

Cation Exchange Chemistry as a Route to Induce Noncentrosymmetry in Layered Perovskite Oxides

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This work is focused on the synthesis and characterisation of $n = 2$ Layered Perovskite Oxides.

KNdM_2O_7 ($M = \text{Ta}, \text{Nb}$) were synthesized by a two-step cation exchange reaction from RbNdM_2O_7 via NaNdM_2O_7 . The K-phases adopt a polar $Im2m$ structure. A competition between the requirement of bonding optimization of the K^+ and Nd^{3+} -cation sites is demonstrated.

$A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb}, \text{Li}, \text{Na}, \text{K}$) were synthesized and their structures were determined using neutron diffraction and second harmonic generation data. All four compounds adopt noncentrosymmetric crystal structures. Comparison with the spherical Nd-analogues demonstrates that although the Rb and Li phases adopt polar structures described in the same space group, the presence of the asymmetric Bi^{3+} enhances the polarity in these structures. In the $\text{NaBiNb}_2\text{O}_7$ phase, the noncentrosymmetry is generated from the $6s^2$ electronic configuration of the Bi^{3+} . The KBiNb_2O_7 phase exhibits frequent “axis switch” stacking faults in which the $(0, \frac{1}{2}, z)$ stacking changes to $(\frac{1}{2}, 0, z)$ stacking and *vice versa*.

Members of the solid solution with composition $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ were synthesized and demonstrated that a structural transformation takes place from hybrid improper $A2_1am$ structure to proper $Pna2_1$ structure with Ca-substitution. Some of the room temperature $A2_1am$ phases in this series of compounds were shown to have a phase transition to the $Pna2_1$ structure at low temperature. Similar phase transition behaviour was observed for the $\text{Li}_2\text{SrNb}_2\text{O}_7$ phase. The polarity in the $Pna2_1$ phase is driven by the SOJT effect of the $4d^0\text{-Nb}^{5+}$ cation. Substitution of $4d\text{-Nb}$ by $5d\text{-Ta}$ in the $\text{Li}_2\text{SrNb}_2\text{O}_7$ structure lowers the SOJT effect which lowers the stability region of the $Pna2_1$ phase.

The lifting of inversion symmetry in the polar structures of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ occurs via two different mechanisms: a trilinear coupled hybrid-improper mechanism for the Li-phase and a more conventional SOJT-driven mechanism for the Na-phase. The operation of these two different mechanisms in materials with a common $\text{La}(\text{TaTi})\text{O}_7$ core suggests they compete against each other, and further suggests this competition is also occurring in other hybrid-improper ferroelectric phases which contain SOJT active cations.

$\text{MnCaTa}_2\text{O}_7$ was synthesized by a topochemical cation exchange reaction from $\text{Li}_2\text{CaTa}_2\text{O}_7$. $\text{MnCaTa}_2\text{O}_7$ adopts a polar $P2_1nm$ structure where Mn^{2+} cations are ordered in chequerboard arrangement. Mn^{2+} magnetic moments order antiferromagnetically below 56 K. Further cation exchange reactions were performed to synthesize $\text{MnCaTa}_2\text{O}_7$ ($M = \text{Fe}, \text{Co}, \text{Zn}$). Successful synthesis of these phases indicates that the cation exchange chemistry could be used to incorporate divalent transition metal cations within the distorted double perovskite frameworks of $n = 2$ Ruddlesden-Popper phases.

Declaration

The work described in this thesis was carried out at the Inorganic Chemistry Laboratory at the University of Oxford between October 2018 and January 2022 under the supervision of Professor Michael A. Hayward. All the work presented in this thesis is my own except where I have either acknowledged help from a named person or given reference to a published source. None of the work has been submitted by the author for any degree at any other university.

Subhadip Mallick

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To Maa and Baba

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Chapter 1 – Introduction

1.1 Perovskites

Perovskite is a mineral of formula CaTiO_3 . As with many minerals, Perovskite has given its name to a family of compounds called *Perovskites*, which have a general formula close to or derived from the composition ABX_3 . A is usually a large cation, B is usually a medium-sized cation and X is an anion.¹ In a typical ABO_3 perovskite oxide, the A -cations are typically alkaline earth metals or lanthanides and the B -cations are usually transition metals. In this structure, the A -cations sit in 12-coordinate sites, while the B -cations sit in 6-coordinate sites forming a 3-dimensional array of corner linked BO_6 octahedra. A “perfect” perovskite network adopts a cubic structure described in $Pm\bar{3}m$ space group. One such example of aristotype structure is the room temperature structure of SrTiO_3 ,² shown in Figure 1.1. An ideal perovskite structure requires an ideal ratio in the sizes of the A and B -cations, which is defined by the Goldschmidt tolerance factor.³ If we consider a cubic unit cell of ABO_3 perovskite, the B -O bond distance, $\langle B - O \rangle$ is equal to $a/2$ (Figure 1.1) and the A -O bond distance $\langle A - O \rangle$ is equal to $a/\sqrt{2}$ (where a is the cubic unit cell parameter); which gives the following relation: $\langle A - O \rangle = \sqrt{2} \langle B - O \rangle$. The tolerance factor (t) is defined as:

$$t = \frac{\langle A - O \rangle}{\sqrt{2} \langle B - O \rangle} = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)}$$

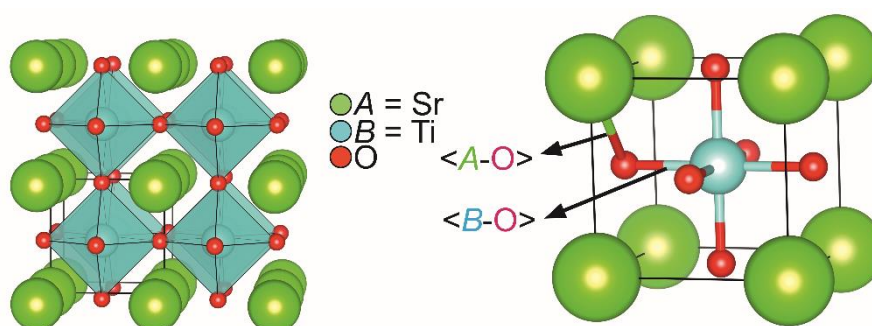


Figure 1.1. (Left) Cubic perovskite structure of SrTiO_3 . (Right) $\langle A-O \rangle$ and $\langle B-O \rangle$ bond lengths of an ideal ABO_3 perovskite.

1.2 Layered perovskite

The Dion-Jacobson structure is one of the derivatives of the 3D perovskite structure. The general formula of Dion-Jacobson phases can be described as $A'A_{n-1}B_nO_{3n+1}$, where n is the number of perovskite slabs in each perovskite unit.^{4,5} In the Dion Jacobson structure, adjacent perovskite blocks have a (0, 0, z) stacking as shown in Figure 1.2. The aristotype structure of this family is described in $P4/mmm$ space group. In the Dion-Jacobson structure, the A' -cation is usually a large alkali metal ion e.g. Rb^+ or Cs^+ , which occupies an 8-coordinate interlayer site. The large monovalent cations in the A' -site are quite mobile due to low charge density and small lattice energy, which make the Dion-Jacobson phases suitable precursors for cation exchange reactions.

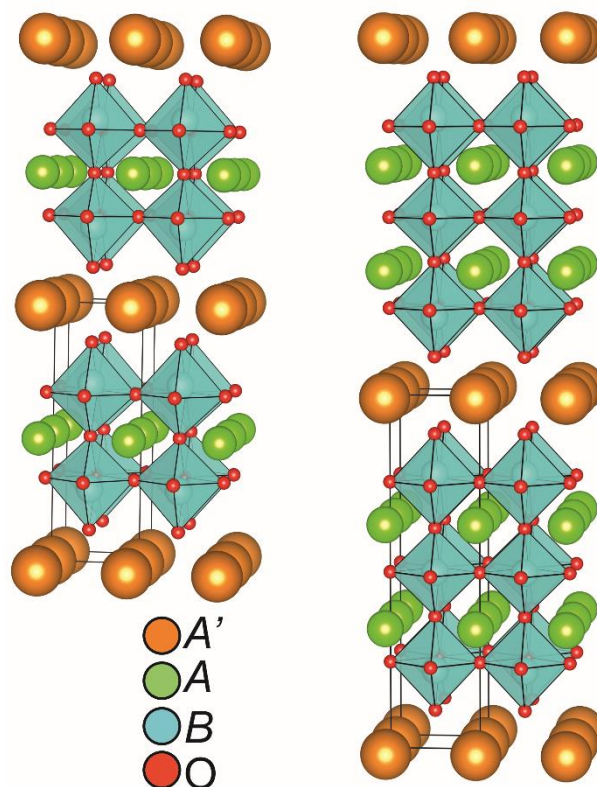


Figure 1.2. (Left) $n = 2$ and (right) $n = 3$ Dion-Jacobson structures.

The Ruddlesden-Popper series of phases⁶ are another modification of the 3D perovskite structure. The general formula of this class of layered perovskites can be expressed as $A'A_{n-1}B_nO_{3n+1}$ where n is the number of perovskite slabs in each perovskite unit. Ruddlesden-Popper

structures can be viewed as an intergrowth of ABO_3 perovskite blocks and $A'O$ rock salt layers. In this structure, the A' -cations usually sit in 9-coordinate sites, whereas the A -cations occupy the traditional 12-coordinate sites as shown in Figure 1.3. The A -site and the A' -site cations can be the same (hence the composition will be $A_3B_2O_7$ for $n=2$ phase, Figure 1.3) or different (composition $A'_2AB_2O_7$ for $n=2$ phase, Figure 1.3) chemical species. If the A' -cation size is small, (e.g. Li^+)⁷ these ions can sit in pseudo tetrahedral sites in between the perovskite blocks (e.g. $Li_2SrTa_2O_7$) as shown in Figure 1.3. In the Ruddlesden-Popper structures, the adjacent perovskite blocks are related by a $(\frac{1}{2}, \frac{1}{2}, z)$ translational stacking. The aristotype Ruddlesden-Popper structure is described in the tetragonal $I4/mmm$ space group.

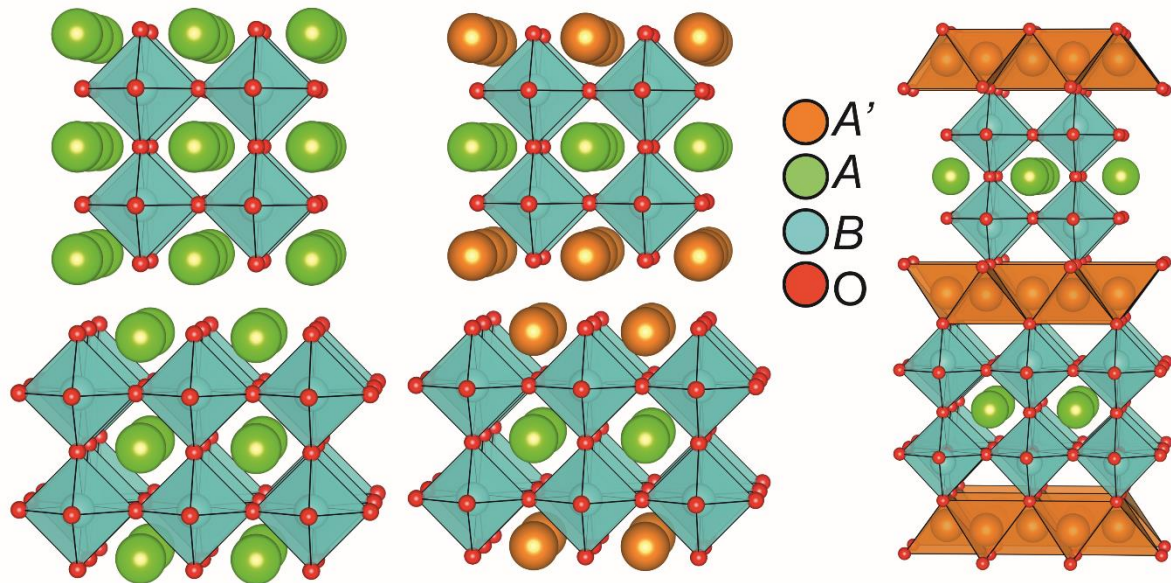


Figure 1.3. $n = 2$ Ruddlesden-Popper structures with general formula $A_3B_2O_7$ (left), $A'_2AB_2O_7$ (middle) and $A'_2AB_2O_7$ with tetrahedral A' -site (right).

1.3 Octahedral tilting distortions

For a “perfect” cubic perovskite, the tolerance factor (t) is equal to 1. A value of $t < 1$, indicates that the A -cation is too small for the 12-coordinate site. Hence the bonding of the A -site is not optimized. The only way to shorten the A -O bond length without changing the B -O bond length is to have rotation and tilting of BO_6 octahedra while maintaining their corner-sharing connectivity as described next. The tilting distortion of perovskites and related structures can

be described using Glazer notation.^{8–10} In the ABO_3 perovskite structure the BO_6 octahedra can tilt along the three Cartesian axes. Due to the corner-sharing nature of BO_6 octahedra, the octahedral tilting distortion in a plane is cooperative; meaning if an octahedron has a clockwise rotation, its four neighbouring octahedra in that plane (say xy) must have an anti-clockwise rotation. However, the adjacent octahedra perpendicular to this plane (along the z -direction) are not restricted and can tilt in either a clockwise or an anti-clockwise direction. In Glazer notation, the rotations about each axis are described by two parameters. The first of these parameters is a letter specifying the magnitude of the rotation about that axis, relative to the magnitude of the rotations about the other Cartesian axes. The second parameter is a superscript indicating whether the rotations of the adjacent layers are in the same or opposite directions. A positive superscript (+) indicates that the rotations of two neighbouring octahedra, along the tilt axis, are in the same direction (called in-phase, Figure 1.4), while a negative superscript (–) is used when the neighbouring octahedra tilt in opposite directions (called out-of-phase, Figure 1.4). A zero (0) superscript is used when no rotations occur about an axis.

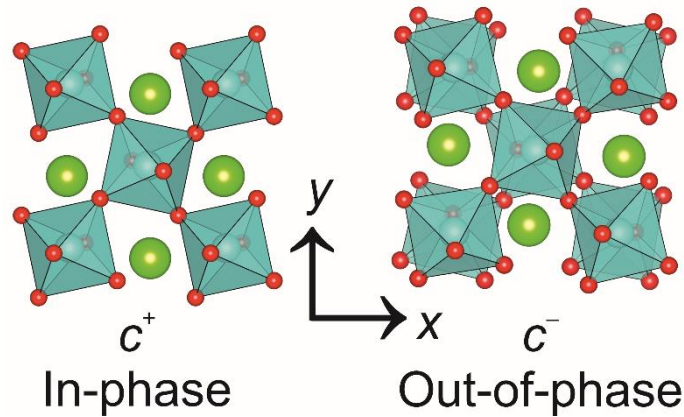


Figure 1.4. In-phase and out-of-phase tilting distortion of BO_6 octahedra along the z -direction.

For example, an $a^+a^+a^+$ notation means that the tilting distortions along all the Cartesian axes are in phase with the same magnitude of tilting distortions. An $a^-a^-c^+$ notation indicates that along x and y axes the rotation of BO_6 octahedra are out of phase but they have the same

magnitude of tilting distortion and along the z-direction, the tilt is in phase with a different magnitude of tilting distortion.

In layered perovskites, for example, Dion-Jacobson or Ruddlesden-Popper phases, the tilting distortions in individual perovskite blocks can be described in the same way as in the ABO_3 perovskites. But there is an additional complexity when it comes to expressing the tilting distortion of the whole structure as the adjacent perovskite blocks do not necessarily have the same tilting distortion. Let's take the example of room temperature structures of $CsNdNb_2O_7$ and $RbNdNb_2O_7$.¹¹ The crystal structures of $CsNdNb_2O_7$ and $RbNdNb_2O_7$ can be described in $P2_1am$ and $I2cm$ space groups respectively. The Cs-phase has $a^-a^-c^+$ tilting distortions in both the perovskite layers as shown in Figure 1.5. In contrast, layer 2 of the Rb-phase, although has local $a^-a^-c^+$ tilting, with respect to layer 1, the senses of $a^-a^-c^+$ tilting distortions are inverted (Figure 1.5). A negative (-) sign is used in front of the tilting distortions to indicate this inversion of the sense of tilting.

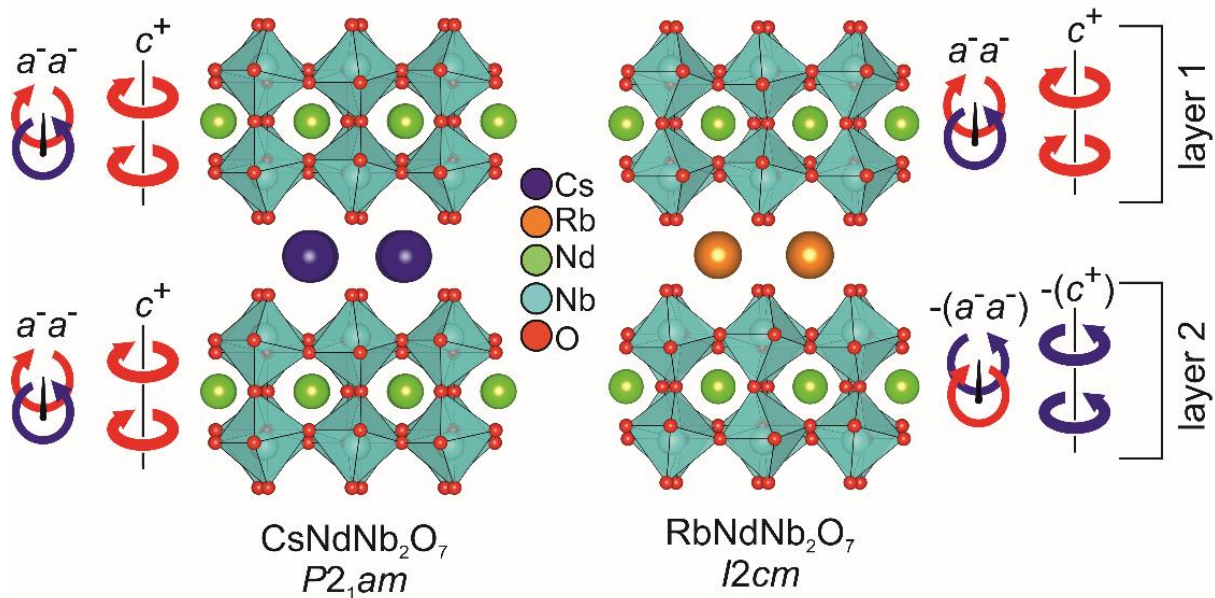


Figure 1.5. The $P2_1am$ and $I2cm$ structures of $CsNdNb_2O_7$ and $RbNdNb_2O_7$ respectively.

1.4 Ferroelectrics and magnetoelectric multiferroic materials

1.4.1 Ferroelectric materials

Ferroelectrics are a class of compounds which exhibit spontaneous and switchable electrical polarisation. Ferroelectrics are used in capacitors, electromechanical transducers and actuators¹² because the change in electric polarisation is accompanied by a change in shape. For a material to be ferroelectric, the crystal structure must be noncentrosymmetric.¹³ However, for macroscopic polarisation, noncentrosymmetry is not sufficient. We can elaborate on this point by taking the example of some molecular symmetries. In an octahedral symmetry, the inversion point is present at the centre of the octahedra, hence it is centrosymmetric, thus it cannot be polar. In a tetrahedral symmetry, while there is no inversion centre, it is not polar because the polarity of any two dipoles is cancelled out by the polarity of the other two dipoles. However, in a trigonal pyramidal symmetry, there is no centre of inversion and it is polar as shown in Figure 1.6.

