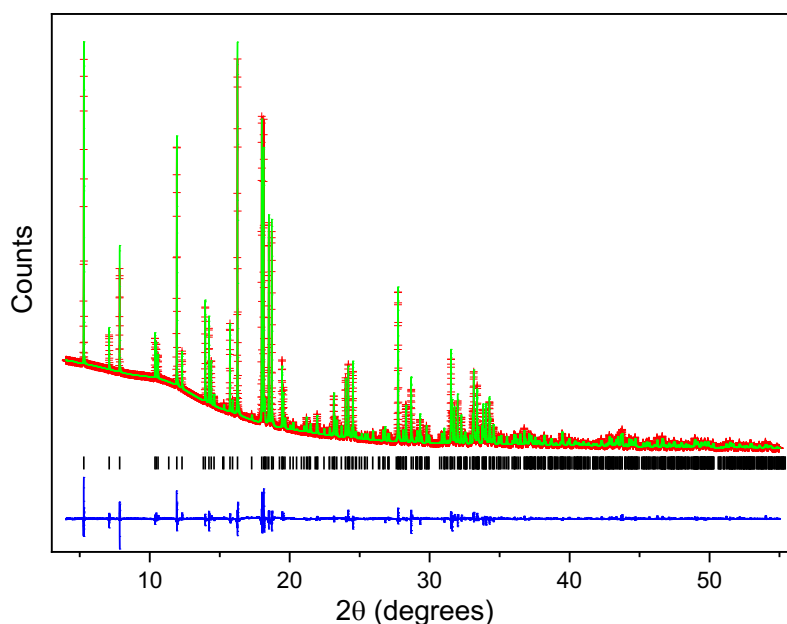


Figure 9a. 1. Observed, calculated and difference plots from the structural refinement of $\text{Na}_3\text{Fe}_4\text{GaO}_9$ against SXRD data

Table 9a.1. Parameters from the structural refinement of $\text{Na}_3\text{Fe}_4\text{GaO}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Fe1/Ga1	8f	0.1155(1)	0.3190(1)	0.2171(1)	0.74(1)/0.26(1)	0.065(15)
Fe2/Ga2	8f	0.3592(1)	0.3390(1)	0.2821(2)	0.74(1)/0.26(1)	0.065(15)
Fe3	4e	0	0.0643(1)	0.25	1	0.069(44)
Na1	8f	0.2385(2)	0.0772(3)	0.2268(6)	1	0.791(59)
Na2	4e	0	0.5894(3)	0.25	1	0.791(59)
O1	8f	0.0846(2)	0.0525(3)	-0.0687(7)	1	0.070(48)
O2	8f	0.3665(2)	0.2042(3)	0.1276(7)	1	0.070(48)
O3	8f	0.2293(3)	0.3893(3)	0.3232(7)	1	0.070(48)
O4	8f	0.4071(2)	0.3175(3)	0.6170(7)	1	0.070(48)
O5	4e	0	0.4004(4)	0.25	1	0.070(48)
$\text{Na}_3\text{Fe}_4\text{GaO}_9$ – space group $C2/c$ (#15) $a = 13.3543(1) \text{ \AA}$, $b = 12.0839(1) \text{ \AA}$, $c = 5.2861(1) \text{ \AA}$, $\beta = 89.1298(2)^\circ$ volume = $852.950(4) \text{ \AA}^3$ Formula weight = $508.85 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.26 \%$, $wR_p = 2.35 \%$, $R_{\text{Bragg}} = 1.17$						

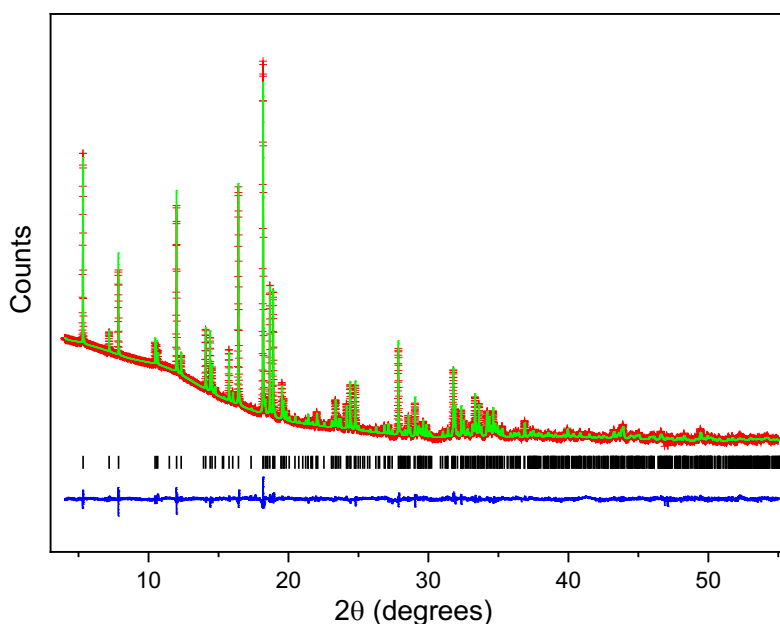


Figure 9a. 2. Observed, calculated and difference plots from the structural refinement of $\text{Na}_3\text{FeGa}_4\text{O}_9$ against SXRD data

Table 9a.2. Parameters from the structural refinement of $\text{Na}_3\text{FeGa}_4\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Ga1	8f	0.1158(1)	0.3156(1)	0.2169(3)	1	0.39(3)
Ga2	8f	0.3584(1)	0.3390(1)	0.2806(3)	1	0.39(3)
Fe3	4e	0	0.0633(2)	0.25	1	0.1
Na1	8f	0.2392(4)	0.0750(4)	0.2306(11)	1	0.1
Na2	4e	0	0.5889(5)	0.25	1	0.1
O1	8f	0.0804(4)	0.0516(5)	0.9478(15)	1	0.88(8)
O2	8f	0.3645(5)	0.1984(5)	0.1286(12)	1	0.88(8)
O3	8f	0.2304(5)	0.3925(5)	0.3303(11)	1	0.88(8)
O4	8f	0.4091(4)	0.3250(5)	0.6069(13)	1	0.88(8)
O5	4e	0	0.3937(7)	0.25	1	0.88(8)
$\text{Na}_3\text{FeGa}_4\text{O}_9$ – space group $C2/c$ (#15) $a = 13.1929(1) \text{ \AA}$, $b = 12.0724(1) \text{ \AA}$, $c = 5.2335(1) \text{ \AA}$, $\beta = 89.0362(2)^\circ$ volume = $833.436(4) \text{ \AA}^3$ Formula weight = $547.69 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.09 \%$, $wR_p = 1.63 \%$, $R_{\text{Bragg}} = 0.93$						