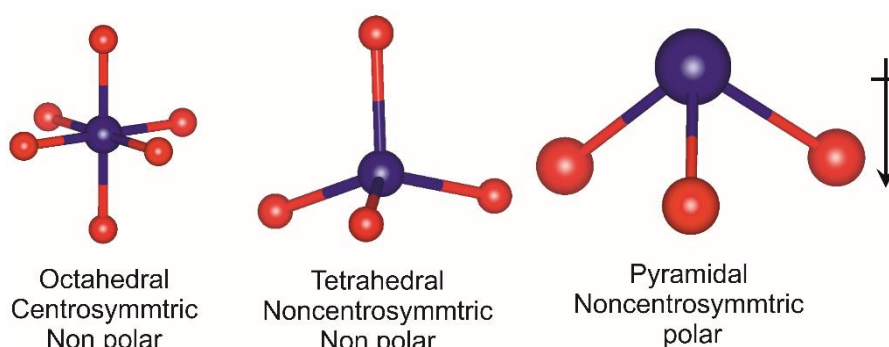


Figure 1.6. Octahedral, tetrahedral and pyramidal symmetry describing the distinction between noncentrosymmetry and polarity.

Only a small group of noncentrosymmetric crystal classes are polar. Hence, in order to exhibit ferroelectricity, the compound needs to crystallize in one of the polar point groups.¹⁴

Synthesizing solids with noncentrosymmetric crystal structures is very challenging because centrosymmetric crystal packing is generally more stable than acentric analogues. The most common approach to break inversion symmetry is to use a Second-Order Jahn Teller (SOJT) distortion.¹³ If a transition metal ion with d^0 electronic configuration resides in an octahedral coordination environment of oxide ions, the transition metal displaces away from the centre of the octahedra because it would allow the empty metal d -orbitals to hybridize with the filled

oxygen 2p orbitals, which stabilises the system by lowering its energy as well as lowering the crystal symmetry. Perovskite ferroelectrics e.g. BaTiO₃ and PbTiO₃ are classical examples of SOJT-driven ferroelectrics.

The high-temperature structure of both BaTiO₃ and PbTiO₃ perovskite can be described in cubic $Pm\bar{3}m$ space group. BaTiO₃ has three phase transitions, from cubic to tetragonal (393 K), (Figure 1.7) tetragonal to orthorhombic (278 K) and orthorhombic to rhombohedral (183 K); whereas PbTiO₃ has only one, cubic to tetragonal at 766 K. In both cases, the hybridisation between Ti 3d states with O 2p states is essential to allow the ferroelectric distortion. In BaTiO₃, the Ba-O interaction is largely ionic. However, in PbTiO₃, Pb 6s states hybridise with O 2p, which indirectly changes the Ti-O interaction.

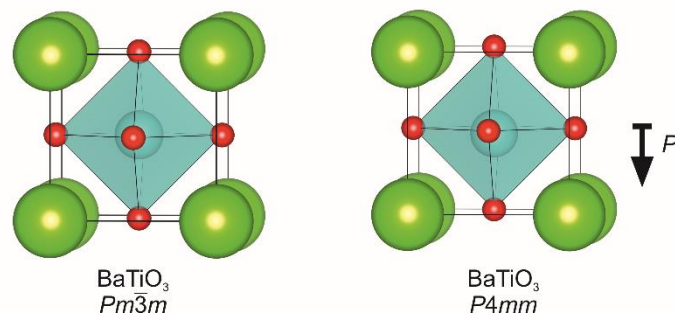


Figure 1.7. High-temperature paraelectric $Pm\bar{3}m$ and tetragonal ferroelectric $P4mm$ symmetry structure of BaTiO₃.

Both materials are also ferroelastic. Tetragonal BaTiO₃ has a 1% c/a strain, whereas, tetragonal PbTiO₃ shows a large 6% c/a strain. Without the strain, the rhombohedral phase has lower energy in both BaTiO₃ and PbTiO₃.¹⁵ However, the smaller ionic radius of Pb²⁺ compared to Ba²⁺ leads to a larger strain in PbTiO₃, which stabilizes the tetragonal phase over the rhombohedral phase.

It is observed that two changes occur simultaneously in this kind of ferroelectric phase transition: atomic displacement causing the polarisation, and the change in unit cell size and shape resulting in strain. The polarisation is the primary order parameter here and the strain is a secondary order parameter coupled to the polarisation. The strain only appears in the presence

of the ferroelectric polarisation but the polarisation could appear in the absence of strain. Since the polarisation is the primary order parameter, BaTiO₃ can be considered as a proper ferroelectric and an improper ferroelastic.

It is also possible that the polarisation is a secondary order parameter in a ferroelectric phase transition. These are known as improper ferroelectrics.¹⁶ One example of such improper ferroelectrics is the hexagonal manganite, YMnO₃. This phase undergoes a phase transition from high-temperature paraelectric $P6_3/mmc$ to low temperature ferroelectric $P6_3cm$, which is accompanied by a tripling of the unit cell volume. The primary order parameter for this phase transition transforms as the K_3 irreducible representation of the high symmetry $P6_3/mmc$ structure.¹⁷ The K_3 distortion mode buckles the MnO₅ trigonal bipyramids, which also displaces the Y³⁺ cations along the c -direction as shown in Figure 1.8. The polarisation arises from the coupling between this K_3 mode and the polar Γ_2^- distortion mode. The polar Γ_2^- mode is only stabilized in presence of the K_3 mode. Hence the Γ_2^- distortion mode is secondary order parameter and YMnO₃ is an improper ferroelectric. Theoretical calculations show that there is hardly any hybridisation between Mn-O or Y-O orbitals.¹⁸ Also, neither Mn³⁺ nor Y³⁺ has any “stereo-active” lone pair. Hence the ferroelectric phase transition cannot be proper.

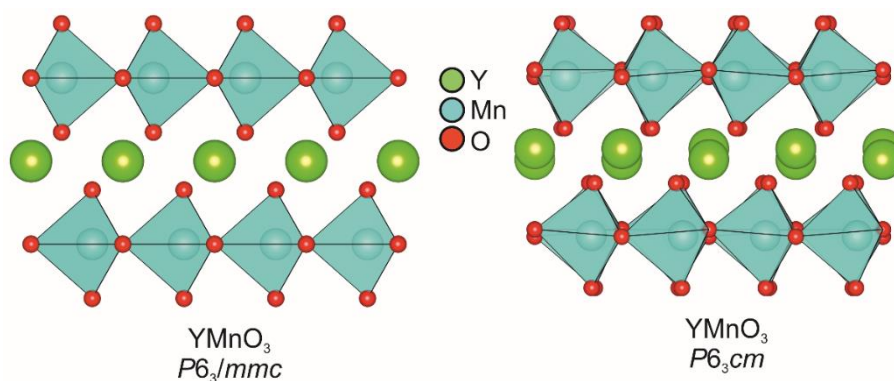


Figure 1.8. The paraelectric $P6_3/mmc$ and ferroelectric $P6_3cm$ structure of YMnO₃.

1.4.2 Magnetoelectric multiferroic materials

The term “magnetoelectric multiferroic” is used to describe the materials in which spontaneous electrical and magnetic, generally ferromagnetic polarisations occur in the same phase.¹⁹ This

means they have spontaneous magnetisation which can be reoriented by applying a magnetic field as well as by applying an electric field. One typical example of a multiferroic compound is BiFeO_3 , in which ferroelectricity is induced by the stereo-active Bi^{3+} cations and the antiferromagnetic order is due to the Fe^{3+} cations.^{20,21} Multiferroic materials have potential applications in multiple state memory devices, transducers, actuators and magnetic sensors.²² Despite the multifunctional properties of magnetoelectric multiferroics, only a few have been reported. This is because of the contraindicative requirement of a material to be simultaneously ferroelectric and ferromagnetic.²³

Ferromagnetism requires a material to have unpaired electrons whose magnetic moments are coupled together to yield a collective spontaneous response. On the other hand, the common approach to induce ferroelectricity is to use the SOJT mechanism where the presence of a d^0 transition metal cation (Ti^{4+} , Nb^{5+} , W^{6+}) or a post-transition metal with a stereo-active lone pair (Pb^{2+} , Bi^{3+}) is necessary, as discussed in the previous sections. Neither of these approaches are directly compatible with magnetism. Hence, there has been a great effort to find alternative ways to prepare solids with noncentrosymmetric structures without any kind of electronic requirement. One of the most promising approaches is the use of a trilinear coupling mechanism in which the inversion symmetry is broken by a combination of lattice distortions in layered perovskite structures as discussed later.

1.5 Hybrid improper ferroelectricity

In a hybrid improper ferroelectric, the polarisation is coupled to two other non-polar distortion modes.²⁴ These non-polar distortion modes are usually the primary order parameters in a ferroelectric phase transition. Octahedral tilting and rotations can be considered as the non-polar distortion modes in perovskites and layered perovskite structures. This approach is versatile because there is no electronic requirement for the constituent cations. Although layered perovskites have been investigated mostly as candidates for hybrid improper

ferroelectrics, 3D perovskites also adopt polar structures under strict ordering criteria, as will be discussed now.

Tilting and rotation of BO_6 octahedra in simple ABO_3 perovskites cannot generate polar structures.²⁵ The most common tilting pattern observed in hybrid improper ferroelectric structures is $a^-a^-c^+$. The same tilting pattern in ABO_3 perovskite (e. g. $GdFeO_3$) results in $Pnma$ symmetry structure. Such tilting causes displacement of the A -site cations, which generates local dipoles, but the dipoles in adjacent layers are equal and oriented in opposite directions as shown in Figure 1.9, resulting in zero macroscopic polarisation.

The $a^-a^-c^+$ tilt pattern combined with the layered ordering of A -site cation can generate macroscopic polarisation. However, the synthesis of cation ordered perovskites is challenging because, at high temperatures, cation disordered structures are entropically favoured. Cation ordering is only possible if there is a significant difference in charge and size of the respective cations.^{26,27} There are a few examples of layered A -site cation ordered perovskite which are accompanied by a rock salt ordering of B -site cations as well. Hence the general composition of these double-double perovskites will be $AA'BB'O_6$. It is observed that for layered ordering of the A -site cations, one of the B -site cations must have d^0 electronic configuration, which adds additional constraint. Hence, the A , A' , B and B' cations have to be chosen in such a way that there is a significant difference in charge and size between A -and A' -cations, and B -and B' -cations; also, the average size difference between the A -site and B -site cations will be such that the structure will adopt an $a^-a^-c^+$ tilting. The most widely studied examples of such double-double perovskites are $NaLnMnWO_6$, which adopt a polar $P2_1$ symmetry structure.^{28–30} In this case, also, the local dipoles on the A -O and A' -O layers are opposite to one another. But the magnitudes of the dipoles are not the same because of the different identity of the A -and A' -cations as shown in Figure 1.9; hence there is a finite macroscopic polarisation.

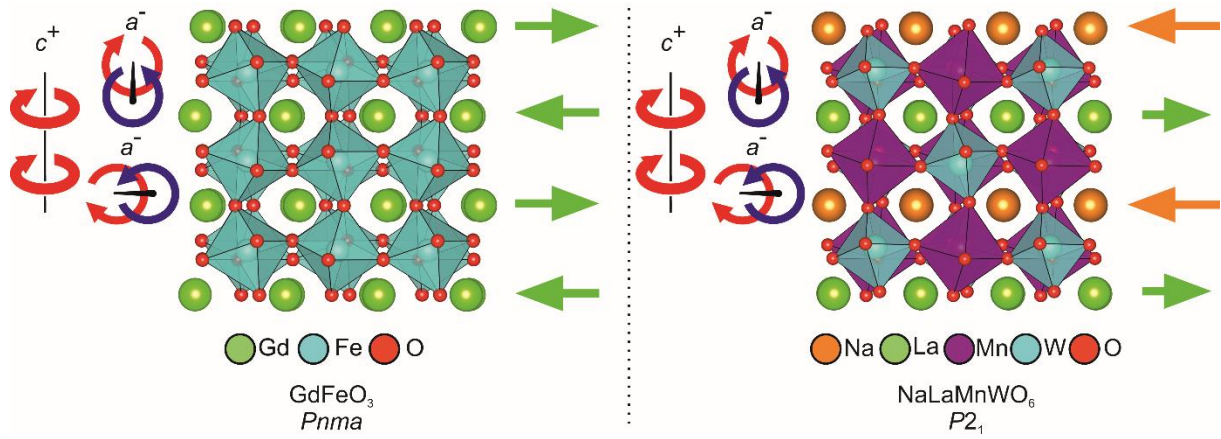


Figure 1.9. *Pnma* and *P2₁* structures of GdFeO₃ and NaLaMnWO₆ respectively.

Now let's see how the trilinear-coupled hybrid improper mechanism breaks inversion symmetry in layered perovskites. In contrast to ABO_3 perovskites, in layered perovskites, the local polarities do not necessarily cancel out between adjacent layers, even without complex cation ordering. One typical example is the polar $n = 2$ Ruddlesden-Popper phase $Ca_3Mn_2O_7$. It adopts $A2_1am$ structure with $a^-a^-c^+/a^-a^-c^+$ tilting of MnO_6 octahedra.^{31,32} The $A2_1am$ structure can be analysed in terms of the distortion modes which need to be applied in order to get the distorted structure from the aristotype $I4/mmm$ symmetry structure. The MnO_6 octahedra adopt an $a^-a^-c^0/a^-a^-c^0$ tilting distortion in the xy -plane, described by the X_3^- irreducible representation of the aristotype $I4/mmm$ structure; and an in-phase $a^0a^0c^+/a^0a^0c^+$ rotation around the z -axis, described by the X_2^+ irreducible representation. The X_3^- and X_2^+ distortion modes are individually non-polar but the combination of these two distortion modes results in a structure that cannot be described in a centrosymmetric space group. The presence of these two nonpolar distortion modes in combination couple to a third polar Γ_5^- distortion mode via a trilinear coupling mechanism to yield the hybrid improper polar $A2_1am$ structure of $Ca_3Mn_2O_7$.

Ca^{2+} cations occupy the 12-coordinated A -site as well as the 9-coordinated A' -site. Each perovskite block has three Ca-O layers; two of which have polarisation in one direction and the other Ca-O layer has polarisation in the opposite, as shown in Figure 1.10. Hence each

perovskite block has a net polarity and the direction of polarity is the same in the adjacent perovskite blocks. Hence the $\text{Ca}_3\text{Mn}_2\text{O}_7$ structure has an overall macroscopic polarisation.

It should also be noted that it is also possible to align the net polarisation of the adjacent perovskite blocks in an opposite direction as shown in Figure 1.10. In that case, the bulk structure will be anti-polar. One example of an anti-polar compound is topochemically prepared $\text{La}_3\text{Ni}_2\text{O}_{5.5}\text{F}_{3.5}$,³³ which adopts a $Pnam$ symmetry structure with $a^-a^-c^+/a^-a^-(-c^+)$ tilting distortion of the NiO_6 octahedra.

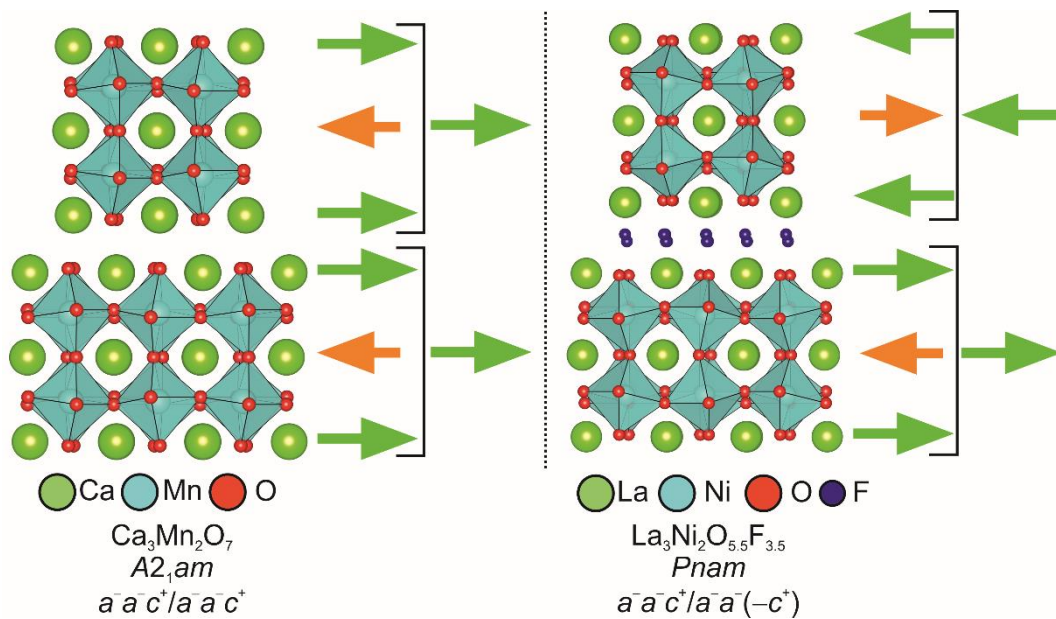


Figure 1.10. The polar $A2_1am$ and anti-polar $Pnam$ structures of $\text{Ca}_3\text{Mn}_2\text{O}_7$ and $\text{La}_3\text{Ni}_2\text{O}_{5.5}\text{F}_{3.5}$ respectively. The arrows indicate the direction of displacement of the cations in that layer.

Utilising tilting distortions of layered perovskites to prepare noncentrosymmetric phases is very attractive since it is free of electronic requirements. However, in order to induce polarity by a trilinear-coupled mechanism, a very small structural tolerance factor (t) is required. A recent study by Yoshida *et. al.* suggested that the Curie temperature (T_c) of $n = 2$ hybrid improper ferroelectrics is inversely proportional to the structural tolerance factor (t)³⁴ and $t = 0.89$ is the highest limit of tolerance factor for which an $A2_1am$ structure could be stabilised. There are two ways to lower the tolerance factor: either by taking a smaller A-site cation or by taking a larger B-site cation. Pitcher *et. al.* have investigated the tuning of tilting distortions by

changing the tolerance factor of a Fe^{3+} Ruddlesden-Popper phase to induce ferroelectricity.³⁵ $\text{La}_2\text{BaFe}_2\text{O}_7$ has an undistorted $I4/mmm$ structure, but the structure of $\text{Tb}_2\text{SrFe}_2\text{O}_7$ can be described in $P4_2/mnm$ space group with $a^-b^0c^0/b^0a^-c^0$ tilting distortion. Further substitution of Sr^{2+} by smaller Ca^{2+} to synthesize the $\text{Tb}_2\text{CaFe}_2\text{O}_7$ phase was not experimentally successful, although this phase was computationally predicted to adopt an $A2_1am$ symmetry structure with the desired $a^-a^-c^+/a^-a^-c^+$ tilting distortions. It was not possible to drive the framework to adopt the polar $A2_1am$ structure with $a^-a^-c^+/a^-a^-c^+$ tilting distortion by A-cation substitution, as the desired tolerance factor is extremely small. The most distorted all- Fe^{3+} compound $(\text{Ca}_{0.6}\text{Sr}_{0.4})_{1.15}\text{Tb}_{1.85}\text{Fe}_2\text{O}_7$ was mixed with $\text{Ca}_3\text{Ti}_2\text{O}_7$ (Ti^{4+} is SOJT active) in order to achieve the polar $A2_1am$ structure which showed magnetoelectric multiferroic behaviour. This indicates that the stabilisation of the $A2_1am$ structure with only paramagnetic transition metals in the B-site is only possible in a few exceptional cases.

Although, hybrid improper ferroelectric mechanism does not impose any electronic constraints on the constituent elements; in practice, it is observed that the large magnitude of tilt required to stabilise the polar phase is only possible by including a large B-site cation in the layered perovskite framework. As the ionic radius of transition metal ions declines across the series, the suitable cations for the B-site of layered perovskites often are early transition metal cations in their group oxidation state. As a result, many of the reported hybrid improper ferroelectric phases contain Ti^{4+} ,³⁶ Zr^{4+} ,³⁷ Nb^{5+} or Ta^{5+} ^{11,38}. The presence of d^0 transition metal ions in hybrid improper ferroelectric phases indicates a competition between the trilinear-coupled hybrid-improper and the SOJT driven proper mechanism.