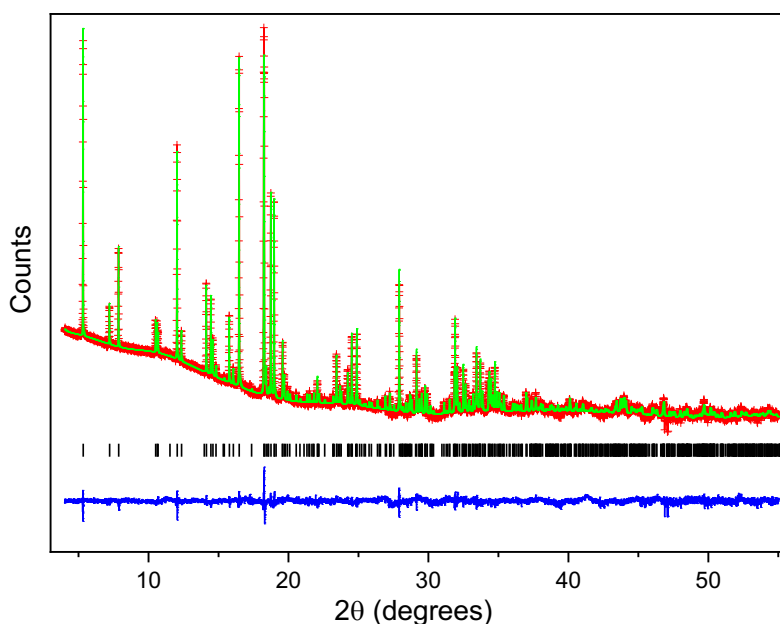


Figure 9a. 3. Observed, calculated and difference plots from the structural refinement of $\text{Na}_3\text{Ga}_5\text{O}_9$ against SXRD data

Table 9a.3. Parameters from the structural refinement of $\text{Na}_3\text{Ga}_5\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Ga1	$8f$	0.1146(1)	0.3160(1)	0.3187(4)	1	0.1
Ga2	$8f$	0.3591(1)	0.3384(1)	0.2819(4)	1	0.1
Ga3	$4e$	0	0.0632(2)	0.25	1	0.1
Na1	$8f$	0.2453(5)	0.0730(5)	0.0730(5)	1	0.1
Na2	$4e$	0	0.5924(7)	0.25	1	0.1
O1	$8f$	0.0855(5)	0.0555(6)	-0.0727(17)	1	0.11(1)
O2	$8f$	0.3651(6)	0.1974(7)	0.1230(16)	1	0.11(1)
O3	$8f$	0.2232(6)	0.3891(6)	0.3290(16)	1	0.11(1)
O4	$8f$	0.4040(6)	0.3183(7)	0.6126(16)	1	0.11(1)
O5	$4e$	0	0.4049(9)	0.25	1	0.11(1)
$\text{Na}_3\text{Ga}_5\text{O}_9$ – space group $C2/c$ (#15) $a = 13.1407(1) \text{ \AA}$, $b = 12.0494(1) \text{ \AA}$, $c = 5.2067(1) \text{ \AA}$, $\beta = 89.0464(2)^\circ$ volume = $824.316(9) \text{ \AA}^3$ Formula weight = $561.56 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.36 \%$, $wR_p = 1.92 \%$, $R_{\text{Bragg}} = 0.92$						

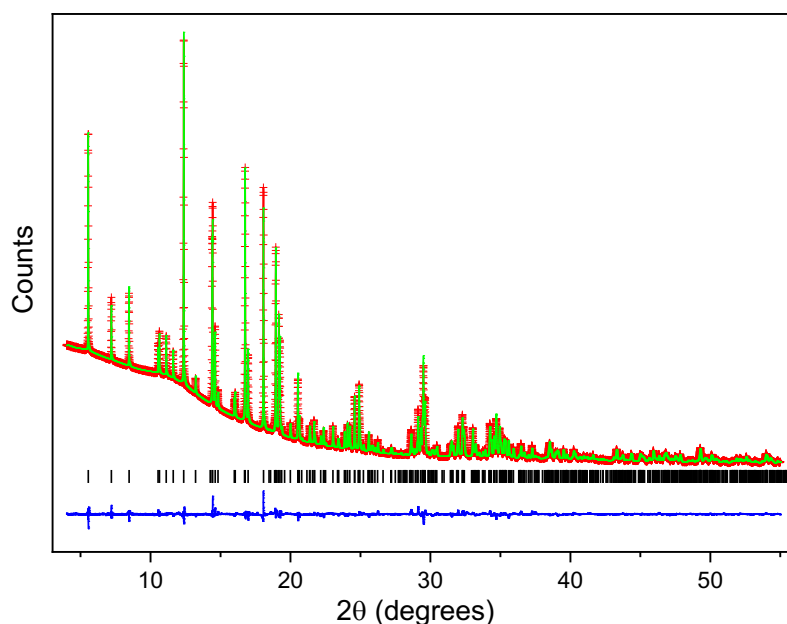


Figure 9a. 4. Observed, calculated and difference plots from the structural refinement of $\text{Li}_3\text{Fe}_4\text{GaO}_9$ against SXRD data

Table 9a.4. Parameters from the structural refinement of $\text{Li}_3\text{Fe}_4\text{GaO}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Fe1/Ga1	$8f$	0.1179(1)	0.3364(1)	0.2937(2)	0.75/0.25	0.35(1)
Fe2/Ga2	$8f$	0.3569(1)	0.3334(1)	0.2123(2)	0.75/0.25	0.35(1)
Fe3	$4e$	0	0.0681(1)	0.25	1	0.1
Li1	$8f$	0.2411	0.0760	0.2320	1	3.57(2)
Li2	$4e$	0	0.5902	0.25	1	3.57(2)
O1	$8f$	0.1011(2)	0.1932(3)	0.1418(7)	1	0.78(3)
O2	$8f$	0.3645(2)	0.1795(3)	0.3462(7)	1	0.78(3)
O3	$8f$	0.2259(2)	0.4139(3)	0.1561(6)	1	0.78(3)
O4	$8f$	0.4186(2)	0.4411(3)	0.4174(6)	1	0.78(3)
O5	$4e$	0	0.4326(5)	0.25	1	0.78(3)
$\text{Li}_3\text{Fe}_4\text{GaO}_9$ – space group $C2/c$ (#15) $a = 13.1594(1) \text{ \AA}$, $b = 11.2033(1) \text{ \AA}$, $c = 5.2653(1) \text{ \AA}$, $\beta = 90.8879 (6)^\circ$ volume = $776.181 (4) \text{ \AA}^3$ Formula weight = $457.925 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.00 \%$, $wR_p = 1.54 \%$, $R_{\text{Bragg}} = 1.35$						