The requirement of a large magnitude of tilting distortions that are associated with the hybrid improper behaviour restricts the chemical diversity of trilinear-coupled hybrid-improper behaviour. One alternative approach to expand the family of hybrid improper ferroelectrics is

to move beyond the thermodynamic limits and investigate metastable phases synthesized by a soft chemical route.

1.6 Low-temperature topochemical synthesis

Traditionally, the synthesis of complex solid oxides is performed at very high temperatures. Although conventional ceramic synthesis has been extremely useful to prepare new functional materials, there are drawbacks to this conventional approach. Firstly, high-temperature reactions can only yield thermodynamically stable products, therefore metastable phases which may have interesting properties are not accessible via this route. Moreover, there is very little predictability for a thermodynamically controlled reaction. Hence the rational design of a particular reaction product is not generally possible in a high-temperature reaction.

Low-temperature solid-state reactions can utilize the differing solid-solid diffusion rates of different ions present in the structure. If a certain chemical species in the complex oxide is more mobile than the rest of the host lattice at a particular temperature, that species can be inserted into or removed from the host structure under conditions in which the rest of the structure stays practically immobile. Such chemical reactions are described as “topochemical” reactions^{39,40} because they reserve the basic structural framework before and after the reaction. Since there is a difference in reactivity between the host lattice and the mobile species, it is possible to have some kinetic control on the reaction products. The products in low-temperature reactions are metastable and usually not accessible by conventional high-temperature pathways.

Layered perovskites are suitable precursors for performing topochemical reactions. For example, the $n = 2$ Dion-Jacobson phase $\text{RbLaNb}_2\text{O}_7$ can undergo a reductive cation insertion when heated in the presence of a controlled amount of rubidium vapour to form $\text{Rb}_2\text{LaNb}_2\text{O}_7$.⁴¹ There is a change in stacking of the double-perovskite blocks associated with the Rb-insertion, from a Dion-Jacobson arrangement where the Rb^+ cations occupy 8-coordinate pseudo-cubic

sites to a Ruddlesden-Popper arrangement where the Rb^+ cations occupy the interlayer 9-coordinate sites within the rock salt layer as shown in Figure 1.11. The change in stacking sequence and the intercalation of a large cationic species demonstrate the relatively weak binding between the A' -cations and the perovskite blocks.

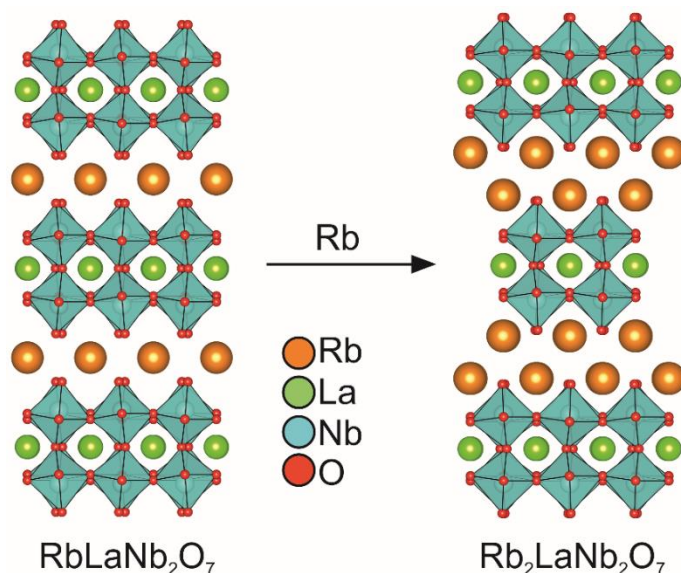


Figure 1.11. Reductive intercalation of rubidium into the Dion-Jacobson phase $\text{RbLaNb}_2\text{O}_7$.

1.6.1 Topochemical cation exchange reactions

Many layered perovskites e.g. Dion-Jacobson phases and Ruddlesden-Popper phases exhibit topochemical cation exchange reactions which lead to metastable phases with interesting functional properties. The interlayer cations in Dion-Jacobson phases are more mobile than the rest of the host lattice, hence it can be exchanged for other cations to make new kinetically stable phases. For example, the Rb^+ cation of $\text{RbNdNb}_2\text{O}_7$ can be exchanged by smaller Li^+ or Na^+ to synthesize metastable $\text{LiNdNb}_2\text{O}_7$ or $\text{NaNdNb}_2\text{O}_7$ by treating with a large excess of LiNO_3 or NaNO_3 respectively.⁴² This exchange reaction is driven by an increase in lattice enthalpy while a larger cation is exchanged by a smaller cation with the same charge. There is a change in stacking of the adjacent double perovskite blocks associated with this cation exchange reaction from a Dion-Jacobson stacking of the Rb-phase to a Ruddlesden-Popper stacking of the Li-or Na-phase. The Li^+ or Na^+ cations are too small to occupy the large pseudo-

cubic sites of the Dion-Jacobson structure; therefore, the perovskite blocks are rearranged to accommodate the smaller Li^+ or Na^+ cations in 4-coordinated tetrahedral sites of a pseudo-Ruddlesden-Popper framework. In addition to simple monovalent cation exchange reactions, it is also possible to intercalate charged layer of transition metal salts into the interlayer space via cation exchange reactions. For example, $(\text{CuCl})^+$ can be intercalated in the interlayer of $n = 2$ Dion-Jacobson phase, $\text{RbLaNb}_2\text{O}_7$ in exchange of Rb^+ to form $(\text{CuCl})\text{LaNb}_2\text{O}_7$ ⁴³ as shown in Figure 1.12. Ruddlesden-Popper phases with monovalent cations in the interlayer sites can also undergo aliovalent substitution where two of the existing cations are replaced by a divalent transition metal ion.^{44,45}

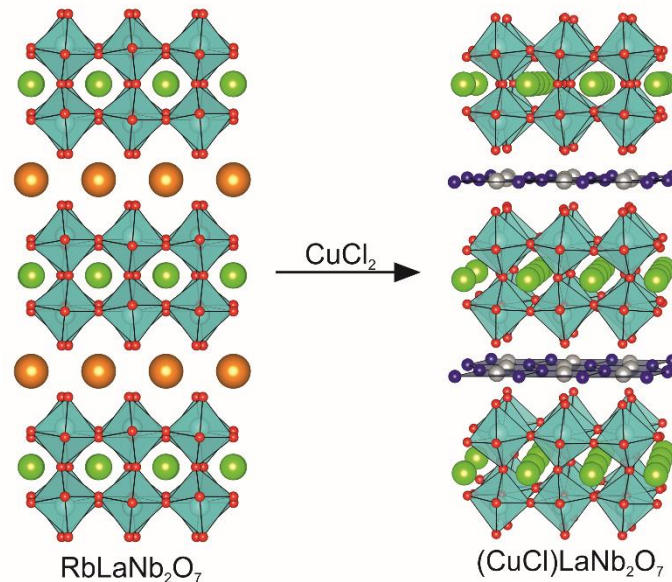


Figure 1.12. Cation exchange reaction from $\text{RbLaNb}_2\text{O}_7$ to $(\text{CuCl})\text{LaNb}_2\text{O}_7$.

The requirement of a large tilting magnitude limits the chemical diversity of phases which are stabilized via a tri-linear coupled hybrid-improper mechanism. One promising avenue to synthesize new hybrid improper ferroelectric materials is to move beyond the thermodynamic region and explore metastable phases. As described above, layered perovskites undergo a series of cation exchange reactions which can be utilized to make new materials with the potential of ferroelectric and multiferroic behaviour.

Chapter 2 – Experimental methods and techniques

2.1 Synthesis methods

2.1.1 Ceramic synthesis

A widely used approach for synthesizing complex oxides is high-temperature solid-state ceramic synthesis, which involves mixing and grinding binary metal oxides and/or metal salts (carbonates, nitrates, etc.) and heating them at high temperatures. Solid-state reactions are limited by the intrinsic low mobility of the chemical constituents of the metal oxide phases. At the contact point of different phases, the reaction is rapid but then the reaction proceeds by slow interdiffusion of reactant particles to form the product phases. Reaction rates can be increased by grinding the sample mixture regularly to expose fresh reagents and by pressing pellets to increase the degree of inter grain contact. As the overall reaction rates are slow, reactions require multiple heating periods of days, even weeks, at elevated temperatures (>1000 °C) to reach completion. If a reactant has a high vapour pressure at the reaction temperature (e.g. group 1 metal carbonates), additional quantities of that reactant (typically 5% to 25% excess) are added to compensate for the weight loss at high temperature.

2.1.2 Cation exchange reactions

The cation exchange reactions carried out as a part of this thesis were performed by mixing the starting material with group 1 metal nitrates or transition metal chlorides and heating the reaction mixture at relatively low temperatures (typically from 300 °C to 500 °C). The reagents and products of the exchange reactions with group 1 nitrates were air-stable at the reaction temperature but those of the exchange reactions with transition metal chlorides were air-sensitive at the reaction temperature.

2.1.2.1 Air stable reactions

The air-stable reactions were performed in open-ended tubes. The starting oxide phase was ground together with a 10-fold excess of the group 1 nitrate and placed in an open-ended pyrex

tube which was then placed vertically in a low-temperature furnace as shown in Figure 2.1. We have used LiNO_3 , NaNO_3 and KNO_3 to perform exchange reactions using this experimental setup. These nitrates have low melting points ($255\text{ }^\circ\text{C}$ for LiNO_3 , $308\text{ }^\circ\text{C}$ for NaNO_3 and $334\text{ }^\circ\text{C}$ for KNO_3)⁴⁶ and the reaction temperatures are usually higher than the melting point of the nitrate salts. As the nitrates are liquid at the reaction temperature, the ionic diffusion of Li^+ , Na^+ or K^+ is much higher than that of a traditional solid-state reaction. The nitrates were hygroscopic so an open-ended tube was required, as this experimental setup allows the water vapour to evaporate safely. After the reaction, the reaction mixture was washed with water to remove the excess nitrate. This reaction procedure was repeated with a further 10-fold excess of nitrate to ensure the complete conversion to the exchanged phase.

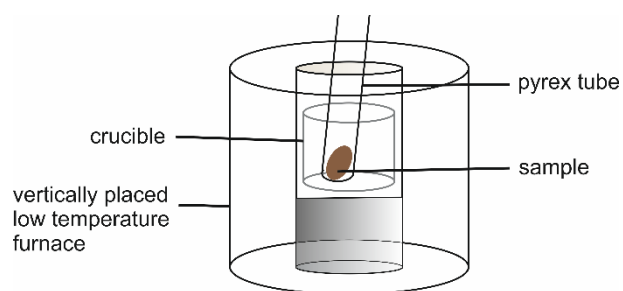


Figure 2.1. Setup for the air-stable cation exchange reactions in an open-ended tube.

2.1.2.2 Air sensitive reactions

An oxygen-free environment is required for the exchange reactions with transition metal chlorides as these chlorides react easily with oxygen to form transition metal oxides at the reaction temperature. Small scale reactions (up to $\sim 1\text{ g}$) were performed in sealed glass tubes and large-scale reactions ($\sim 4\text{ g}$) were performed in a purging system as shown later.

2.1.2.2.1 Sealed glass tube

Usually, a layered perovskite precursor was mixed with 5-molar equivalents of an anhydrous transition metal chloride inside an argon-filled glove box, and ground well using an agate mortar pestle. The mixture was then placed in a pyrex or quartz tube (depending on reaction temperature) and closed with Young's tap. The tube was then evacuated to $\sim 10^{-2}\text{ mbar}$ using a

vacuum pump and sealed using a blowtorch. The sealed tube was then placed in a low-temperature furnace and heated at reaction temperature (350 °C to 400 °C) for 3 to 4 days before being cooled down to room temperature. The glass tube was then broken inside the glove box and the reaction progress was analysed by performing powder X-ray diffraction of the reaction mixture. Due to the presence of a large excess of transition metal chloride, the powder diffraction pattern was often dominated by the diffraction peaks originated from the metal chloride; which could mislead our observation of the reaction progress. To avoid this, a small amount of reaction mixture was taken out of the glove box, washed with water to remove the excess chloride, filtered and dried at 120 °C, and then a powder diffraction pattern was collected. If the reaction is not finished then the original reaction mixture was ground and heated again in a similar fashion at a slightly higher temperature or for a longer time at that temperature. Upon completion, the reaction mixture was washed with water to remove the excess chloride, filtered and dried in a drying oven at 120 °C, and then stored inside the glovebox.

2.1.2.2.2 Purging system

The transition metal halides used for the exchange reactions usually contained a small amount of water and the water vapour in a sealed tube at elevated temperature can cause an explosion. For small-scale reactions (up to ~1g) this is usually not a problem but when we prepared large-scale samples for neutron diffraction (~4g) we used a purging system with flowing Ar instead of a sealed tube to avoid any explosion. The experimental setup is shown in Figure 2.2. Samples were prepared inside an Ar-filled glove box as explained in the 2.1.2.2.1 section and placed in a 19 mm pyrex tube. This tube was then placed in another glass apparatus which has a ground glass joint. The other end of the glass has Young's taps to seal the whole apparatus. The Young's taps were closed inside the glove box and then the purging apparatus was taken out and connected to argon flow. The system was first purged with argon for 30 minutes and then

heated to the reaction temperature (350 °C to 400 °C) in a horizontally placed low-temperature furnace for 3 to 4 days before cooling down to room temperature. After the heating cycle, the tube was evacuated and opened inside the glove box. Reaction progress was monitored by performing powder X-ray diffraction of the reaction mixture. If the reactions were deemed incomplete, they were ground and heated again in a similar fashion. After completion, the reaction mixture was washed with water to remove the excess chloride, filtered, and dried in a drying oven at 120 °C. The products were then stored inside the glove box.

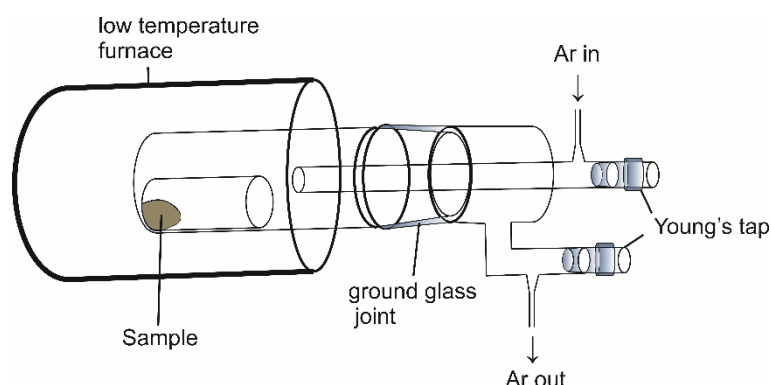


Figure 2.2. Setup for the cation exchange reactions using the purging system.

2.1.3 Drying hygroscopic products

Some products obtained in cation-exchange reactions were hygroscopic. The layered perovskites often absorb water in the interlayer space which leads to expansion of the stacking axis. The crystal structure of the hydrated phase is usually different from the anhydrous phase. Also, strong incoherent and inelastic scattering of hydrogen atoms lowers the quality of the neutron diffraction data collected from the hydrated phase which makes the structural characterisation more difficult. So, for such hydrated compounds, a further drying process is required to remove the interlayer water. The experimental setup is shown in Figure 2.3. The hydrated samples were placed in an alumina boat crucible and placed in a silica tube as shown in Figure 2.3. The tube was then closed using end caps with T-junction taps. The silica tube was then placed in a split tube furnace and connected to gas (Ar or O₂) flow. At first, the tube was purged with the gas for 30 minutes then it was heated to the reaction temperature and kept

there for 12 hours before cooling down to room temperature. After that, the tube was evacuated and transferred into the glove box. The anhydrous product was stored inside the glove box for further analysis.

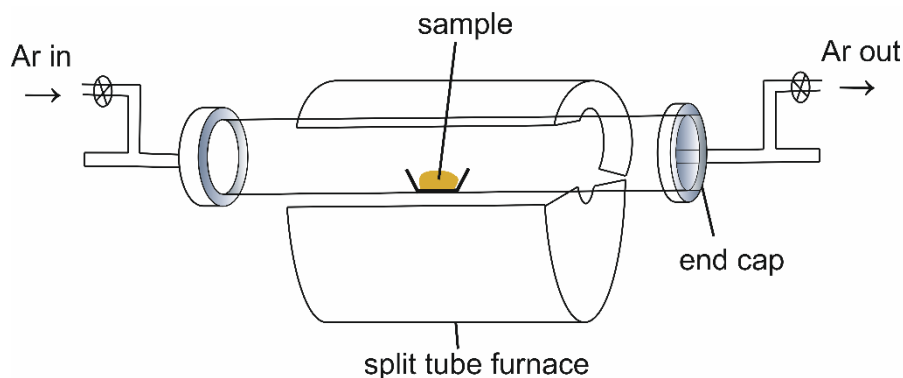


Figure 2.3. Setup for drying hygroscopic samples in a split tube furnace.

2.2 Powder diffraction

Powder diffraction is a widely used structural characterisation technique in solid-state chemistry. X-ray and neutron powder diffraction were essential for the structural characterisations presented in this thesis.

The periodic arrangement of atoms in crystalline solids forms a regular array of lattice planes. Each set of lattice planes are equally spaced, known as the d -spacing. The d -spacings of the crystal lattice are comparable to the wavelengths of X-ray and neutron. The regular array of lattice planes acts as a diffraction grating to diffract incident beams and produce a regular array of scattered rays. In most directions, these scattered rays will be canceled out by destructive interference. However, when their path difference is an integral of their wavelength, they will interfere constructively. This is illustrated by Bragg's law of diffraction⁴⁷:

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

where λ is the wavelength of the incident radiation, d_{hkl} is the interplanar distance, θ is the angle between the incident beam and the lattice plane, and n is an integer. A pictorial description of Bragg's law is shown in Figure 2.4.

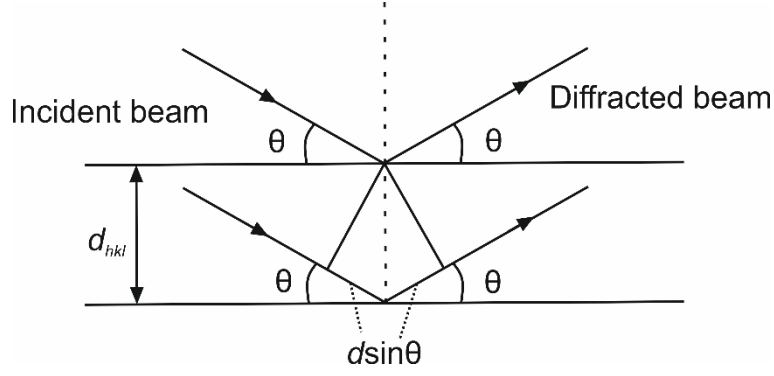


Figure 2.4. Illustration of Bragg's law of diffraction

In a diffraction pattern, the positions of Bragg reflections are defined by d -spacing and hence determined by the unit cell dimensions. The intensity of a given (hkl) reflection is given by:

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

where L is the sample independent Lorentz polarisation function, m is the reflection multiplicity, A is the absorption factor and F_{hkl} is the structure factor⁴⁸. Structure factor depends on the identity and the arrangements of atoms:

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

where f_n is the atomic scattering factor and x_n , y_n and z_n are the atomic coordinates of n^{th} atom in the unit cell, and U_{iso_n} is the isotropic thermal displacement parameter. The second exponential term describes the reduction in intensity as a function of scattering angle⁴⁹.

2.2.1 X-ray powder diffraction

X-ray powder diffraction was used routinely to monitor reaction progress and determine crystal structure due to the ready availability of a monochromatic X-ray source. Since the X-rays interact with the electron densities of atoms, the scattering factor (f_n) of an atom is related to its atomic number (Z). Therefore, X-ray diffraction is relatively insensitive to the light elements especially in presence of heavy ones. Consequently, unambiguous structure determination using only X-rays was not possible for the distorted layered perovskites discussed in this thesis, as they contain very heavy atoms (e.g. Ta, Nb, Bi, etc) as well as light atoms (e.g. Li, O, etc.)

in the same crystal structure and the structural distortions originate from the displacement of light oxide ions.

2.2.1.1 Panalytical Empyrean and X'pert diffractometers

In-house Panalytical Empyrean and X'pert diffractometers were used to collect diffraction data suitable for a routine inspection of reaction progress. Both diffractometers use the Bragg-Brentano geometry and generate monochromatic Cu $K_{\alpha 1}$ radiation. A Ni filter is used to eliminate the K_{β} radiation. A Ge (111) single crystal was used as a monochromator to further eliminate the $K_{\alpha 2}$ radiation so that only Cu $K_{\alpha 1}$ radiation could hit the sample. Soller slits and anti-scatterers were used to adjust the beam optics. Empyrean diffractometer generates high-intensity data whereas the X'pert generates data with higher resolution, which are suitable for Rietveld refinement.

Non-air sensitive samples were ground and sprinkled onto a silicon wafer coated with a thin layer of high-vacuum grease. This wafer was cleaved along the [110] plane which is systematically absent in the diffraction pattern so it does not produce any diffraction peak in the pattern. The wafer was then assembled on a spinning sample holder which rotates during the measurement to minimize the effect of uneven sample distribution and preferred orientation. Air-sensitive samples were prepared in an argon-filled glove box. In this case, the powder samples were sprinkled on a glass slide coated with a thin layer of high vacuum grease. The slide was then inserted in a flat sample holder designed for air-sensitive samples and closed with a brass cap as shown in Figure 2.5.

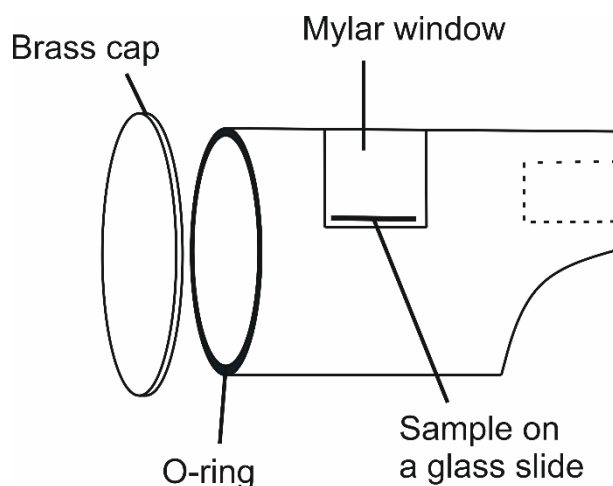


Figure 2.5. Sample holder for measuring X-ray powder diffraction from air-sensitive samples.

2.2.1.2 Synchrotron X-ray powder diffraction

Synchrotron X-rays are generated based on the fundamental physics that accelerated charged particles emit electromagnetic radiation. In a synchrotron, electrons are accelerated in a circular path at a speed close to the speed of light and as a result, electromagnetic radiation of widespread wavelengths is produced; the X-ray part of which is used for diffraction. The intensity of synchrotron radiation is many orders of magnitude higher than the lab X-ray; so, the measurement takes a shorter time. Another advantage of synchrotron radiation is that the wavelength is tunable precisely by using a suitable crystal monochromator and the monochromatic radiation can be well collimated. Such modification of the X-ray beam reduces significant intensity but it can produce very high-resolution diffraction data.

The synchrotron X-ray diffraction data presented in this thesis were collected from I11 beamline⁵⁰ of Diamond Light Source in Didcot, Oxfordshire. The I11 beamline can produce X-rays with energy 5-25 KeV (0.4-2.1 Å) and is dedicated to high-resolution powder diffraction. A double crystal monochromator which is composed of two liquid nitrogen cooled Si (111) crystals; is used to select the wavelength of the incident beam. There are two kinds of detectors at I11. The wide-angle Position Sensitive Detector (PSD) which uses Mythen-2 Si μ strip module⁵¹, is optimized for quick data collection (~2 minutes). The other detector is Multi Analyzing Crystal (MAC)⁵² in which there are 9 Si (111) crystals deployed in each of the five

MAC arms. This detector is optimized for very high-resolution data collection. The intensity is sacrificed largely because of the Si monochromators; hence the data collection takes a longer time (~30 minutes).

Powder samples were loaded in 0.3- or 0.5-mm glass capillaries which were then sealed using a blowtorch. The sealed capillaries were mounted onto a brass holder which has a magnetic base. These holders were placed on a magnetic stage and the capillaries were aligned at the centre of the beam. The capillaries spin during the measurement. Variable temperature measurements are also possible at I11. An Oxford cryostat is used to lower the temperature down to 80 K. On the other hand, a hot air blower is optimized for measurements at high temperatures (300K - 1273 K). These sample environments are important to track down phase transitions and they were used extensively to produce several data presented in this thesis.

2.2.2 Neutron powder diffraction

X-rays are scattered by the electron cloud of atoms, whereas neutrons interact with the atomic nucleus. So, neutron diffraction differs from X-ray diffraction in a few ways: (1) Since neutrons do not interact with electron clouds the neutron scattering length of an element does not vary linearly with its atomic number. So, the total neutron scattering from a structure is almost evenly distributed among its constituent elements, which allows us to precisely locate the light atoms even in presence of heavy ones.⁵³ (2) Unlike the electron cloud, the nucleus is a point scatterer, hence the neutron scattering form factors do not diminish with scattering angle. Consequently, diffraction peaks at low d -spacing are significantly intense, and thus structural information and thermal factors can be extracted correctly. (3) The interaction between neutrons and atomic nuclei is very weak, so for neutron diffraction, we need a large-scale sample. The neutron diffraction measurements carried out as a part of this thesis used approximately 4g powder sample. Neutrons are also very penetrating which allows us to use cryostat, furnace and high-pressure setup to collect diffraction patterns in different sample

environments. (4) Neutrons are spin $\frac{1}{2}$ particle, hence they are scattered by a lattice of ordered unpaired electrons. Neutron scattering from a material where magnetic spins are long-range ordered allows us to determine the magnetic structure of the material. The form factor of magnetic scattering has an angular dependence which decays even faster than the form factor of X-ray. This is because the neutrons interact with the outer shell electrons to result in magnetic scattering.

The magnetic structure factor⁵⁴ $F_{hkl,mag}$ of an unpolarized neutron source can be defined as:

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

where q_j is the magnetic interaction vector, p_j is the magnetic scattering length, and x_j , y_j and z_j are the atomic coordinates of the j^{th} magnetic atom in the unit cell. The observed intensity of a magnetic reflection ($I_{hkl,mag}$) is proportional to $|F_{hkl,mag}|^2$.

For neutron diffraction measurement, the powder samples were loaded in vanadium cans and sealed with steel lids. Vanadium is chosen as the container because of its very low neutron coherent scattering length (-0.3824 fm).⁵³

The neutron diffraction patterns shown in this thesis were collected from HRPD, GEM and WISH instruments at the ISIS Neutron and Muon Source in Didcot, Oxfordshire.

2.2.2.1 ISIS: HRPD, GEM and WISH

Neutrons are generated either in a nuclear reactor (neutrons are generated by the fission process) or by spallation. At ISIS, neutrons are produced by spallation. High energy pulsed protons are accelerated in a synchrotron and fired at the heavy metal target made of tantalum. This causes an intranuclear cascade which results in pulses of neutrons. The neutrons generated by this process have very high thermal energy; which are then slowed down by using hydrogenous moderators (liquid methane in HRPD and GEM) to get wavelengths suitable for the time of flight experiment.

In the TOF technique, the time taken (t , usually measured in μS) for a neutron to travel the total flight path L from the moderator to the detector is measured. d -spacing can be calculated by combining the Bragg's law and De Broglie relationship:

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

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

where h is the Plank's constant, v and m are the velocity and mass of neutron respectively. TOF technique uses a fixed angle detector, so θ is known.

HRPD⁵⁵ has three banks of detectors and is optimized for high-resolution measurements. The resolution of a time of flight diffractometer⁵⁴ can be expressed as:

$$\frac{\Delta d}{d} = \sqrt{\Delta \theta^2 \cot^2 \theta + \frac{\Delta t^2}{t^2} + \frac{\Delta L^2}{L^2}}$$

Contribution of uncertainties in θ , to the uncertainty in d -spacing ranges from infinite at $\theta = 0^\circ$, to zero at $\theta = 90^\circ$. Therefore, a greater resolution is always obtained by placing a detector at a higher 2θ value. In HRPD, Bank1, which is the back-scattering bank ($2\theta = 168^\circ$) has the highest resolution. The resolution of HRPD is further increased by its long path length (L) which minimizes the $\Delta L/L$ term. The very high resolution of HRPD makes it suitable for studying small structural distortions originated from octahedral tilting. Hence, HRPD data were used extensively for structural characterisations in this thesis. The HRPD setup is shown in Figure 2.6.

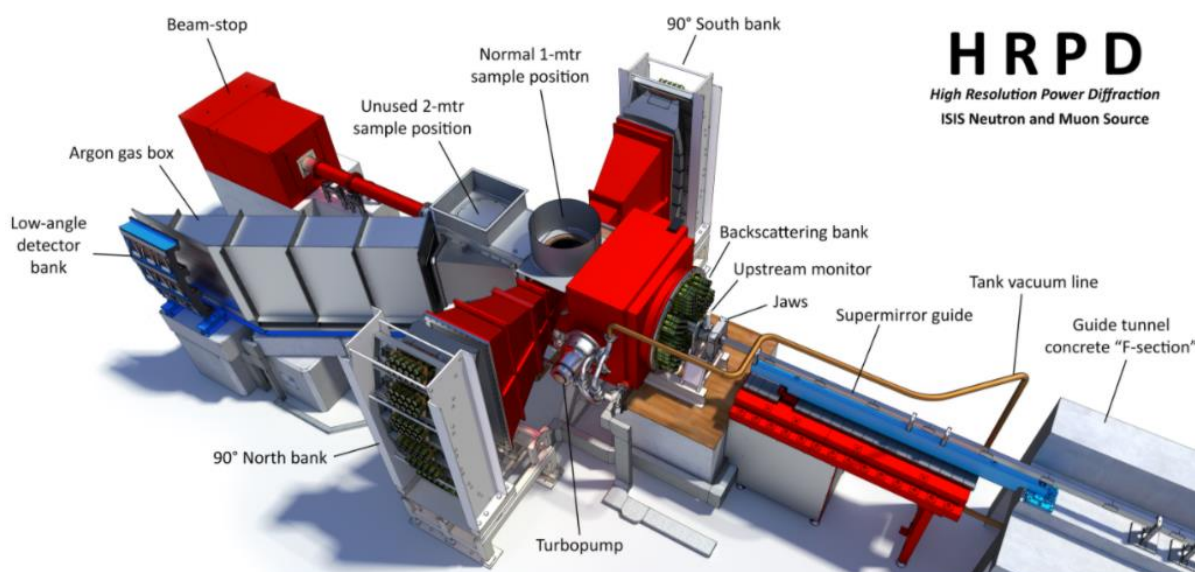


Figure 2.6. Instrumentation of HRPD⁵⁶ at ISIS.

The General Materials Diffractometer (GEM)⁵⁷ is used for high-resolution and high-intensity neutron diffraction. Six detector banks collect the data covering scattering angles from 9° to 154°. Its high resolution at high d -spacing makes it a suitable instrument for magnetic characterisation.

WISH⁵⁸ is a long wavelength diffractometer optimized for powder diffraction at high d -spacing to solve magnetic structures. WISH data are also useful for solving and refining structures with large unit cell. Wish provides high-resolution data over a d -spacing range from 0.7 Å - 17 Å and it uses pixelated ^3He detectors covering scattering angles from 10° to 170°.

2.3 Rietveld refinement

Rietveld refinement is a powerful technique for structural characterisation of polycrystalline samples. Extraction of structural information from powder diffraction data is intrinsically difficult as the reflections from Miller indices with the same d -spacing but different hkl values overlap with each other. As all these overlapping peaks could contribute to the observed intensity, the exact structure factor cannot be calculated for the individual reflections. Rietveld method⁵⁹ overcomes this problem by calculating the intensity at each point and comparing it

with the observed peak intensity at that point. In Rietveld refinement a least square algorithm is used to minimize the difference between observed and calculated patterns:

$$S = \sum_i w_i (y_{io} - y_{ic})^2$$

where w_i is the weighting factor, y_{io} and y_{ic} are the observed and calculated intensities at point i . S is the residual function that needs to be minimized. The refinement is started from an approximate model and different degrees of freedom are allowed to vary which will change the calculated pattern in a way such that S is minimized. In a typical refinement, the background, lattice parameters, peak shape parameters, zero-point; and atomic coordinates, occupancy and thermal parameters of the atomic sites are refined. The fitting statistics can be expressed using three parameters: reduced χ^2 , residual parameter R_p and the weighted residual parameter wR_p , which are defined as:

$$R_p = \frac{\sum_i |y_{io} - y_{ic}|}{\sum_i y_{io}} \times 100 \%$$

$$wR_p = \sqrt{\frac{\sum_i w_i (y_{io} - y_{ic})^2}{\sum_i w_i y_{io}^2}} \times 100 \% = \sqrt{\frac{S}{\sum_i w_i y_{io}^2}}$$

$$\chi^2 = \frac{\sum_i w_i (y_{io} - y_{ic})^2}{N - V + C} = \frac{S}{N - V + C}$$

where N is the number of observations in all histograms, V is the number of variables and C is the number of constraints used in the least square refinement. The structural refinements presented in this thesis were performed using GSAS⁶⁰ and Topas V6⁶¹ suite of programmes.

2.3.1 Peak broadening

Fitting the peak shape is a crucial part of Rietveld refinement. In an ideal case, the diffraction peaks will be extremely sharp. But in practice, the diffraction peaks always have some broadening and it depends on three main factors:

- (1) From the uncertainty principle, the exact knowledge of the position of the photon implies that there is uncertainty about its momentum and consequently uncertainty in

wavelength. This results in Bragg reflections to have a finite width. Although broadening due to uncertainty is negligible compared to the other factor responsible for broadening as discussed below.

- (2) Imperfect instrument setup leads to broadening in diffraction peaks. Radiation sources are not perfectly monochromatic, but rather consist of a small range of wavelengths around the mean wavelength. The diffraction volume within the sample is finite and therefore diffraction does not occur at the true centre of the diffractometer, resulting in peak broadening. Axial divergence of incident or diffracted beam or other diffractometer misalignments could also lead to peak broadening.
- (3) The theory of diffraction considers an infinite perfect crystal. But imperfections in crystallites; which are mainly attributed to crystallite size and strain, will lead to peak broadening in the diffraction pattern. The larger the particle size, the narrower is the peak width. Particle size also depends on its shape, consequently, irregular shape particles will lead to anisotropic peak broadening. Strain broadening is reflected in the displacement of lattice planes. A homogeneous strain will shift the whole diffraction pattern to a higher angle. But if the strain is inhomogeneous, the shifting of diffraction peaks is not consistent, resulting in peaks with different widths.

The broadening effect from an instrument is modelled with a Gaussian function while a Lorentzian function is required to model the effect of sample broadening. In most refinement programmes, a linear combination of Gaussian and Lorentzian functions known as the Pseudo-Voigt function is used to define the peak shape.

2.4 DC SQUID magnetometry

Superconducting quantum interference devices (SQUID) are capable of measuring very small changes in a magnetic field by using the Josephson effect.⁶² In a SQUID, two pieces of superconducting rings are separated by very thin insulating layers called Josephson Junction

which allow superconducting electrons to tunnel through. When a magnetic sample is moved through the superconducting coils, the magnetic field generated by the sample induces a current in the ring. When this induced current is larger than the critical current of the Josephson junction, a voltage appears across the junction. This voltage is proportional to the magnetic moment of the sample. A schematic of SQUID magnetometry is shown in Figure 2.7.

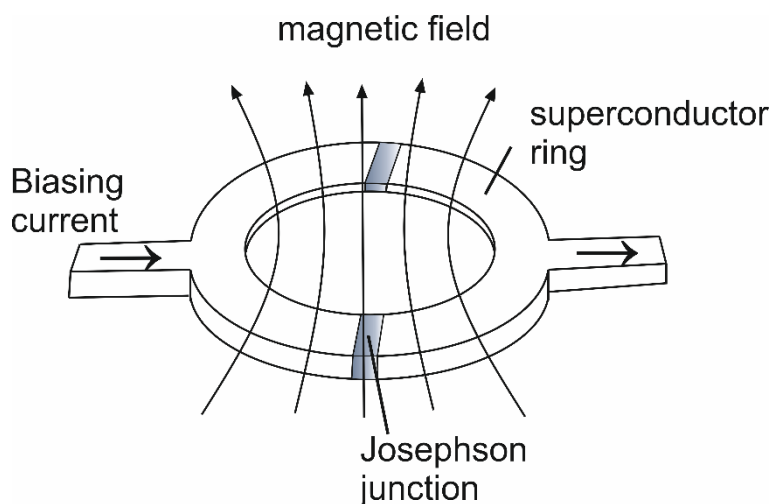


Figure 2.7. Schematic of a SQUID magnetometer.

Magnetic data shown in this thesis were collected from a Quantum Design MPMS XL SQUID magnetometer. Approximately 40 mg of the sample were weighed and loaded in a gelatine capsule. The capsule was then inserted in a straw with four empty capsules on either side of the sample capsule. The top capsule was wrapped with a layer of diamagnetic tape and at the bottom, a plastic tip was used to ensure that the sample did not move during the measurement. The empty capsules were pierced with a needle so that they could be evacuated properly. The straw was then connected to a steel rod and loaded into the SQUID.

Magnetisation data were collected either as a function of temperature at a constant field or as a function of applied field at a fixed temperature. Zero field cooled (ZFC) and field cooled (FC) measurements were performed from 5K to 300K in an applied field of 100 Oe. In ZFC measurement, the sample was cooled at zero field and in FC measurement the sample was

cooled under 100 Oe applied field. The magnetisation-field (M–H) isotherms were collected over the field range of -5 Tesla to 5 Tesla at usually 5 K and 300 K.

2.4.1 Curie-Weiss law

The susceptibility of a material indicates how responsive it is to an applied magnetic field. Curie law describes the relationship between the susceptibility of a paramagnet and temperature:

$$\chi = \frac{C}{T}$$

where C is a constant known as the Curie constant and T is the temperature in K. Curie law assumes that the individual magnetic moments do not interact with each other. But that is only true for magnetically dilute systems. Change in susceptibility for the systems with correlated behaviour; for example, ferromagnets or antiferromagnets with temperature cannot be described by Curie law. In this case, Curie law is modified to give an accurate description of susceptibility, known as Curie-Weiss law:

$$\chi = \frac{C}{T - \theta} + K$$

where θ is the Weiss temperature, which is a measure of the strength of magnetic interactions and K is a constant which accounts for any temperature-independent part. By plotting $1/\chi$ against the temperature, the values of C and θ can be obtained. The Curie constant C , is related to the effective magnetic moment of the sample as⁶³:

$$C = \frac{N_A \mu_B g^2 S(S + 1)}{3K_B} \approx \frac{\mu_{eff}^2}{8}$$

where N_A is Avogadro's number, μ_B is the Bohr magneton, g is the gyromagnetic constant, S is the spin quantum number, K_B is the Boltzmann constant and μ_{eff} is the effective magnetic moment.