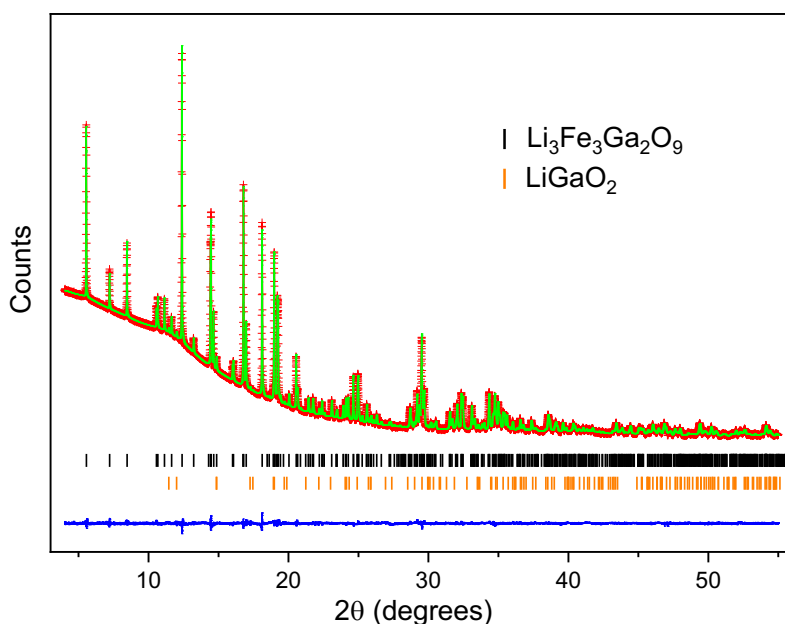


Figure 9a. 5. Observed, calculated and difference plots from the structural refinement of $\text{Li}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ against SXRD data

Table 9a.5. Parameters from the structural refinement of $\text{Li}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Fe1/Ga1	8f	0.1179(1)	0.3349(1)	0.2945(1)	0.5/0.5	0.15(1)
Fe2/Ga2	8f	0.3569(1)	0.3332(1)	0.2125(1)	0.5/0.5	0.15(1)
Fe3	4e	0	0.0681(1)	0.25	1	0.15(1)
Li1	8f	0.2411	0.0760	0.2320	1	2.03(1)
Li2	4e	0	0.5902	0.25	1	2.03(1)
O1	8f	0.1028(2)	0.1908(2)	0.1294(6)	1	0.81(3)
O2	8f	0.3632(2)	0.1976(2)	0.3539(6)	1	0.81(3)
O3	8f	0.2280(2)	0.4078(3)	0.1550(5)	1	0.81(3)
O4	8f	0.4194(2)	0.4392(5)	0.4247(5)	1	0.81(3)
O5	4e	0	0.4230(4)	0.25	1	0.81(3)
$\text{Li}_3\text{Fe}_3\text{Ga}_2\text{O}_9$ — space group $C2/c$ (#15) $a = 13.1261(1) \text{ \AA}$, $b = 11.2978(1) \text{ \AA}$, $c = 5.2501(1) \text{ \AA}$, $\beta = 90.9016(6)^\circ$ volume = $771.595(4) \text{ \AA}^3$ Formula weight = $471.79 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.61 \%$, $wR_p = 0.88 \%$, $R_{\text{Bragg}} = 0.48$						

Secondary phase: 1.14% LiGaO_2

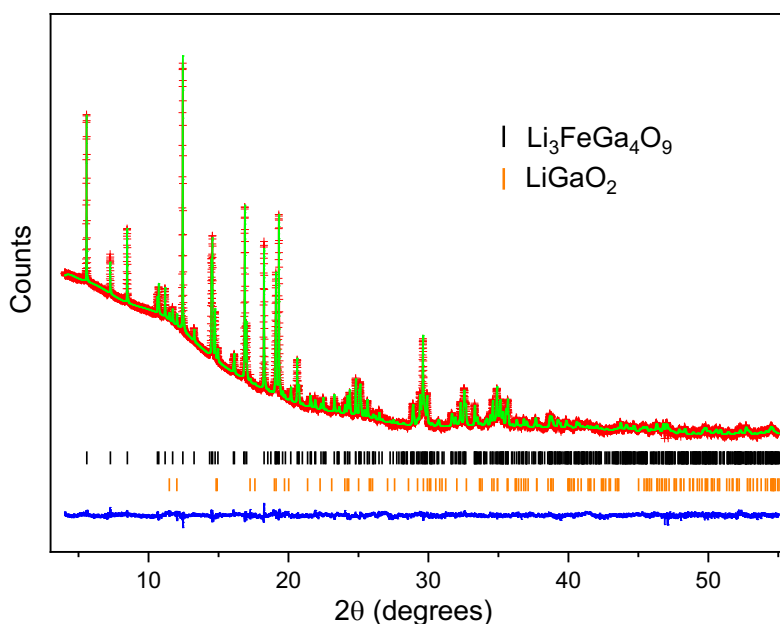


Figure 9a. 6. Observed, calculated and difference plots from the structural refinement of $\text{Li}_3\text{FeGa}_4\text{O}_9$ against SXRD data

Table 9a.6. Parameters from the structural refinement of $\text{Li}_3\text{FeGa}_4\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Ga1	8f	0.1180(1)	0.3344(1)	0.2935(3)	1	0.43(2)
Ga2	8f	0.3573(1)	0.3335(1)	0.2130(3)	1	0.43(2)
Fe3	4e	0	0.0685(2)	0.25	1	0.1
Li1	8f	0.2411	0.0760	0.2320	1	0.1
Li2	4e	0	0.5902	0.25	1	0.1
O1	8f	0.0989(4)	0.1872(5)	0.1271(12)	1	0.97(7)
O2	8f	0.3606(4)	0.1809(5)	0.3533(12)	1	0.97(7)
O3	8f	0.2312(4)	0.4109(5)	0.1443(10)	1	0.97(7)
O4	8f	0.4247(4)	0.4465(5)	0.4355(12)	1	0.97(7)
O5	4e	0	0.4210(10)		1	0.97(7)
$\text{Li}_3\text{FeGa}_4\text{O}_9$ – space group $C2/c$ (#15) $a = 13.0804(1) \text{ \AA}$, $b = 11.1916(1) \text{ \AA}$, $c = 5.2328(1) \text{ \AA}$, $\beta = 90.8661(6)^\circ$ volume = $765.955(7) \text{ \AA}^3$ Formula weight= $499.54 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.81 \%$, $wR_p = 1.11 \%$, $R_{\text{Bragg}} = 0.66$						