2.5 Bond valence sum (BVS)

Bond valence sum calculations allow the estimation of the valence of an ion based on the bond lengths, and identity of the atom it is bonded to, in its coordination sphere.⁶⁴ The total valence V_i of an atom is defined as the sum of the valence contributions from all the bonds:

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

where v_{ij} is the valence of a bond between i and j , R_{ij} is the observed bond length between ion i and j , b is an empirical constant usually considered to be 0.37, R_0 is the bond valence parameter. For the bond valence sum calculation, we have used the bond valence parameters reported by Brese and O'Keeffe.⁶⁵ Bond valence sums were used to compare related structures and justify the best structure description among different possible structures of a compound.

2.6 Second harmonic generation

Second harmonic generation is a nonlinear optical process where two photons with the same wavelength combine to produce a photon with half of that wavelength (ie. twice the energy).¹⁴ Subtle structural distortions are challenging to determine with the help of only powder diffraction data. Thus, SHG data were used to assist the structural characterisation of newly synthesized materials. Most of the noncentrosymmetric crystal classes are SHG active (except for 432) as shown in Figure 2.8. So SHG activity from a sample indicates that the structure must belong to a noncentrosymmetric space group. SHG activity/inactivity from a material can be used to reduce the number of possible space groups. Usually, an infrared laser is used as the incident light, hence after interacting with a noncentrosymmetric material a blue/green light will be observed in the detector. For standard measurements, approximately 100 mg sample was loaded in a sample holder and placed into the device. For particle size-dependent measurements, a dense pellet was sieved into particle sizes in the range 20 μm to 125 μm and SHG intensity was measured with respect to a standard SHG active material. The SHG results

shown in this thesis were performed by Dr. Weiguo Zhang and Prof. Shiv Halasyamani from the University of Houston.

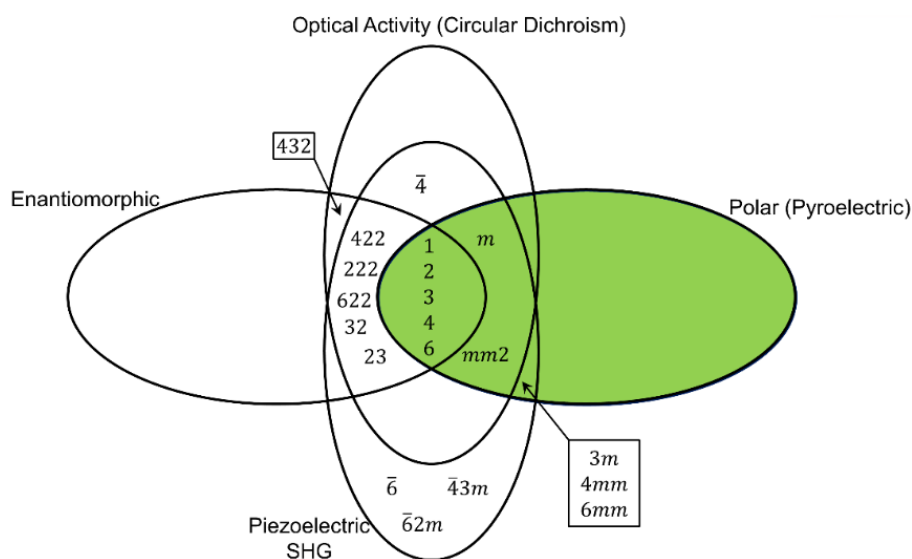


Figure 2.8. Interrelationships of noncentrosymmetric crystal classes.¹³

2.7 ISODISTORT

ISODISTORT is an online applet for generating and exploring distorted crystal structures in terms of the symmetry modes of the irreducible representations of the parent space group symmetry.⁶⁶ Some of the symmetry elements are lost when the distortion arises. The symmetry that remains comprises an isotropy subgroup of the parent space group. Different physical parameters e.g. atomic displacement, magnetic moment, site occupancy, lattice strain can be classified as basis functions of the irreducible representations of the parent space group symmetry.

To use ISODISTORT, a CIF file is first uploaded to the applet. Next, the types of distortions we are looking for (strain, displacive, occupational, magnetic, or rotational) are selected. Selection of more than one type of distortion is also allowed. There are four available methods of child space group searching. Method 1 is the simplest approach, where we can specify the crystal system, space group symmetry and the basis of the child space group we are interested in. In method 2, we choose the number of superposed irreps and select them from a drop-down menu, which will then be used to generate the child space group at a later stage. In method 3,

we have to specify the space group or the point group symmetry of the child structure. We can also choose a basis vector of the child unit cell. Method 4 is used to deconvolute a distorted structure with respect to the distortion modes of the parent structure.

Once we get the distorted structure, ISODISTORT provides a variety of outputs, including tools for visualisation and interactively manipulating the distorted structure and its diffraction pattern. Figure 2.9 shows such an output where Z_1^+ distortion mode on a $(0, \frac{1}{2}, z)$ shifted $n = 2$ layered perovskite results in $a^0b^+c^0/a^0b^+c^0$ tilting of oxygen octahedra as can be seen in the left-hand side of the figure.

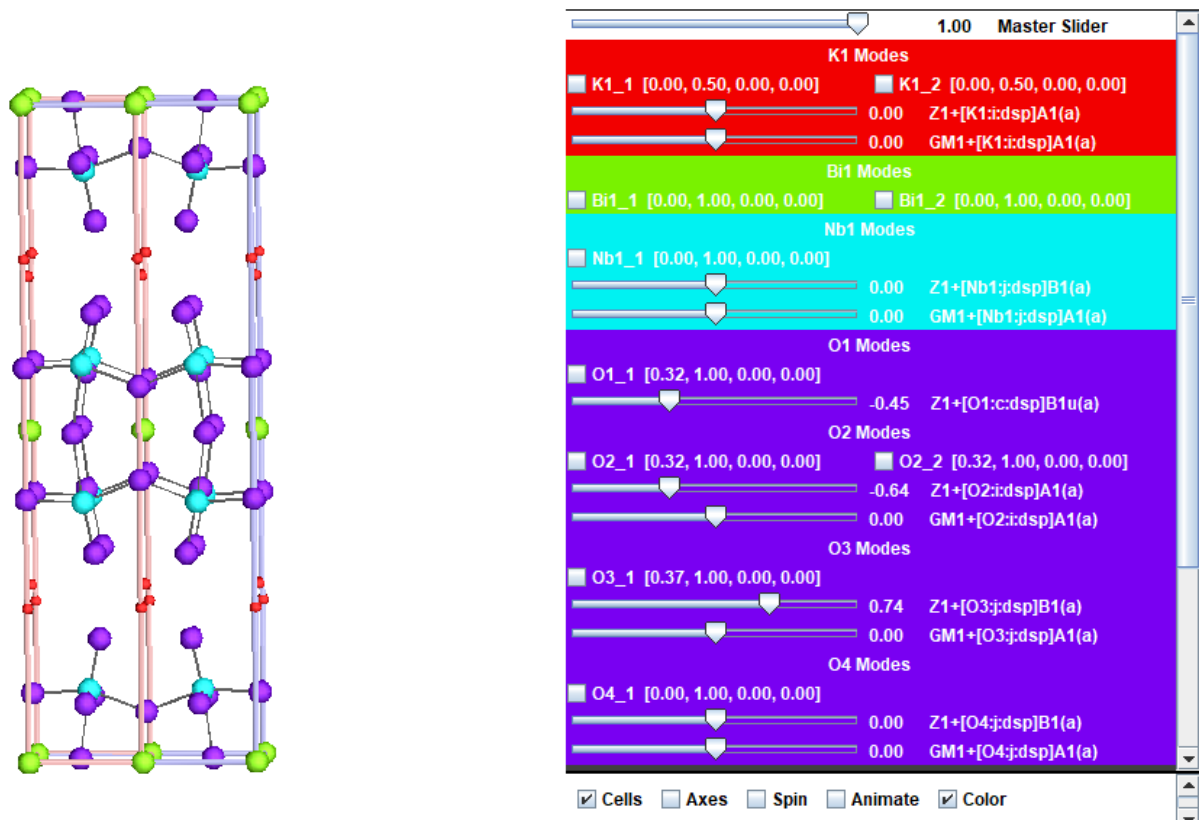


Figure 2.9. Snapshot from an ISODISTORT output which shows the effect of Z_1^+ irreducible representation on a $(0, \frac{1}{2}, z)$ shifted $n = 2$ layered perovskite.

2.8 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is usually a suspension on a grid. The image is formed by the interaction of the electrons with the sample

and then magnified and focused onto an imaging device. TEM is capable of imaging at a significantly high resolution and capturing fine details as small as a single column of atoms. The electron Microscopy results shown in this thesis were performed by Dr. Maria Batuk and Prof. Joke Haddermann from the University of Antwerp. Electron diffraction (ED) patterns were acquired on an FEI Tecnai transmission electron microscope operated at 200 kV. High angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images and energy dispersive X-ray spectroscopy (EDX) maps were acquired using a probe aberration-corrected FEI Titan 80-300 “cubed” microscope operated at 300 kV.

Chapter 3 – Synthesis and structural characterisation of polar KNdM_2O_7 ($M = \text{Ta}, \text{Nb}$)

3.1 Introduction

Recent theoretical calculations suggested that some of the previously reported undistorted $n = 2$ Dion-Jacobson phases are in fact distorted and might even have polar crystal structures.⁶⁷ Some of these predicted materials were reinvestigated and experimentally verified to have noncentrosymmetric crystal structures. For example, $A'\text{LaM}_2\text{O}_7$ ($A' = \text{Rb}, \text{Cs}; M = \text{Nb}, \text{Ta}$)⁶⁸ phases were shown to be noncentrosymmetric and piezoelectric with the help of synchrotron powder X-ray diffraction (SXRD), second harmonic generation (SHG) and Piezoelectric force microscopy (PFM) data. CsLaM_2O_7 ($M = \text{Ta}, \text{Nb}$) and $\text{RbLaNb}_2\text{O}_7$ were shown to adopt polar $P2_1am$ structures with an $a^-a^-c^+$ octahedral distortion. Further investigation into the $A'\text{NdM}_2\text{O}_7$ ($A' = \text{Rb}, \text{Cs}; M = \text{Ta}, \text{Nb}$)¹¹ phases reveals that the caesium phases have the same $P2_1am$ structure as the lanthanum compounds, but the rubidium phases adopt an $I2cm$ structure with an $a^-a^-c^+/- (a^-a^-c^+)$ octahedral tilting. Low temperature cation-exchange reactions performed on RbNdM_2O_7 ($M = \text{Ta}, \text{Nb}$) phases enable the synthesis of metastable $A'\text{NdM}_2\text{O}_7$ ($A' = \text{Li}$ and Na).⁴² When the large alkali metals, Cs and Rb, are exchanged for smaller cations, such as Na or Li, the resulting $A'\text{NdM}_2\text{O}_7$ phases adopt Ruddlesden-Popper structures with the change from a $(0, 0, z)$ to a $(\frac{1}{2}, \frac{1}{2}, z)$ stacking of the NdM_2O_7 double perovskite sheets. This transformation is motivated by the need to accommodate the small Li or Na ions in 4-coordinate, pseudo tetrahedral sites. The Li phases have polar $B2cm$ structures whereas the Na phases are centrosymmetric but distorted. Both the Li and Na phases were previously reported as undistorted $I4/mmm$ aristotype structures.

If K^+ ions are substituted in the A' -cation site of $A'\text{NdM}_2\text{O}_7$ phases, the resulting KNdM_2O_7 ($M = \text{Ta}, \text{Nb}$) compounds adopt layered perovskite structures in which the NdM_2O_7 layers stack in

a $(0, \frac{1}{2}, z)$ arrangement with the K^+ cations accommodated within the 6-coordinate trigonal prismatic sites. These two K-phases were previously reported⁶⁹ to have undistorted structures described in *Ammm* space group. But given that the phases with Cs, Rb, Na and Li in the A' -cation site of A' NdM₂O₇ series are distorted, it is likely that the K-phases are also distorted. In this chapter the KNdM₂O₇ (M = Ta, Nb)^{69,70} phases were reinvestigated with the help of SHG, synchrotron X-ray and neutron powder diffraction data to find out the detailed structure of these two phases, and to understand the dependence of structural distortion with the identity of alkali metal ion in the A' -cation site.

Results from this chapter are published as: **Mallick, S.**; Gibbs, A. S.; Zhang, W.; Halasyamani, P. S.; Benedek, N. A.; Hayward, M. A. Polar Structures of KNdNb₂O₇ and KNdT_a2O₇. *Chem. Mater.* **2020**, 32 (18), 7965–7972.

3.2 Synthesis

Samples of KNdNb₂O₇ and KNdT_a2O₇ were prepared by first synthesizing the corresponding RbNdM₂O₇ (M = Nb, Ta) phases,¹¹ then converting them to the corresponding NaNdM₂O₇ phases via Na-for-Rb cation exchange,⁴² and finally converting them to the KNdM₂O₇ phases via K-for-Na cation exchange.

Specifically, samples of RbNdNb₂O₇ and RbNdT_a2O₇ were prepared from Rb₂CO₃ (99.8%), Nd₂O₃ (99.99%, dried at 900 °C) and Nb₂O₅ (99.9985%, dried at 900 °C) or Ta₂O₅ (99.993%, dried at 900 °C) as described previously.¹¹ Suitable stoichiometric ratios of the oxides were ground together in an agate pestle and mortar and then combined with a 50% excess of Rb₂CO₃ (to compensate for metal loss due to volatility at high temperature). These mixtures were then heated at 850 °C in air for 12 h, reground, and pressed into pellets. Samples of RbNdNb₂O₇ were heated in air for four periods of 48 h at 1000 °C and a further 48 h at 1050 °C. Samples of RbNdT_a2O₇ were heated in air for four periods of 48 h at 1050 °C. All samples were reground and pressed into pellets between heating cycles. After heating, all samples were

washed with distilled water to remove any remaining excess rubidium oxide, filtered, and then dried for 12 h at 140 °C in air.

Sodium cation-exchange reactions were performed by reacting $\text{RbNdNb}_2\text{O}_7$ and $\text{RbNdTa}_2\text{O}_7$ with 10 mole-equivalents of NaNO_3 (>99.0%) as described previously.⁴² These mixtures were ground together and loaded into an open-ended silica tube and heated in air for two periods of 48 h at 400 °C. Between heating cycles, samples were washed with distilled water, dried for 12 h at 140 °C in air, and mixed with a further 10 mole-equivalents of NaNO_3 . After the final heating step, all samples were washed with distilled water to remove the NaNO_3 and then dried for 12 h at 140 °C in air.

Potassium cation-exchange reactions were performed by reacting $\text{NaNdNb}_2\text{O}_7$ and $\text{NaNdT}_a_2\text{O}_7$ with 10 mole-equivalents of KNO_3 (99.995%). These mixtures were ground together and loaded into an open-ended silica tube and heated in air for two periods of 48 h at 370 °C. Between heating cycles, samples were washed with distilled water, dried for 12 h at 110 °C in air, and mixed with a further 10 mole-equivalents of KNO_3 . After the final heating step, all samples were washed with distilled water to remove the remaining NaNO_3 and then dried for 12 h at 110 °C in air.

3.3 Results

3.3.1 Cation exchange route to synthesize KNdM_2O_7 phases

While the high-temperature solid-state synthesis of KLaNb_2O_7 has been reported^{71,72} the analogous neodymium phase is not accessible by direct heating of K_2CO_3 , Nd_2O_3 and Nb_2O_5 . When this combination of reagents is heated at 1100 °C the major product obtained is NdNbO_4 . This indicates that KNdNb_2O_7 is not the thermodynamically most stable product of these reagents, and so cannot be prepared by their direct combination at high temperatures. Therefore, the metastable potassium phases KNdNb_2O_7 and $\text{KNdT}_a_2\text{O}_7$ were synthesized by a

two-step cation exchange route starting from the corresponding RbNdM_2O_7 Dion-Jacobson phases and proceeding via the NaNdM_2O_7 Ruddlesden-Popper phases.

3.3.2 Optical SHG measurements

Powder SHG measurements collected from KNdTa_2O_7 and KNdNb_2O_7 indicate that both compounds are SHG active and the activity is 0.5 and 0.56 times $\alpha\text{-SiO}_2$ respectively. This observation suggests that KNdTa_2O_7 and KNdNb_2O_7 both adopt non-centrosymmetric crystal structures.

3.3.3 Symmetry analysis of KNdM_2O_7 phases

Deducing the subtle structural distortions of layered perovskite phases from diffraction data can be challenging. To assist this process, symmetry analyses were performed using the ISODISTORT software⁶⁶ to produce a list of ‘chemically plausible’ distortions of the $n = 2$ (0, $\frac{1}{2}$, z) stacked framework. ‘Chemically plausible’ distortions are defined as those which retain the equivalence of the BO_6 octahedra, and our initial assumption was that KNdNb_2O_7 and KNdTa_2O_7 adopt structures on the list in Table 3.1.

IRs	Glazer Tilt	Space Group	Lattice parameters
	$a^0b^0c^0$	$Ammm$ (65)	a, b, c
Z_1^+	$a^0b^+c^0/a^0b^+c^0$	$Ammm$ (65)	$a' = 2a, b' = b, c' = c$
T_1^+	$a^0b^+c^0/a^0(-b^+)c^0$	$Immm$ (71)	$a' = b, b' = c, c' = 2a$
$R_2^-(0;a)$	$a^0b^-c^0/a^0b^-c^0$	$C2/m$ (12)	$a' = 2b, b' = 2a, c' = \frac{1}{2}c$
$R_2^-(a;b)$	$a^0b^-c^0/a^0(-b^-)c^0$	$C2/m$ (12)	$a' = 2b, b' = 2a, c' = c$
$S_1^+(0;a)$	$a^+b^0c^0/a^+b^0c^0$	$P2/m$ (10)	$a' = 2b, b' = a, c' = \frac{1}{2}c$
$S_1^+(a;b)$	$a^+b^0c^0/(-a^+)b^0c^0$	$P2/m$ (10)	$a' = 2b, b' = a, c' = c$
$R_1^-(0;a)$	$a^-b^0c^0/a^-b^0c^0$	$C2/m$ (12)	$a' = 2b, b' = 2a, c' = \frac{1}{2}c$
$R_1^-(a;b)$	$a^-b^0c^0/(-a^0)b^0c^0$	$C2/m$ (12)	$a' = 2b, b' = 2a, c' = c$
$R_1^+(0;a)$	$a^0b^0c^+/a^0b^0c^+$	$C2/m$ (12)	$a' = 2b, b' = 2a, c' = \frac{1}{2}c$
$R_1^+(a;b)$	$a^0b^0c^+/a^0b^0(-c^+)$	$C2/m$ (12)	$a' = 2b, b' = 2a, c' = c$
$S_1^+ \cdot Z_1^+(0;a b)$	$a^+b^+c^0$	$P2/m$ (10)	$a' = 2b, b' = 2a, c' = \frac{1}{2}c$

$S_1^+ \cdot Z_1^+ (a;b c)$	$a^+b^+c^0/(-a^+)b^+c^0$	$P2/m (10)$	$a' = 2b, b' = 2a, c' = \frac{1}{2}c$
$S_1^+ \cdot T_1^+ (0;a b)$	$a^+b^+c^0/a^+(-b^+)c^0$	$C2/m (12)$	$a' = c, b' = 2a, c' = 2b$
$S_1^+ \cdot T_1^+ (a;b c)$	$a^+b^+c^0/-(a^+b^+)c^0$	$P2/m (12)$	$a' = 2b, b' = 2a, c' = c$
$R_2^- \cdot R_1^- (0;a 0;b)$	$a^-b^-c^0/a^-b^-c^0$	$P-1 (2)$	$a' = \sqrt{2}a, b' = \sqrt{2}b, c' = \frac{1}{2}c$
$R_2^- \cdot R_1^- (a;b c;d)$	$a^-b^-c^0/-(a^-b^-)c^0$	$P-1 (2)$	$a' = \sqrt{2}a, b' = \sqrt{2}b, c' = c$
$R_2^- \cdot R_1^- (0;a b;0)$	$a^-b^-c^0/(-a^-)b^-c^0$	$C2/c (15)$	$a' = 2b, b' = 2a, c' = c$
$R_1^- \cdot Z_1^+ (a 0;b)$	$a^-b^+c^0/a^-b^+c^0$	$P2/c (13)$	$a' = \frac{1}{2}c, b' = 2a, c' = 2b$
$R_1^- \cdot Z_1^+ (a b;c)$	$a^-b^+c^0/(-a^-)b^+c^0$	$P2/c (13)$	$a' = c, b' = 2a, c' = 2b$
$R_1^- \cdot T_1^+ (a 0;b)$	$a^-b^+c^0/a^-(-b^+)c^0$	$C2/c (15)$	$a' = c, b' = 2a, c' = 2b$
$R_1^- \cdot T_1^+ (a b;c)$	$a^-b^+c^0/-(a^-b^+)c^0$	$P2/c (13)$	$a' = c, b' = 2a, c' = 2b$
$R_2^- \cdot S_1^+ (0;a 0;b)$	$a^+b^-c^0/a^+b^-c^0$	$P2_1/m (11)$	$a' = 2b, b' = 2a, c' = \frac{1}{2}c$
$R_2^- \cdot S_1^+ (a;b c;d)$	$a^+b^-c^0/-(a^+b^-)c^0$	$P2_1/m (11)$	$a' = 2b, b' = 2a, c' = c$
$R_2^- \cdot S_1^+ (0;a b;0)$	$a^+b^-c^0/a^+(-b^-)c^0$	$C2/m (12)$	$a' = c, b' = 2a, c' = 2b$

Table 3.1. Chemically plausible distortions of the $n = 2$ ($0, \frac{1}{2}, z$) stacked perovskite structure. The first column describes the irreducible representations for each distortion (labels as for the *Ammm* space group). The second column lists the glazer-tilt description of the distortions. Column 3 lists the space-group of the distorted structure, and column 4 the unit cell expansion relative to the *Ammm* aristotype structure.