Secondary phase: 2.04 % LiGaO_2

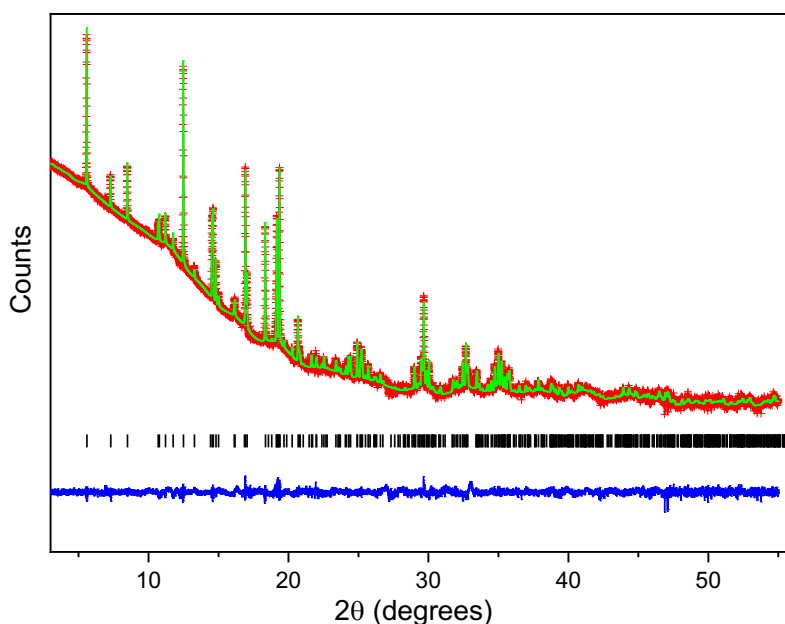


Figure 9a. 7. Observed, calculated and difference plots from the structural refinement of $\text{Li}_3\text{Ga}_5\text{O}_9$ against SXRD data

Table 9a.7. Parameters from the structural refinement of $\text{Li}_3\text{Ga}_5\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Ga1	8f	0.1177(2)	0.3345(2)	0.2927(5)	1	0.28(4)
Ga2	8f	0.3577(2)	0.3324(2)	0.2145(5)	1	0.28(4)
Ga3	4e	0	0.0696(3)	0.25	1	0.28(4)
Li1	8f	0.2411	0.0760	0.2320	1	2.70(48)
Li2	4e	0	0.5902	0.25	1	2.70(48)
O1	8f	0.1028(8)	0.1953(8)	0.1197(21)	1	0.312(139)
O2	8f	0.3548(7)	0.1684(10)	0.36631(21)	1	0.312(139)
O3	8f	0.2344(8)	0.4094(10)	0.1356(18)	1	0.312(139)
O4	8f	0.4207(7)	0.4337(10)	0.4402(21)	1	0.312(139)
O5	4e	0	0.4323(17)	0.25	1	0.312(139)
$\text{Li}_3\text{Ga}_5\text{O}_9$ – space group $C2/c$ (#15) $a = 12.9919(1) \text{ \AA}$, $b = 11.1574(2) \text{ \AA}$, $c = 5.1846(2) \text{ \AA}$, $\beta = 90.7778 (6)^\circ$ volume = $751.485 (20) \text{ \AA}^3$ Formula weight= $513.41 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.90 \%$, $wR_p = 1.30 \%$, $R_{\text{Bragg}} = 0.64$						

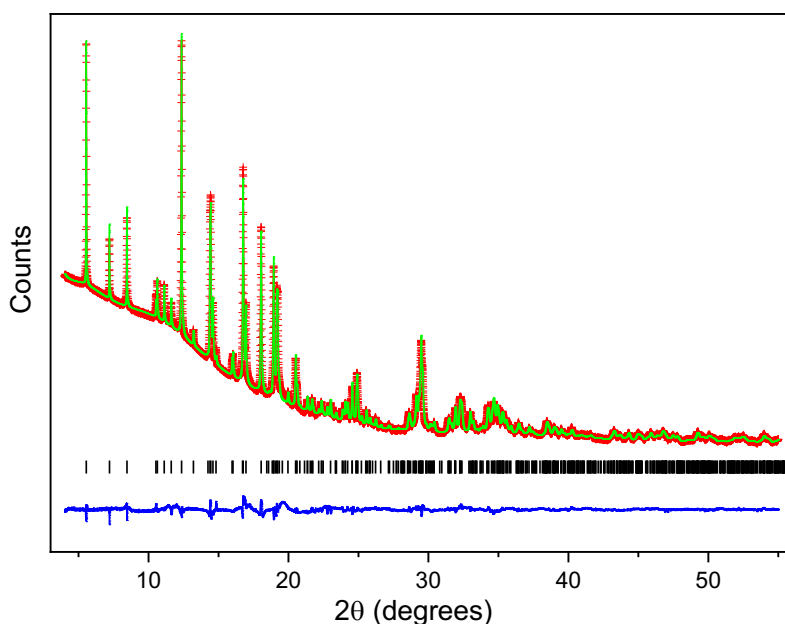


Figure 9a. 8. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$ against SXRD data

Table 9a.8. Parameters from the structural refinement of $\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Fe1/Ga1	8f	0.1180(1)	0.3370(1)	0.2937(2)	0.75/0.25	0.16(2)
Fe2/Ga2	8f	0.3581(1)	0.3322(1)	0.2116(3)	0.75/0.25	0.16(2)
Fe3	4e	0	0.0680(2)	0.25	1	0.16(2)
Li1	8f	0.2683(13)	0.0842(16)	0.1880(28)	1	0.1
Li2	4e	0	0.5871(24)	0.25	1	0.1
O1	8f	0.1068(4)	0.1896(4)	0.1381(10)	1	1.66(7)
O2	8f	0.3685(4)	0.1752(4)	0.3555(10)	1	1.66(7)
O3	8f	0.2267(3)	0.4069(4)	0.1346(8)	1	1.66(7)
O4	8f	0.4233(3)	0.4342(4)	0.4109(9)	1	1.66(7)
O5	4e	0	0.4200(7)	0.25	1	1.66(7)
$\text{Li}_{3+x}\text{Fe}_4\text{GaO}_9$ — space group $C2/c$ (#15) $a = 13.1552(1) \text{ \AA}$, $b = 11.2137(1) \text{ \AA}$, $c = 5.2736(1) \text{ \AA}$, $\beta = 90.9293 (10)^\circ$ volume = $777.852 (17) \text{ \AA}^3$ Formula weight= $457.925 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.31 \%$, $wR_p = 1.87 \%$, $R_{\text{Bragg}} = 1.02$						