3.3.4 Structural characterisation of KNdTa_2O_7

3.3.4.1 Room temperature synchrotron X-ray diffraction

High-resolution synchrotron X-ray powder diffraction data collected from KNdTa_2O_7 was initially indexed using the lattice parameters reported for KLaNb_2O_7 .⁷² However, close inspection of the diffraction data revealed a series of small peaks which can only be indexed using an $a' = 2 \times a$, $b' = b$, $c' = c$ geometric expansion of the aristotype unit cell ($a = 7.702 \text{ \AA}$, $b = 3.862 \text{ \AA}$, $c = 21.772 \text{ \AA}$) as shown in Figure 3.1.

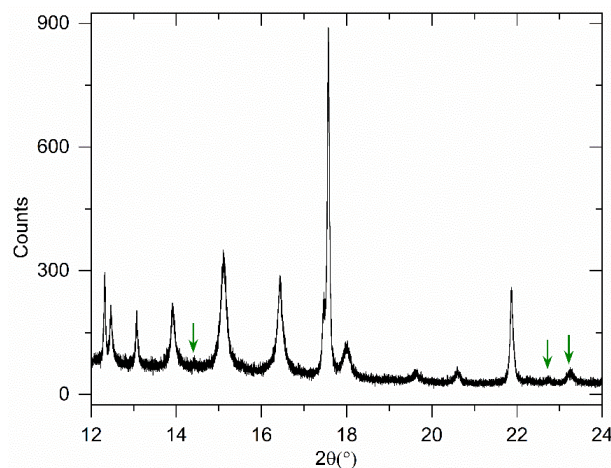


Figure 3.1. Synchrotron X-ray diffraction pattern collected from KNdTa_2O_7 . The green arrows indicate the superlattice peak positions attributed to the doubling of the aristotype a -axis.

Only the $Ammm$ (Glazer tilt $a^0b^+c^0/a^0b^+c^0$) and $Immm$ (Glazer tilt $a^0b^+c^0/a^0-b^+c^0$) structures from Table 3.1 are consistent with the observed lattice parameters of the KNdTa_2O_7 phases. Both these models were constructed and refined against synchrotron X-ray diffraction data which yielded statistically good fit. The observed, calculated and difference plots of the structural refinement in the $Immm$ space group is shown in Figure 3.2.

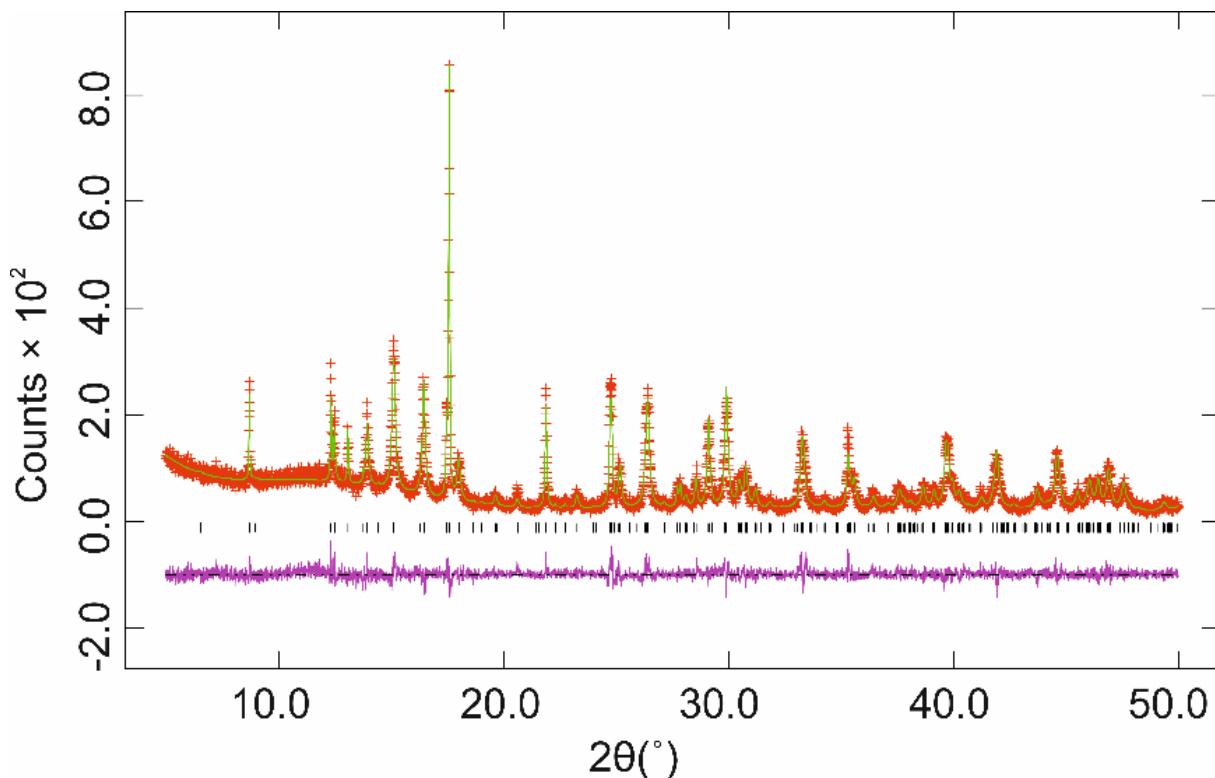


Figure 3.2. Observed, calculated and difference plots from the structural refinement of $Immm$ model with respect to synchrotron X-ray diffraction data collected at room temperature.

3.3.4.2 Room temperature neutron powder diffraction

Although the *Ammm* and *Immm* structures of KNdTa_2O_7 are consistent with the observed lattice parameters, close examination of the neutron diffraction data allows us to eliminate the *Ammm* space group based on extinction conditions as shown in Figure 3.3.

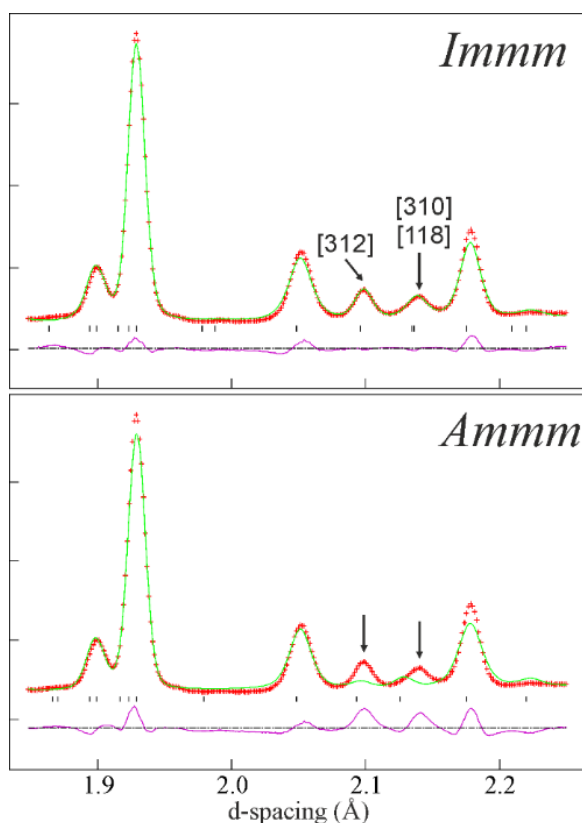


Figure 3.3. Observed, calculated and difference plots from the refinement of structural models in space groups *Ammm* and *Immm* against powder neutron diffraction collected from KNdTa_2O_7 . Arrows indicate systematically absent [312] and [310]/[118] reflections in the space group *Ammm*.

A structural model was constructed based on the *Immm* symmetry ($a^0b^+c^0/a^0-b^+c^0$) distortion. In this structure, there are two independent trigonal prismatic crystallographic sites ($4i$ and $4j$) to locate 4 potassium cations. As a result, the potassium cations can either be ordered on one or other of these sites or disordered across both while maintaining the stoichiometry. A potassium disordered *Immm* structural model was constructed for KNdTa_2O_7 and refined against neutron diffraction data which results in unreasonable U_{iso} values for both the potassium sites. U_{iso} values for $4i$ and $4j$ site were -0.039 and 0.222 respectively. However, when the

occupancy of the potassium sites was refined within the constraint of total occupancy being 1, the occupancy of the 4*i* site approached unity, while that of the 4*j* site approached zero. Thus, a model with the potassium ions ordered on the 4*i* site was constructed for KNdTa₂O₇ and refined against the neutron diffraction data which results in a better fit to the data and reasonable U_{iso} of the K-site compared to the disordered model.

SHG data collected from KNdTa₂O₇ indicates that it is SHG active (0.5 times α -SiO₂) and thus adopts a non-centrosymmetric crystal structure, so the *Immm* symmetry model cannot be correct. Given that none of the distortions in Table 3.1 are non-centrosymmetric, and noting the good fit achieved by the *Immm* ($a^0b^+c^0/a^0-b^+c^0$) distorted model, non-centrosymmetric structures based on a further distortion of this *Immm* model were constructed, again using the ISODISTORT software.⁶⁶ This analysis revealed two candidate non-centrosymmetric structures, described in the space groups *Im2m* and *I222*, which are generated by applying the Γ_4^- and Γ_1^- irreducible representations to the centrosymmetric *Immm* model. Refinement of the structural models described in space groups *Im2m* and *I222* against the NPD data proceeded smoothly. A visual comparison of the fits to the data by the different models shown in Figure 3.4, and the fitting statistics listed in Table 3.2, indicate that the *Im2m* model gives a marginally better fit to the data than either the centrosymmetric *Immm* model or the non-centrosymmetric *I222* model.

	χ^2	R _p (%)	wR _p (%)	Number of variables
KNdTa ₂ O ₇				
<i>Immm</i>	35.59	6.09	6.67	67
<i>Im2m</i>	28.26	5.50	5.94	77
<i>I222</i>	34.99	6.04	6.61	70

Table 3.2. Fitting statistics for the structural refinement of different KNdTa₂O₇ models against neutron powder diffraction data.

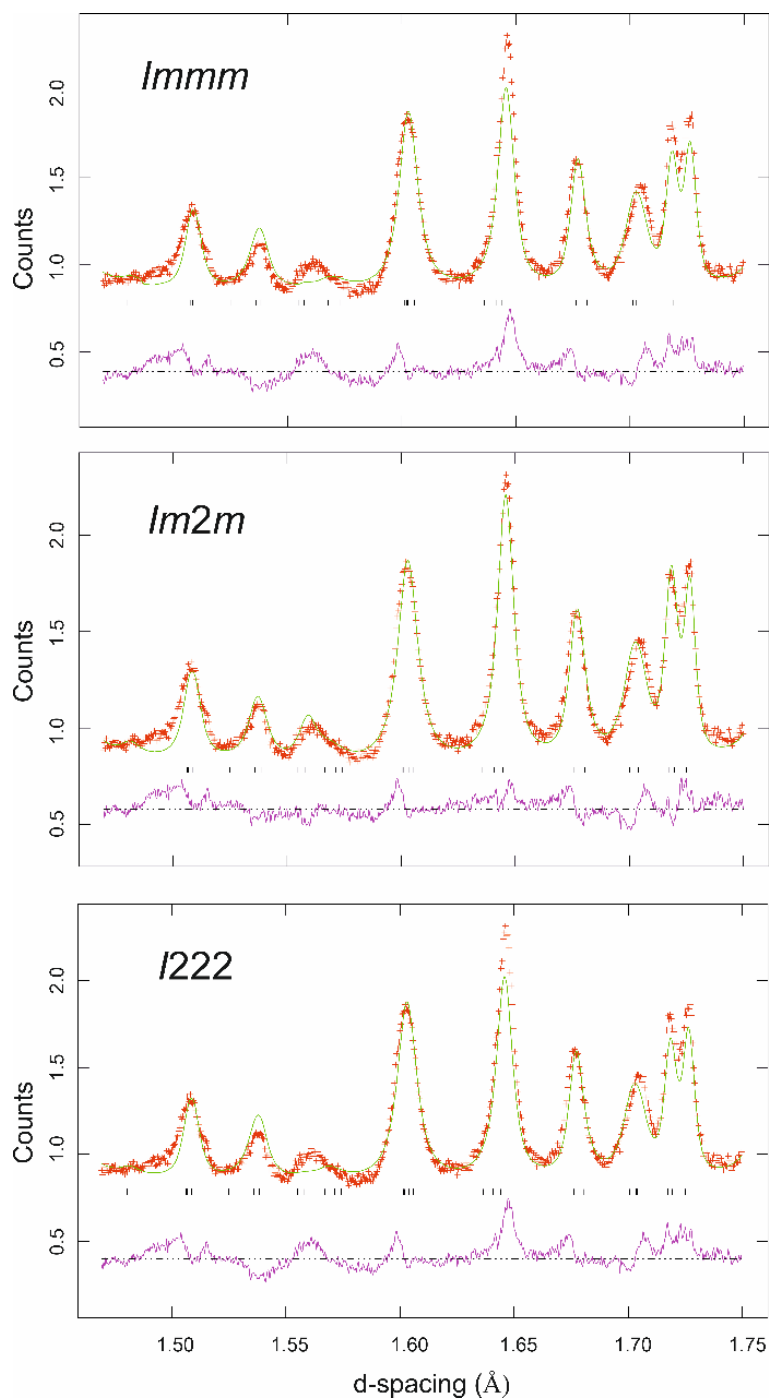


Figure 3.4. Observed, calculated and difference plots from the structural refinement of models described in the space groups *Immm*, *Im2m* and *I222* space against the neutron powder diffraction data collected from KNdTa_2O_7 .

Close inspection of the different refined structures of KNdTa_2O_7 provides further confirmation that the *Im2m* structural model is the best description of the phase. As shown in Table 3.3, lowering the symmetry from *Immm* to *I222* lowers the site symmetry of the Ta position from $8m$ to $8k$, allowing the y -coordinate of this site to take a non-zero value. However, in the refined

I222 model the Ta cation remains at $y = 0$, within error, although it is allowed to displace from the special position. Thus, the atomic configuration of the *I222* model remains centrosymmetric, within error. In contrast, lowering the symmetry to *Im2m* allows all 4 crystallographically distinct cation sites to adopt non-zero y -coordinates, and as can be seen in Table 3.3, in the refined *Im2m* structure all 4 cations displace from $y = 0$ by amounts significantly greater than the error bounds, providing further validation of the *Im2m* model. A complete description of the refined structure of KNdTa_2O_7 is given in Table 3.4, with a list of selected bond lengths from the structural refinement given in Table 3.5. The Observed, calculated and difference plots from the structure refinement of KNdTa_2O_7 are shown in Figure 3.5, and a representation of the refined structure of KNdTa_2O_7 is shown in Figure 3.6.

		Site	x	y	z	BVS
<i>Immm</i>	K	$4i$	0	0	0.2334(4)	0.943
	Nd(1)	$2a$	0	0	0	2.923
	Nd(2)	$2b$	0.5	0	0	2.585
	Ta	$8m$	0.7541(5)	0	0.3991(1)	5.522
<i>Im2m</i>	K	$4c$	0	0.0074(37)	0.2354(4)	0.973
	Nd(1)	$2a$	0	0.0182(36)	0	3.023
	Nd(2)	$2a$	0.5	0.0405(27)	0	2.672
	Ta	$8e$	0.7516(5)	0.0194(11)	0.3992(1)	5.293
<i>I222</i>	K	$4i$	0	0	0.2325(5)	0.956
	Nd(1)	$2a$	0	0	0	2.907
	Nd(2)	$2b$	0.5	0	0	2.602
	Ta	$8k$	0.7543(5)	0.0008(18)	0.3991(1)	5.540

Table 3.3. Fractional coordinates and cation bond valence sums from the structural refinement of KNdTa_2O_7 against powder neutron diffraction data.

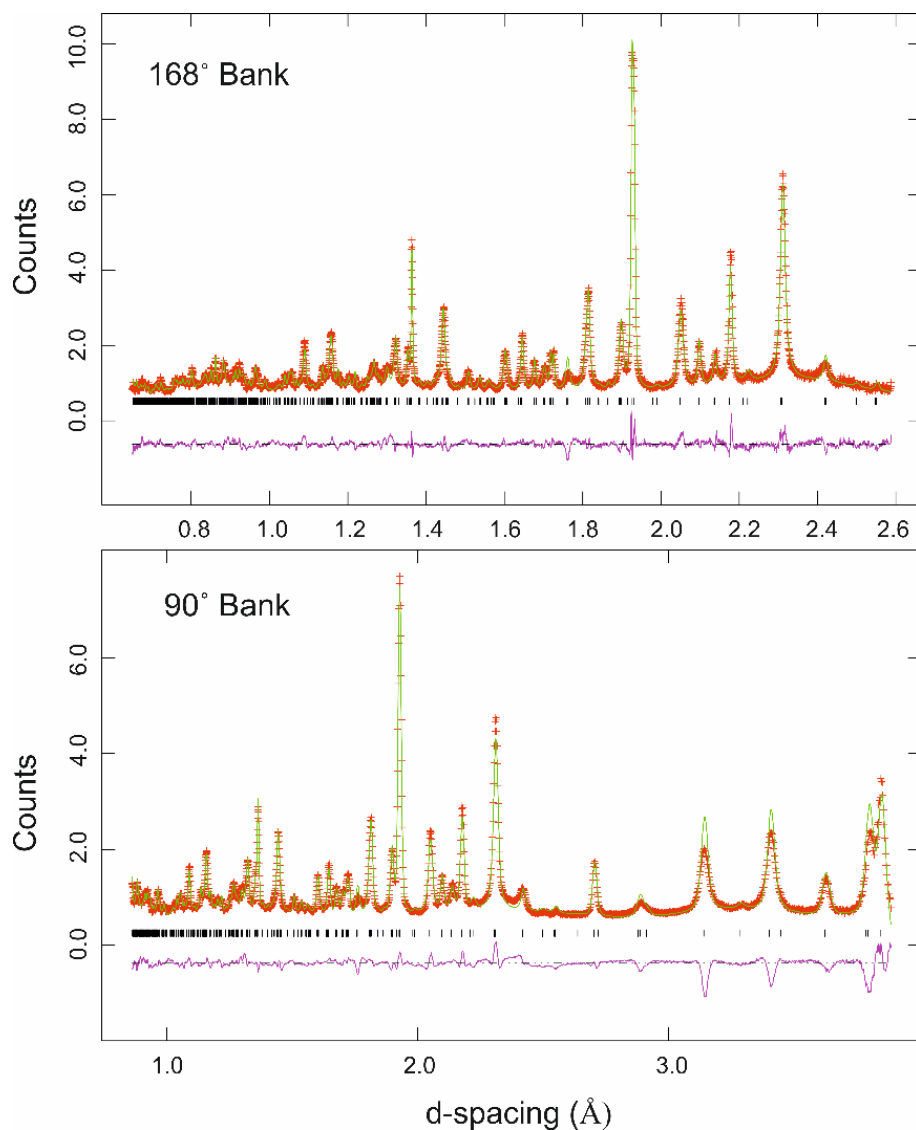


Figure 3.5. Observed, calculated and difference plots from the structural refinement of KNdTa_2O_7 against neutron diffraction data.