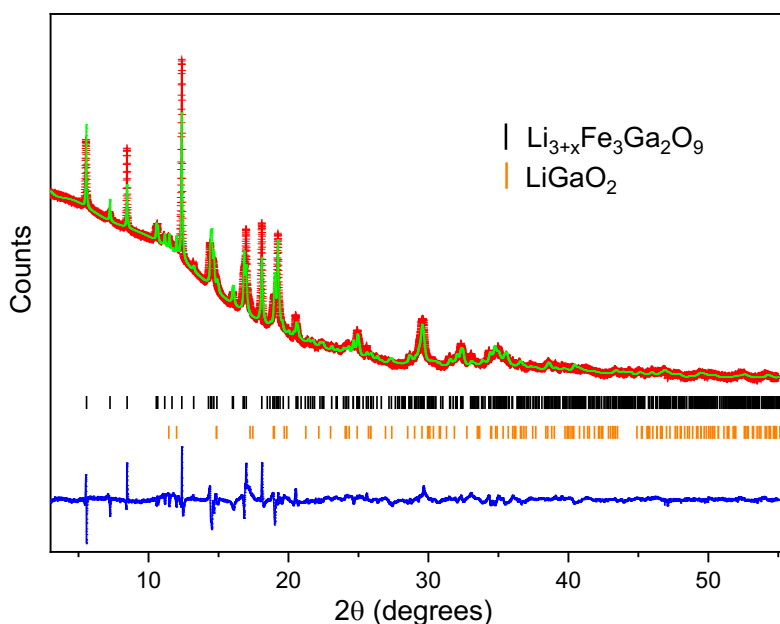


Figure 9a. 9. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3+x}\text{Fe}_3\text{Ga}_2\text{O}_9$ against SXRD data

Table 9a.9. Parameters from the structural refinement of $\text{Li}_{3+x}\text{Fe}_3\text{Ga}_2\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Fe1/Ga1	8f	0.1137(3)	0.34083(3)	0.3051(7)	0.5/0.5	0.1
Fe2/Ga2	8f	0.3566(3)	0.3356(3)	0.2157(7)	0.5/0.5	0.1
Fe3	4e	0	0.0745(5)	0.25	1	0.1
Li1	8f	0.2411	0.0760	0.2320	1	0.1
Li2	4e	0	0.5902	0.25	1	0.1
O1	8f	0.1007(2)	0.1907(3)	0.1311(7)	1	0.1
O2	8f	0.3654(3)	0.1801(3)	0.3490(8)	1	0.1
O3	8f	0.2285(3)	0.4119(3)	0.1558(6)	1	0.1
O4	8f	0.4203(2)	0.4428(3)	0.4221(7)	1	0.1
O5	4e	0	0.4259(5)	0.25	1	0.1
$\text{Li}_{3+x}\text{Fe}_3\text{Ga}_2\text{O}_9$ – space group $C2/c$ (#15) $a = 13.0888(6) \text{ \AA}$, $b = 11.1967(5) \text{ \AA}$, $c = 5.2577(2) \text{ \AA}$, $\beta = 90.8724(3)^\circ$ volume = $770.442(64) \text{ \AA}^3$ Formula weight = $471.7975 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.86 \%$, $wR_p = 3.01 \%$, $R_{\text{Bragg}} = 2.41$ Secondary phase: 7.7% LiGaO_2						

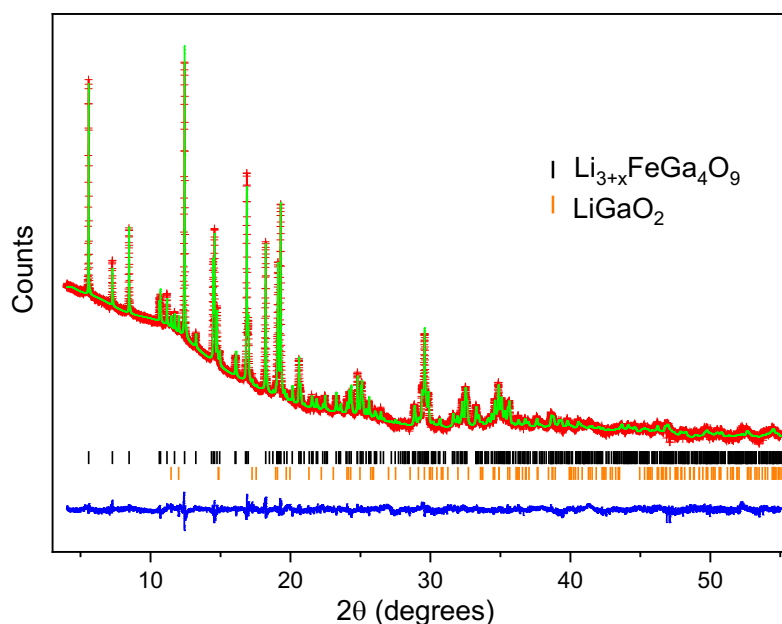


Figure 9a. 10. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$ against SXRD data

Table 9a.10. Parameters from the structural refinement of $\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Ga1	8f	0.1174(1)	0.3345(2)	0.2896(4)	1	0.16(3)
Ga2	8f	0.3579(2)	0.3317(2)	0.2119(4)	1	0.16(3)
Fe3	4e	0	0.0701(4)	0.25	1	0.1
Li1	8f	0.2411	0.0760	0.2320	1	0.1
Li2	4e	0	0.5902	0.25	1	0.1
O1	8f	0.1009(7)	0.1813(8)	0.1397(20)	1	0.68(11)
O2	8f	0.3593(7)	0.1825(9)	0.3688(20)	1	0.68(11)
O3	8f	0.2304(7)	0.4164(9)	0.1434(16)	1	0.68(11)
O4	8f	0.4296(6)	0.4446(9)	0.4325(21)	1	0.68(11)
O5	4e	0	0.4223(16)	0.25	1	0.68(11)
$\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$ — space group $C2/c$ (#15) $a = 13.0373(2) \text{ \AA}$, $b = 11.1982(2) \text{ \AA}$, $c = 5.2208(1) \text{ \AA}$, $\beta = 90.7804(12)^\circ$ volume = $762.182(21) \text{ \AA}^3$ Formula weight = 499.545 mol^{-1} , $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 1.18 \%$, $wR_p = 1.63 \%$, $R_{\text{Bragg}} = 0.73$ Secondary phase: 2.81% LiGaO_2						

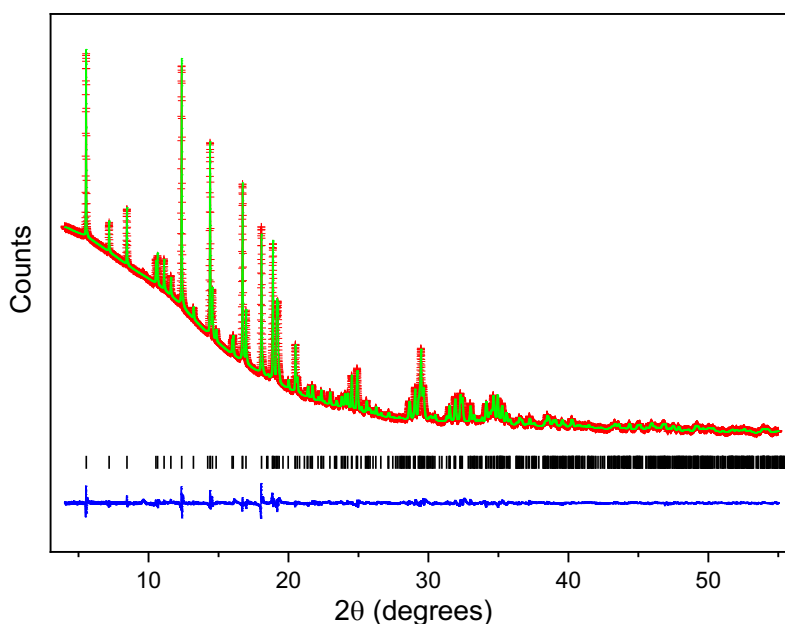


Figure 9a. 11. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3-x}\text{Fe}_4\text{GaO}_9$ against SXRD data

Table 9a.11. Parameters from the structural refinement of $\text{Li}_{3-x}\text{Fe}_4\text{GaO}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Fe1/Ga1	8f	0.1198(1)	0.3366(1)	0.2905(2)	0.75/0.25	0.55(3)
Fe2/Ga2	8f	0.3568(1)	0.3310(1)	0.2107(2)	0.75/0.25	0.79(4)
Fe3	4e	0	0.0678(15)	0.25	1	0.1
Li1	8f	0.2411	0.0760	0.2320	1	0.1
Li2	4e	0	0.5902	0.25	1	0.1
O1	8f	0.0968(3)	0.1951(3)	0.1410(8)	1	2.00(6)
O2	8f	0.3571(3)	0.1796(3)	0.3679(8)	1	2.00(6)
O3	8f	0.2305(3)	0.4099(4)	0.1469(6)	1	2.00(6)
O4	8f	0.4215(3)	0.4412(3)	0.4274(7)	1	2.00(6)
O5	4e	0	0.4286(6)	0.25	1	2.00(6)
$\text{Li}_{3-x}\text{Fe}_4\text{GaO}_9$ – space group $C2/c$ (#15) $a = 13.1973$ (1) Å, $b = 11.2096$ (1) Å, $c = 5.2657$ (3) Å, $\beta = 91.1287$ (7)° volume = 778.855 (10) Å ³ Formula weight= 457.925 mol ⁻¹ , $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268$ Å Temperature: 298 K $R_p = 0.84$ %, $wR_p = 1.34$ %, $R_{\text{Bragg}} = 0.66$						

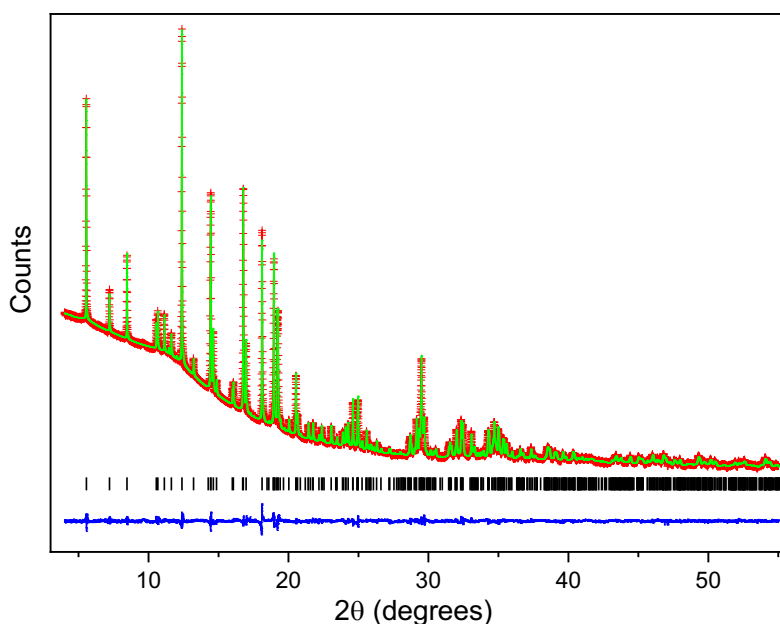


Figure 9a. 12. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3-x}\text{Fe}_3\text{Ga}_2\text{O}_9$ against SXR data

Table 9a.12. Parameters from the structural refinement of $\text{Li}_{3-x}\text{Fe}_3\text{Ga}_2\text{O}_9$ sample against synchrotron powder diffraction data

Atom	site	x	y	z	Fraction	B_{iso}
Fe1/Ga1	8f	0.1184(1)	0.3355(1)	0.2928(2)	0.5/0.5	0.35(2)
Fe2/Ga2	8f	0.3569(1)	0.3331(1)	0.2116(2)	0.5/0.5	0.35(2)
Fe3	4e	0	0.0676(1)	0.25	1	0.1
Li1	8f	0.2567(11)	0.0781(12)	0.2058(24)	1	0.1
Li2	4e	0	0.5890(18)	0.25	1	0.1
O1	8f	0.1008(3)	0.1915(3)	0.1311(8)	1	1.38(5)
O2	8f	0.3598(3)	0.1808(3)	0.3626(8)	1	1.38(5)
O3	8f	0.2293(3)	0.4091(3)	0.1514(6)	1	1.38(5)
O4	8f	0.4198(3)	0.4399(3)	0.4269(7)	1	1.38(5)
O5	4e	0	0.4219(6)	0.25	1	1.38(5)
$\text{Li}_{3-x}\text{Fe}_3\text{Ga}_2\text{O}_9$ – space group $C2/c$ (#15) $a = 13.1447(1) \text{ \AA}$, $b = 11.2058(1) \text{ \AA}$, $c = 5.2529(3) \text{ \AA}$, $\beta = 91.0080(7)^\circ$ volume = $773.634(10) \text{ \AA}^3$ Formula weight = $471.7975 \text{ mol}^{-1}$, $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268 \text{ \AA}$ Temperature: 298 K $R_p = 0.86 \%$, $wR_p = 1.28 \%$, $R_{\text{Bragg}} = 0.51$						