Atom	Label	Site	x	y	z	Occ.	U_{iso}
K	K1	$4c$	0	0.0074(37)	0.2354(4)	1	0.0036(19)
Nd	Nd1	$2a$	0	0.0182(36)	0	1	0.0176(22)
	Nd2	$2a$	0.5	0.0405(27)	0	1	0.0110(19)
Ta	Ta1	$8e$	0.7516(5)	0.0194(11)	0.3992(1)	1	0.0041(5)
O	O1	$4d$	0.2812(6)	0.5869(14)	0	1	0.0104(17)
	O2	$4c$	0	0.1071(16)	0.4076(2)	1	0.0007(15)
	O3	$4c$	0	0.5570(23)	0.9224(2)	1	0.0094(15)
	O4	$8e$	0.7169(5)	0.0196(21)	0.3174(1)	1	0.0251(11)
	O5	$8e$	0.7457(11)	0.0294(24)	0.0831(1)	1	0.0508(12)
KNdTa_2O_7 – space group $Im2m$ (#44)							

$a = 7.7018(6) \text{ \AA}$, $b = 3.8613(3) \text{ \AA}$, $c = 21.7688(17) \text{ \AA}$, volume = $647.37(14) \text{ \AA}^3$ Formula weight = $657.23 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Neutron Time of Flight Temperature: 298 K $\chi^2 = 28.26$, $R_p = 5.50 \%$, $wR_p = 5.94 \%$
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Table 3.4. Parameters from the structural refinement of KNdTa₂O₇ against neutron powder diffraction data collected at 298 K.

	Anion	Bond length (Å)	Bond valence sum
K1	O4 × 2	2.818(7)	+0.973
	O4 × 2	2.768(13)	
	O4 × 2	2.833(13)	
Nd2	O1 × 2	2.431(10)	+3.023
	O1 × 2	2.700(10)	
	O5 × 4	2.618(8)	
	O2 × 2	2.617(9)	
	O2 × 2	2.972(10)	
Nd1	O1 × 2	2.732(10)	+2.672
	O1 × 2	3.084(12)	
	O3 × 2	2.455(13)	
	O3 × 2	2.680(14)	
	O5 × 4	2.667(7)	
Ta	O1 × 1	2.221(3)	+5.293
	O2 × 1	1.951(5)	
	O3 × 1	2.008(5)	
	O4 × 1	1.801(4)	
	O5 × 1	1.931(11)	
	O5 × 1	2.007(11)	

Table 3.5. Selected bond lengths from the structural refinement of KNdTa₂O₇.

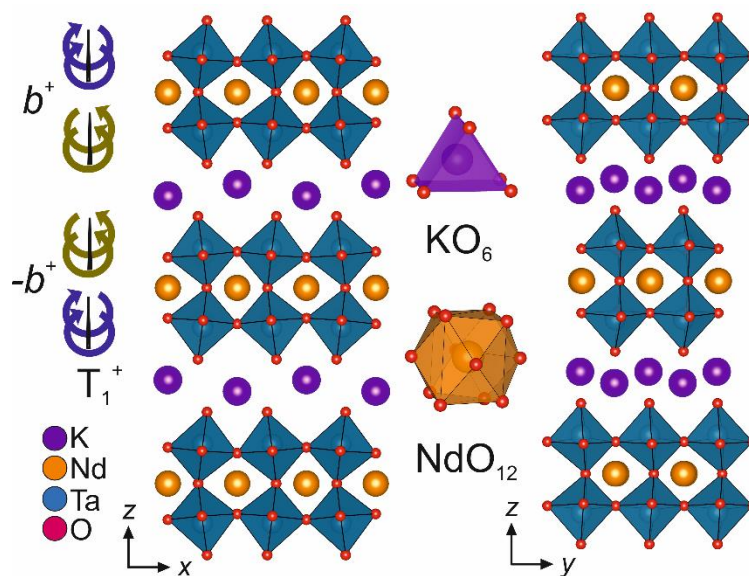


Figure 3.6. The structure of KNdTa_2O_7 in space group $Im2m$ with $a^0b^+c^0/a^0-b^+c^0$ tilting.

3.3.5 Structural characterisation of KNdNb_2O_7

3.3.5.1 Room temperature synchrotron X-ray diffraction

High-resolution synchrotron X-ray diffraction data collected from KNdNb_2O_7 could initially be indexed using the unit cell that was previously reported for KNdTa_2O_7 .⁶⁹ However, close inspection of the diffraction data revealed a series of small peaks which can only be indexed using an $a' = 2 \times a$, $b' = b$, $c' = c$ geometric expansion of the aristotype unit cell ($a = 7.709 \text{ \AA}$, $b = 3.871 \text{ \AA}$, $c = 21.553 \text{ \AA}$) as shown in Figure 3.7.

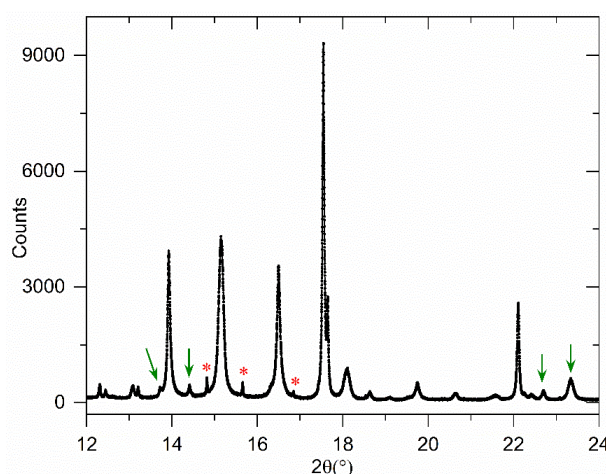


Figure 3.7. Synchrotron X-ray diffraction data collected from KNdNb_2O_7 . The green arrows indicate the superlattice peak positions attributed to the doubling of the aristotype a -axis. Red asterisks correspond to the peaks from NdNbO_4 secondary phase.

Only *Ammm* (Glazer tilt $a^0b^+c^0/a^0b^+c^0$) and *Immm* (Glazer tilt $a^0b^+c^0/a^0-b^+c^0$) structures from Table 3.1 are consistent with the observed lattice parameters of the KNdNb_2O_7 phases. Both these models were constructed and refined against synchrotron X-ray diffraction data which yielded a statistically good fit. The observed, calculated and difference plots of the structural refinement in *Immm* space group are shown in Figure 3.8.

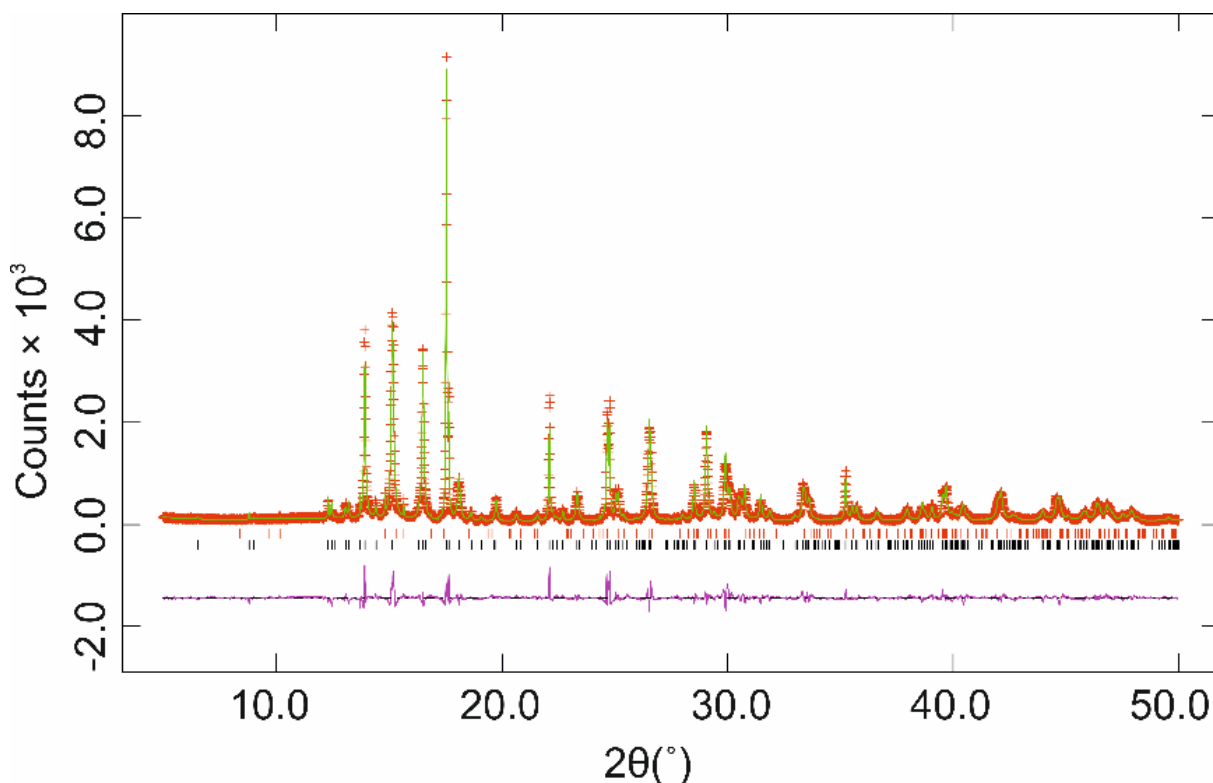


Figure 3.8. Observed, calculated and difference plots from the structural refinement of *Immm* model of KNdNb_2O_7 with respect to synchrotron X-ray diffraction data collected at room temperature. The black ticks show the Bragg positions for the majority KNdNb_2O_7 phase and the red ticks show the position of the NdNbO_4 secondary phase.

3.3.5.2 Room temperature neutron powder diffraction

Although *Ammm* and *Immm* structures of KNdNb_2O_7 are consistent with the observed lattice parameters, close examination of the neutron diffraction data allows us to eliminate the *Ammm* space group based on extinction conditions as shown in Figure 3.9.

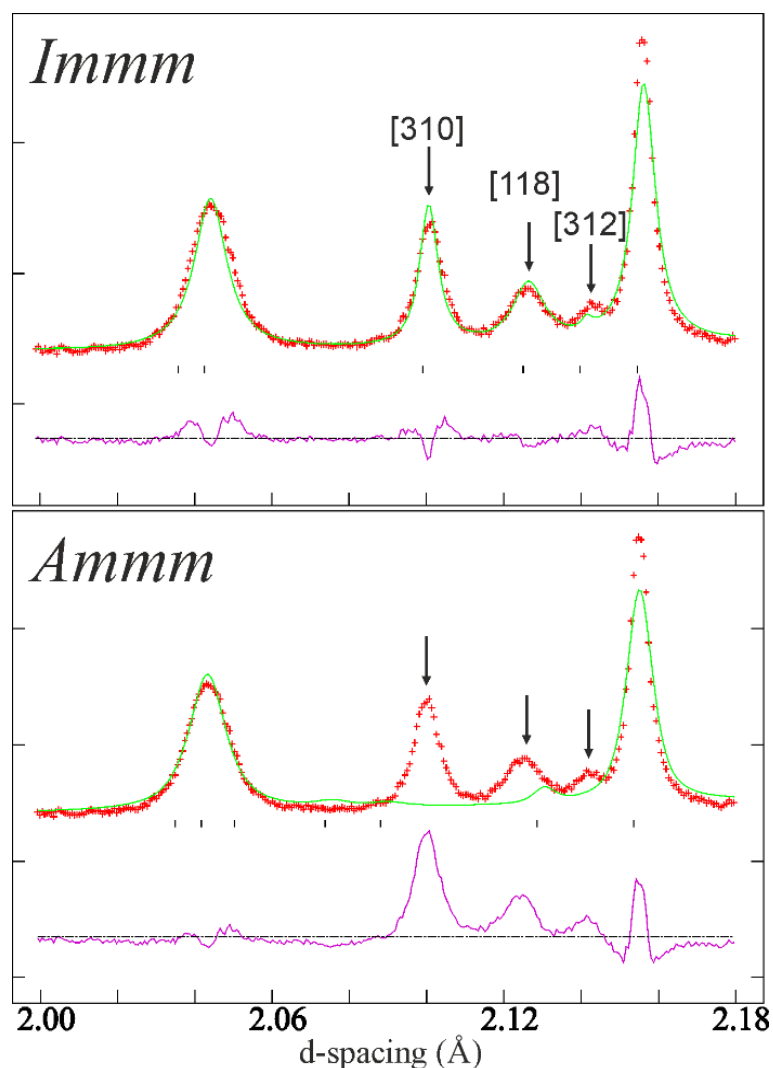


Figure 3.9. Observed, calculated and difference plots from the refinement of structural models in space groups *Ammm* and *Immm* against powder neutron diffraction collected from KNdNb₂O₇. Arrows indicate systematically absent [312] and [310]/[118] reflections in the space group *Ammm*.

A structural model was constructed based on the *Immm* space group with $(a^0b^+c^0/a^0-b^+c^0)$ distortion. In this structure, there are two independent trigonal prismatic crystallographic sites (*4i* and *4j*) to locate 4 potassium cations. As a result, the potassium cations can either be ordered on one or other of these sites or disordered across both while maintaining the stoichiometry. Potassium disordered *Immm* structural model was constructed for KNdNb₂O₇ and refined against neutron diffraction data which results in unreasonable thermal parameters for both *4i* and *4j* sites of potassium. The corresponding U_{iso} values were -0.045 and 0.536 for *4i* and *4j* sites respectively. However, when the occupancy of the potassium sites was refined within the

constraint of total occupancy being 1, the occupancy of the 4i site approached unity, while that of the 4j site approached zero. Thus, the model with the potassium ions ordered on the 4i site was constructed for KNdNb₂O₇ and refined against the neutron diffraction data which gave a better fit to the data, and reasonable thermal parameter for the K-site compared to the disordered model.

SHG data collected from KNdNb₂O₇ indicate that it is SHG active (0.56 times α -SiO₂) and thus adopts a noncentrosymmetric crystal structure, so the *Immm* symmetry model cannot be correct. Given that none of the distortions in Table 3.1 are non-centrosymmetric, and noting the good fit achieved by the *Immm* ($a^0b^+c^0/a^0-b^+c^0$) distorted model, non-centrosymmetric structures based on a further distortion of this *Immm* model were constructed, again using the ISODISTORT software.⁶⁶ This analysis revealed two candidate non-centrosymmetric structures, described in the space groups *Im2m* and *I222*, which are generated by applying the Γ_4^- and Γ_1^- irreducible representations of the *Immm* space group respectively to the centrosymmetric *Immm* model. Refinement of the structural models described in space groups *Im2m* and *I222* against the neutron diffraction data proceeded smoothly. A visual comparison of the fits to the data by the different models shown in Figure 3.10, and the fitting statistics listed in Table 3.6, indicate that the *Im2m* model gives a marginally better fit to the data than either the centrosymmetric *Immm* model or the non-centrosymmetric *I222* model.

	χ^2	R _p (%)	wR _p (%)	Number of variables
KNdNb ₂ O ₇				
<i>Immm</i>	48.91	7.17	7.52	69
<i>Im2m</i>	38.88	6.61	6.70	77
<i>I222</i>	44.74	6.63	7.19	72

Table 3.6. Fitting statistics for the structural refinement of KNdNb₂O₇ against neutron powder diffraction data.

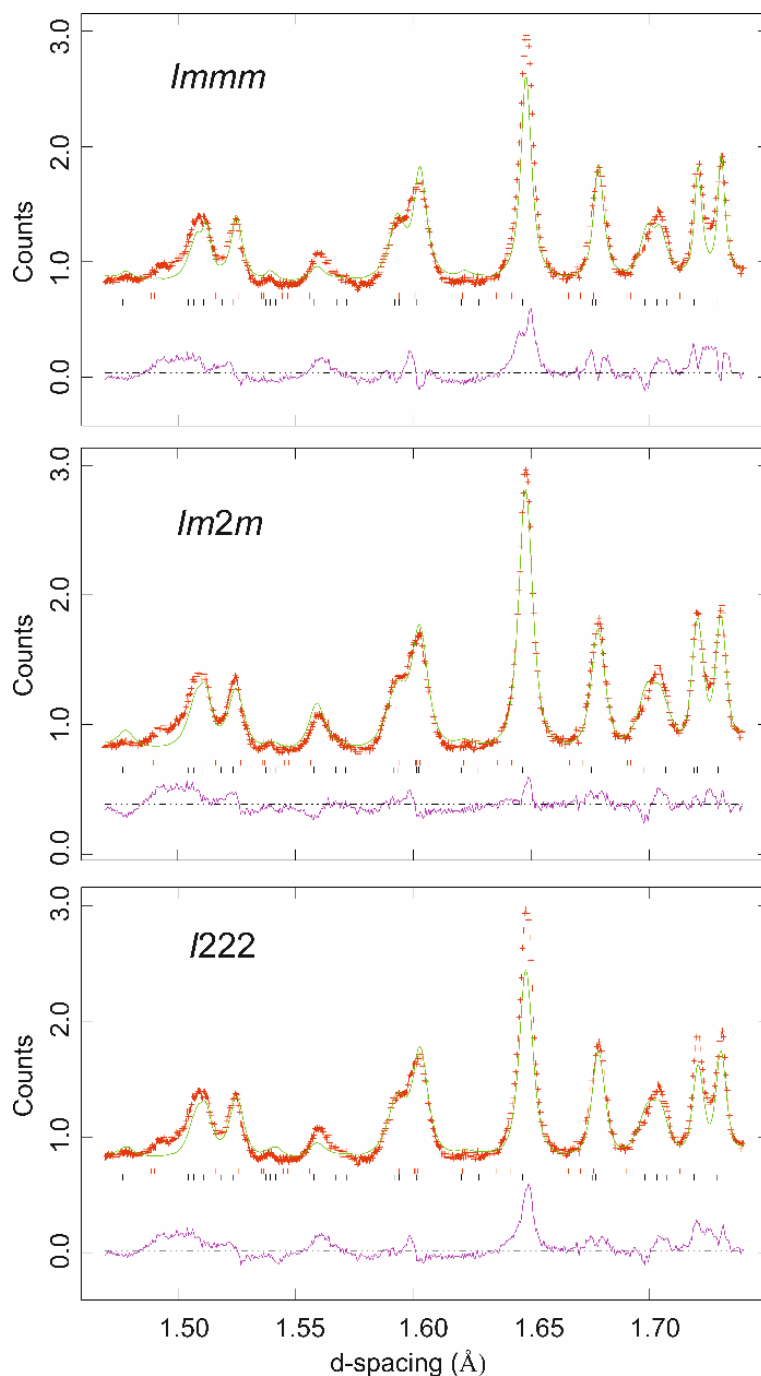


Figure 3.10. Observed, calculated and difference plots from the structural refinement of models described in the space groups *Immm*, *Im2m* and *I222* space against the neutron powder diffraction data collected from KNdNb_2O_7 . NdNbO_4 was added as a secondary phase; Bragg positions of which are indicated by the red ticks.