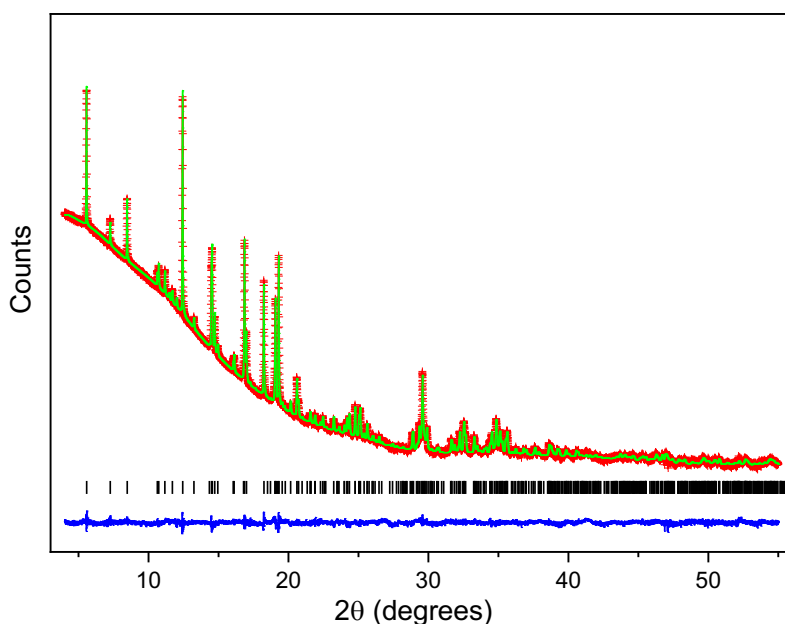


Figure 9a. 13. Observed, calculated and difference plots from the structural refinement of $\text{Li}_{3-x}\text{FeGa}_4\text{O}_9$ against SXRD data

Table 9a.13. Parameters from the structural refinement of $\text{Li}_{3-x}\text{FeGa}_4\text{O}_9$ sample against synchrotron powder diffraction data

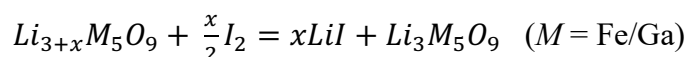
Atom	site	x	y	z	Fraction	B_{iso}
Ga1	8f	0.1171(1)	0.3341(2)	0.2900(4)	1	0.36(3)
Ga2	8f	0.3572(1)	0.3330(2)	0.2119(4)	1	0.36(3)
Fe3	4e	0	0.0697(3)	0.25	1	0.1
Li1	8f	0.2529(22)	0.0902(21)	0.2177(50)	1	0.1
Li2	4e	0	0.5844(36)	0.25	1	0.1
O1	8f	0.1019(7)	0.1808(7)	0.1292(18)	1	0.90(8)
O2	8f	0.3575(6)	0.1823(8)	0.3702(20)	1	0.90(8)
O3	8f	0.2297(7)	0.4117(9)	0.1465(15)	1	0.90(8)
O4	8f	0.4282(6)	0.4446(8)	0.4311(18)	1	0.90(8)
O5	4e	0	0.4168(15)	0.25	1	0.90(8)
$\text{Li}_{3-x}\text{FeGa}_4\text{O}_9$ — space group $C2/c$ (#15) $a = 13.0561$ (1) Å, $b = 11.1857$ (1) Å, $c = 5.2153$ (3) Å, $\beta = 90.9320$ (7)° volume = 761.757 (25) Å ³ Formula weight= 499.545 mol ⁻¹ , $Z = 4$ Radiation source: synchrotron X-ray, $\lambda = 0.8268$ Å Temperature: 298 K $R_p = 0.82$ %, $wR_p = 1.17$ %, $R_{\text{Bragg}} = 0.58$						

Table 9a.14. Table of ICP-MS data for lithium intercalation

Sample	Elements		
	Li	Fe	Ga
Li ₃ Fe ₅ O ₉	2.99	5	--
Li _{3+x} Fe ₅ O ₉	3.78	5	--
Li ₃ Fe ₂ Ga ₃ O ₉	2.93	2	2.50
Li _{3+x} Fe ₂ Ga ₃ O ₉	4.51	2	2.51

An increase in the lithium concentration for both Li_{3+x}Fe₅O₉ and Li_{3+x}Fe₂Ga₃O₉ was observed in comparison to Li₃Fe₅O₉ and Li₃Fe₂Ga₃O₉. These results confirm lithium intercalation in the structure.

Iodometric titrations: To check the reversibility of lithium cations intercalation and to further quantify the reversible lithium cations, Li_{3+δ}Fe_{5-x}Ga_xO₉ phases were treated with a known concentration of iodine in acetonitrile. The remaining iodine in solution was titrated against a standardised thiosulphate solution.



Concentration of thiosulphate solution used = 0.0106 (M)

Table 9a.15. Titrations table for Li_{3+x}Fe₅O₉

Li _{3+x} Fe ₅ O ₉ taken (mg)	I ₂ (mg)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
17.5	23.1	20	15.8	0.35
18.9	27.7	20	18.8	0.44
27.6	32.2	20	22.1	0.30

Table 9a.16. Titrations table for Li_{3+x}Fe₄GaO₉

Li _{3+x} Fe ₄ GaO ₉ taken (mg)	I ₂ (mg)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
17.4	32.3	20	23.2	0.19
20	23.4	20	16.2	0.27
20.4	28.7	20	20.1	0.29

Table 9a.17. Titrations table for Li_{3+x}Fe₃Ga₂O₉

Li _{3+x} Fe ₃ Ga ₂ O ₉ taken (mg)	I ₂ (mg)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
19.4	28.4	20	17.2	1.03
21.6	30.1	20	17.5	1.17
27.4	25.8	20	14.1	0.96

Table 9a.18. Titrations table for $\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$

$\text{Li}_{3+x}\text{Fe}_2\text{Ga}_3\text{O}_9$ taken (mg)	I_2 (mg)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
18.2	26.4	20	11.5	2.56
22.1	24.4	20	8.4	2.53
24.5	23.7	20	8.1	2.21

Table 9a.19. Titrations table for $\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$

$\text{Li}_{3+x}\text{FeGa}_4\text{O}_9$ taken (mg)	I_2 (mg)	Acetonitrile solution(mL)	Thiosulphate solution consumed(mL)	Li intercalated (x)
20.8	26.1	20	15.4	1.05
23.3	28.2	20	17.5	0.90
31.7	28.6	20	14.6	1.16

Table 9a.20 Table of ICP-MS data for lithium deintercalation

Sample	Elements		
	Li	Fe	Ga
$\text{Li}_3\text{Fe}_5\text{O}_9$	2.33	5	--
$\text{Li}_{3-x}\text{Fe}_5\text{O}_9$	1.62	5	--
$\text{Li}_{3-x}\text{Fe}_5\text{O}_9 + \text{LiI}$	1.96	5	--
$\text{Li}_3\text{Fe}_2\text{Ga}_3\text{O}_9$	2.62	2	2.50
$\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$	2.21	2	2.50
$\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9 + \text{LiI}$	2.49	2	2.46

Table 9a.21. Table of titration values of reversibility check of $\text{Li}_{3-x}\text{Fe}_5\text{O}_9$ ($3-x = 1.62$ determined by ICP-MS data) [conc. of thiosulphate solution = 0.0106 (M)]

$\text{Li}_{1.62}\text{Fe}_5\text{O}_9$ taken (mg)	LiI (mg)	Thiosulphate solution consumed (mL)	Reversibly lithium intercalated (y)
53.4	300	4.7	0.8143
70.4	300	5.6	0.7360

Table 9a.22. Table of titration values of reversibility check of $\text{Li}_{3-x}\text{Fe}_2\text{Ga}_3\text{O}_9$ ($3-x = 2.21$ determined by ICP-MS data) [conc. of thiosulphate solution = 0.0106 (M)]

$\text{Li}_{2.21}\text{Fe}_2\text{Ga}_3\text{O}_9$ taken (mg)	LiI (mg)	Thiosulphate solution consumed (mL)	Reversibly lithium intercalated (y)
42.9	300	2.8	0.6674
48.1	300	3.6	0.7653

ICP-MS and iodometric data confirms reversible lithium insertion and extraction in Li_3Fe_5 .
 $_x\text{Ga}_x\text{O}_9$.

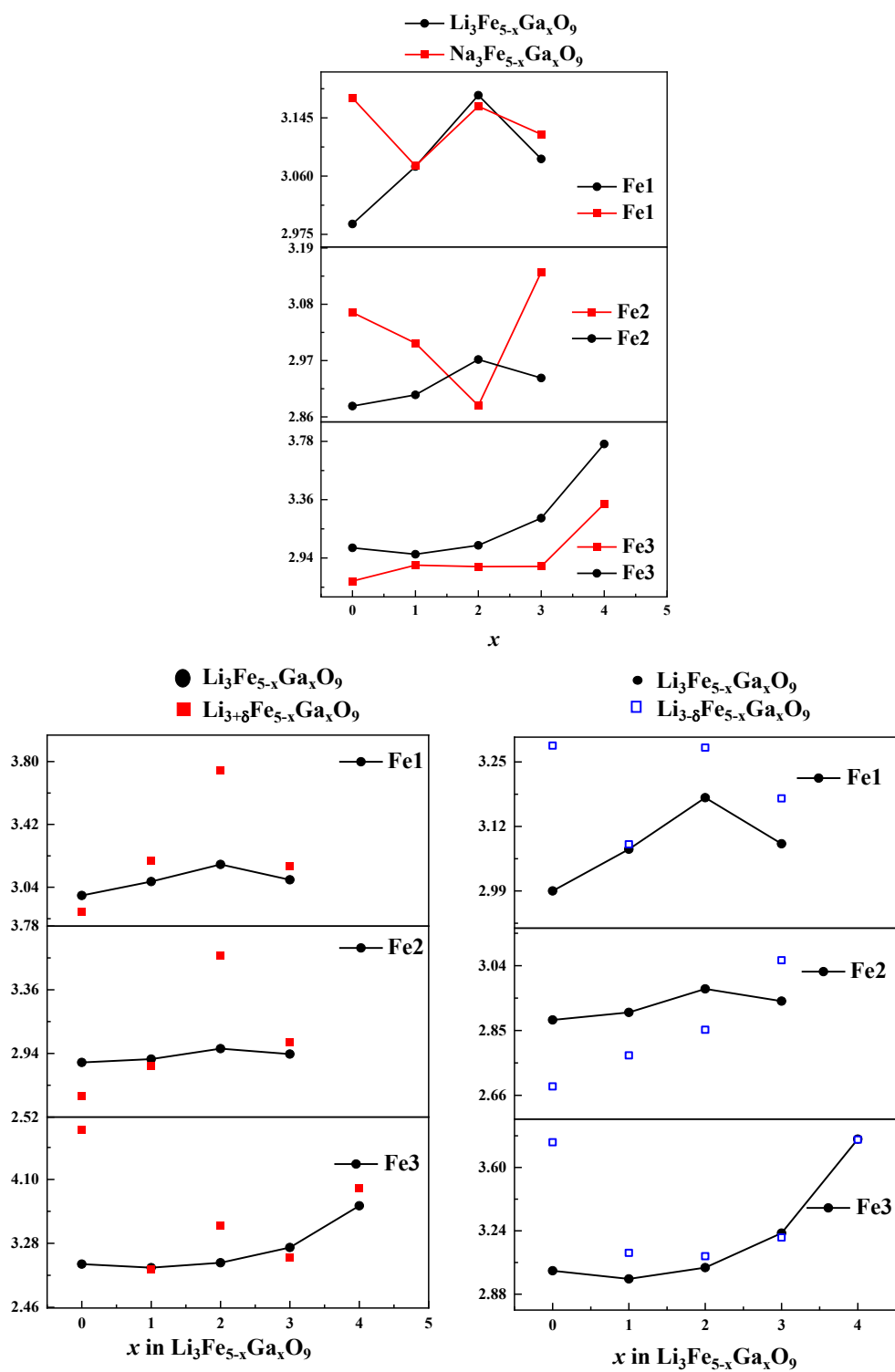


Figure 9a. 14 Bond valence sum comparison of $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Na}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ samples (top); comparison of Fe-BVS in $\text{Li}_{3+\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ (bottom left); comparison of Fe-BVS in $\text{Li}_{3-\delta}\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ and $\text{Li}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_9$ (bottom right)

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