Close inspection of the different refined structures of KNdNb_2O_7 provides further confirmation that the *Im2m* structural model is the best description of this phase. As shown in Table 3.7, lowering the symmetry from *Immm* to *I222* lowers the site symmetry of the Nb position from $8m$ to $8k$, allowing the y -coordinate of this site to take a non-zero value. However, it can be

seen that in the refined $I222$ model the Nb cation remains at $y = 0$, within error, thus the atomic configuration of the $I222$ model remains centrosymmetric, within error. In contrast, lowering the symmetry to $Im2m$ allows all 4 crystallographically distinct cation sites to adopt non-zero y -coordinates, as can be seen in Table 3.7, in the refined $Im2m$ structure all 4 cations displace from $y = 0$ by amounts significantly greater than the error bounds, providing further validation of the $Im2m$ model. A complete description of the refined structure of KNdNb_2O_7 is given in Table 3.8, with a list of selected bond lengths from the structural refinement given in Table 3.9. The observed, calculated and difference plots from the structure refinement of KNdNb_2O_7 against the neutron powder diffraction data are shown in Figure 3.11, and a representation of the refined structure of KNdNb_2O_7 is shown in Figure 3.13.

		Site	x	y	z	BVS
$Immm$	K	$4i$	0	0	0.2358(4)	0.961
	Nd(1)	$2a$	0	0	0	2.584
	Nd(2)	$2b$	0.5	0	0	2.924
	Nb	$8m$	0.7505(5)	0	0.3987(1)	5.397
$Im2m$	K	$4c$	0	0.0078(38)	0.2371(4)	0.972
	Nd(1)	$2a$	0	0.0123(29)	0	2.894
	Nd(2)	$2a$	0.5	0.0113(25)	0	2.996
	Nb	$8e$	0.7515(5)	0.0230(10)	0.3985(1)	5.324
$I222$	K	$4i$	0	0	0.2362(4)	0.973
	Nd(1)	$2a$	0	0	0	2.642
	Nd(2)	$2b$	0.5	0	0	2.849
	Nb	$8k$	0.7512(5)	0.9983(15)	0.3986(1)	5.402

Table 3.7. Fractional coordinates and cation bond valence sums from the structural refinement of KNdNb_2O_7 against powder neutron diffraction data.

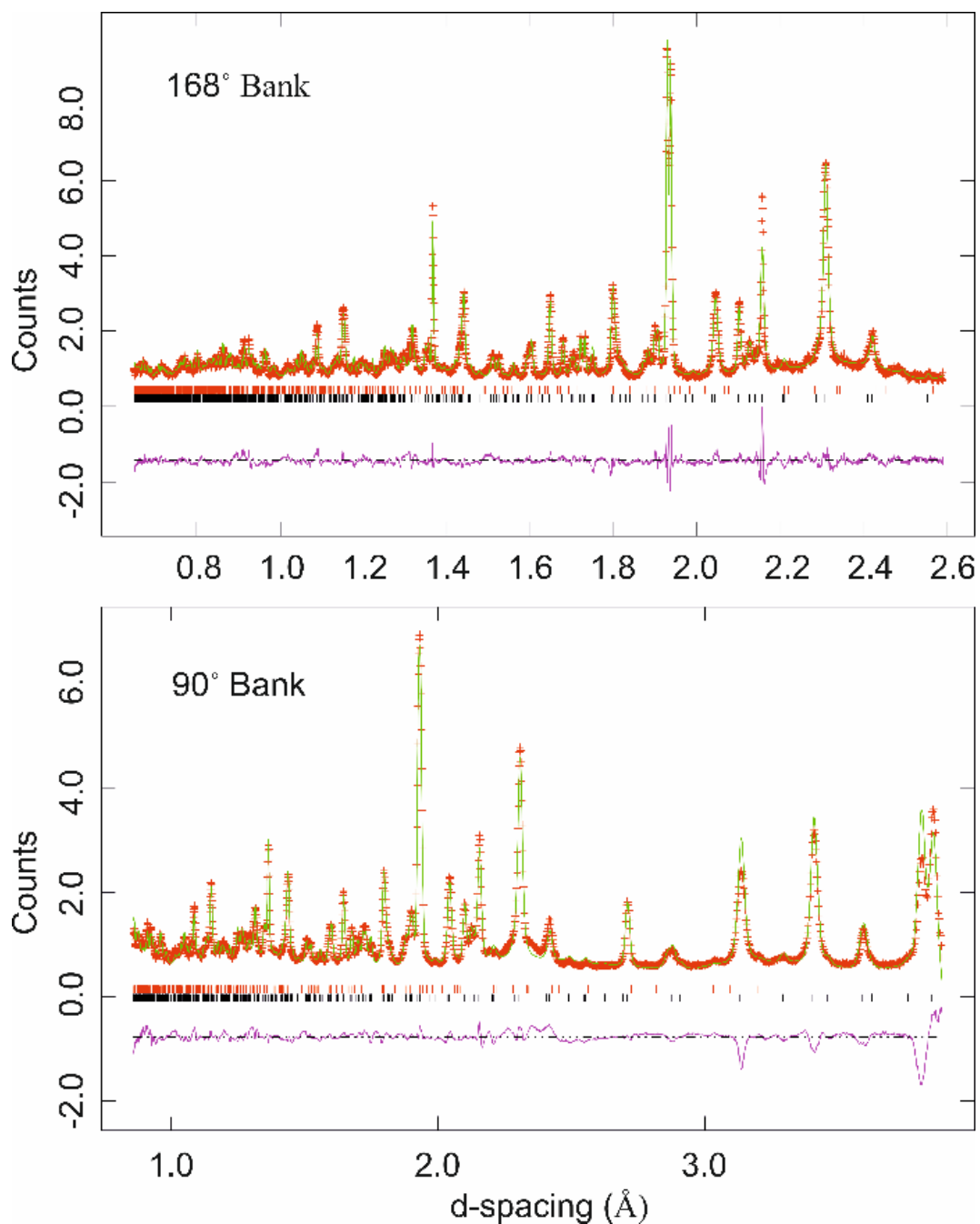


Figure 3.11. Observed, calculated and difference plots from the structural refinement of KNdNb_2O_7 against neutron diffraction data.

Atom	Label	Site	x	y	z	Occ.	U_{iso}
K	K1	4c	0	0.0078(38)	0.2371(4)	1	0.0175(22)
Nd	Nd1	2a	0	0.0123(29)	0	1	0.0122(18)
	Nd2	2a	0.5	0.0113(25)	0	1	0.0136(18)
Nb	Nb1	8e	0.7515(5)	0.0230(10)	0.3985(1)	1	0.0034(5)
O	O1	4d	0.2862(6)	0.5934(13)	0	1	0.0125(17)
	O2	4c	0	0.1073(14)	0.4020(2)	1	0.0134(18)

	O3	4c	0	0.5254(25)	0.9267(2)	1	0.0095(12)
	O4	8e	0.7160(4)	0.0411(18)	0.3180(2)	1	0.0219(10)
	O5	8e	0.7617(9)	0.0408(24)	0.0856(2)	1	0.0445(11)
KNdNb₂O₇ – space group <i>Im2m</i> (#44) a = 7.7093(5) Å, b = 3.8709(2) Å, c = 21.5558(16) Å, volume = 643.28(13) Å³ Formula weight = 481.14 g mol⁻¹, Z = 4 Radiation source: Neutron Time of Flight Temperature: 298 K χ^2 = 38.88, R_p = 6.61%, _wR_p = 6.70 %							

Table 3.8. Parameters from the structural refinement of KNdNb₂O₇ against neutron powder diffraction data collected at 298 K.

	Anion	Bond length (Å)	Bond valence sum
K1	O4 × 2	2.802(7)	+0.972
	O4 × 2	2.729(12)	
	O4 × 2	2.906(13)	
Nd2	O1 × 2	2.309(9)	+2.996
	O1 × 2	2.792(10)	
	O5 × 4	2.736(6)	
	O2 × 2	2.628(8)	
	O2 × 2	3.128(9)	
Nd1	O1 × 2	2.738(9)	+2.894
	O1 × 2	3.151(10)	
	O3 × 2	2.459(12)	
	O3 × 2	2.538(12)	
	O5 × 4	2.606(6)	
Nb	O1 × 1	2.221(3)	+5.324
	O2 × 1	1.945(4)	
	O3 × 1	2.032(4)	
	O4 × 1	1.758(5)	
	O5 × 1	1.900(10)	
	O5 × 1	2.036(10)	

Table 3.9. Selected bond lengths from the refined structure of KNdNb₂O₇.

3.4 Discussion

3.4.1 Two-step cation exchange reaction

The synthesis of KNdTa_2O_7 via the K-for-Rb cation exchange of $\text{RbNdTa}_2\text{O}_7$ has been reported previously.⁶⁹ However, to prepare the KNdM_2O_7 ($M = \text{Nb, Ta}$) compounds the 2-step process: $\text{RbNdM}_2\text{O}_7 \rightarrow \text{NaNdM}_2\text{O}_7 \rightarrow \text{KNdM}_2\text{O}_7$ was employed using sequential Na-for-Rb and K-for-Na cation exchange. This was to ensure the observed SHG activity of the KNdM_2O_7 phases was not due to the presence of small quantities of the non-centrosymmetric compounds RbNdM_2O_7 and/or LiNdM_2O_7 due to incomplete cation-exchange. So, a route via the centrosymmetric NaNdM_2O_7 intermediates was utilized.

3.4.2 Effect of A' - and A -cation on the structure of $A'\text{NdM}_2\text{O}_7$

The polar structures of KNdTa_2O_7 and KNdNb_2O_7 can be derived from the aristotype $n = 2$ ($0, \frac{1}{2}, z$) structure (space group $Ammm$ #65) by the sequential application of two distortion modes: the T_1^+ mode which adds an $a^0b^+c^0/a^0-b^+c^0$ cooperative tilting distortion of the MO_6 octahedra, and a Γ_4^- polar distortion. Considering the tilting distortion first, the cooperative rotation and tilting of BO_6 octahedra in ABO_3 perovskite phases, and related layered analogues, occurs in response to a size mismatch between the A - and B -site cations. If a small cation is placed in the 12-coordinate A -site of an ABO_3 perovskite phase, the cooperative rotation of the BO_6 units can optimize the A -site bonding by shortening the A -O bond length without changing the B -O bond length. For the 3D ABO_3 perovskite structure, the magnitude of the size-mismatch between A - and B -cations can be quantified using the structural tolerance factor, $t = \langle A-O \rangle / (\sqrt{2} \langle B-O \rangle)$.³ A small value of t ($t \ll 1$) indicates a large mismatch in the sizes of A - and B -cations, and thus results in large magnitude tilting and twisting distortions. However, the situation for layered $A'\text{AB}_2\text{O}_7$ phases, such as KNdM_2O_7 , is a bit more complicated because the tilting of the BO_6 units must accommodate the size mismatch between A - and B -cations as well as the mismatch between A' - and B -cations.

The effect of the differing bonding requirements of the A - and A' -cations on the tilting distortions of $n = 2$ layered perovskite phases will now be discussed by taking the structures of $A'\text{NdNb}_2\text{O}_7$ ($A' = \text{Cs}, \text{Rb}, \text{Li}, \text{Na}, \text{K}$) compounds as examples. The analogous compounds in the $A'\text{NdTa}_2\text{O}_7$ series have the same structure as the corresponding Nb-phases. Hence the conclusions derived from the discussion of these Nb-phases can be extended to the Ta analogues.

The tolerance factor of the NdNb_2O_7 perovskite double sheets present in all the $A'\text{NdNb}_2\text{O}_7$ phases can be calculated using the ionic radii of the ions ($\text{Nd}^{3+} = 1.27 \text{ \AA}$, $\text{Nb}^{5+} = 0.64 \text{ \AA}$, $\text{O}^{2-} = 1.40 \text{ \AA}$) to yield a value of $t = 0.925$. This indicates that in the absence of any influence from the A' -cation; the NdNb_2O_7 sheets should exhibit large magnitude tilting and twisting distortions.

When large Cs^+ or Rb^+ cations occupy the interlayer A' -cation site, the $A'\text{NdNb}_2\text{O}_7$ phases adopt the Dion-Jacobson framework with $(0, 0, z)$ stacking of the double perovskite layers. At room temperature the $\text{CsNdNb}_2\text{O}_7$ and $\text{RbNdNb}_2\text{O}_7$ phases adopt polar $P2_1am$ and $I2cm$ structures with relatively large magnitude $a^-a^-c^+$ and $a^-a^-c^+/(a^-a^-c^+)$ tilting distortions (Figure 3.12) respectively. Although the NdNb_2O_7 sheets present in $\text{CsNdNb}_2\text{O}_7$ and $\text{RbNdNb}_2\text{O}_7$ phases are similar (same tilting pattern, same magnitude of tilt), the structures of the Cs and Rb compounds differ in the manner in which these distorted perovskite sheets are stacked. This difference can be attributed to ‘larger’ Cs^+ and ‘smaller’ Rb^+ cations requiring subtly different structures to optimize the bonding requirements of the two different A' -cations and those of the 12-coordinate Nd^{3+} cation simultaneously.¹¹

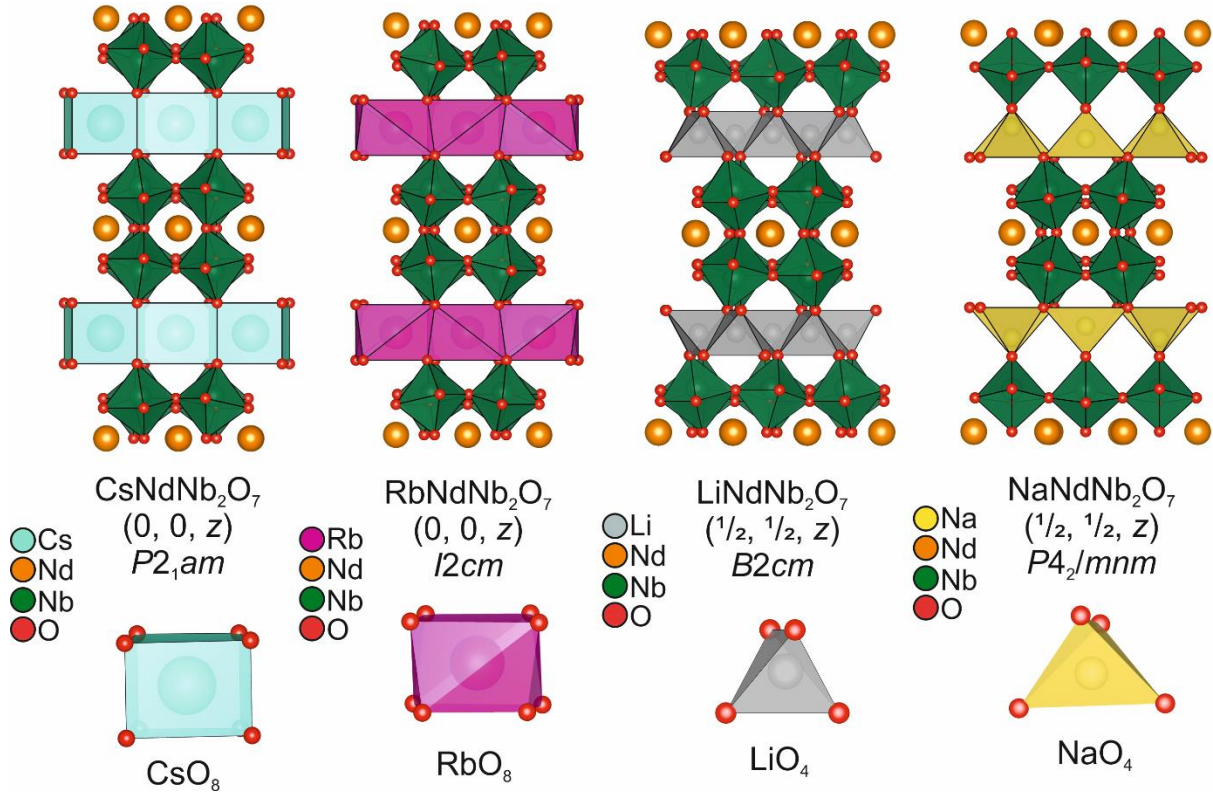


Figure 3.12. Structures of $A'\text{NdNb}_2\text{O}_7$ ($A' = \text{Cs, Rb, Li, Na}$)

Exchanging the large Cs^+/Rb^+ cations for much smaller Na^+/Li^+ cations leads to a change from the $(0, 0, z)$ sheet stacking of the Dion-Jacobson framework to the $(\frac{1}{2}, \frac{1}{2}, z)$ sheet stacking of the Ruddlesden-Popper framework. This is because the Li^+/Na^+ cations are too small to occupy the 8-coordinate A' -cation sites in the Dion-Jacobson framework. $\text{LiNdNb}_2\text{O}_7$ adopts a polar $n = 2$ Ruddlesden-Popper structure with a relatively large magnitude of $a^-a^-c^+/- (a^-a^-c^+)$ tilting of NbO_6 octahedra. (Figure 3.12) This tilting pattern can simultaneously satisfy the bonding requirements of the 4-coordinate Li^+ cations and the 12-coordinate Nd^{3+} cations, as indicated by close to ideal BVS values of Li^+ and Nd^{3+} ions ($\text{Li} = 0.99$, $\text{Nd} = 3.07$).⁴² However, the larger ionic radius of Na^+ means this $\text{LiNdNb}_2\text{O}_7$ framework is unsuitable for $\text{NaNdNb}_2\text{O}_7$. Instead, $\text{NaNdNb}_2\text{O}_7$ adopts a non-polar $P4_2/mnm$ structure in which the NdNb_2O_7 sheets exhibit only a small magnitude $a^-b^0c^0/b^0a^-c^0$ tilting distortion (Figure 3.12).⁴² The smaller distortion of the NdNb_2O_7 layers in the Na compound, compared to the Cs, Rb and Li compounds, is motivated by the need to expand the 4-coordinate A' -cation sites to accommodate Na^+ . However, this also

requires the 12-coordinate Nd^{3+} A-cation site to expand which weakens the bonding of this site. Thus, we observe a potential conflict between the need to optimize the bonding of both the A- and A'-cations simultaneously.

In light of the examples provided by the other $A'\text{NdNb}_2\text{O}_7$ phases, the structure of KNdNb_2O_7 can also be seen as the result of a compromise between the bonding requirements of the A- and A'-cations. The intermediate ionic radius of K^+ drives the adoption of a $(0, \frac{1}{2}, z)$ stacking of the NdNb_2O_7 sheets, which leads to the formation of 6-coordinate trigonal prismatic A'-cation sites to accommodate the K^+ ions. The small magnitude $a^0b^+c^0/a^0-b^+c^0$ tilting distortion of the NdNb_2O_7 sheets in KNdNb_2O_7 (Figure 3.13) can be seen as the result of a need to expand the 6-coordinate A'-cation sites to accommodate K^+ cations, and again this also expands the 12-coordinate A-cation site compromising the bonding of the Nd^{3+} as illustrated by the non-optimal BVS values ($\text{Nd}(1) = 2.894$; $\text{Nd}(2) = 2.996$). To further demonstrate the competition between A- and A'-cation bonding we have constructed a hypothetical structure in which the $a^-a^-c^+$ distorted NdNb_2O_7 layers from $\text{CsNdNb}_2\text{O}_7$ are stacked in a $(0, \frac{1}{2}, z)$ manner, as shown in Figure 3.13. This hypothetical structure represents a situation where the bonding requirements of the Nd^{3+} are satisfied in the NdNb_2O_7 perovskite layers as indicated by the close to ideal BVS value (3.06) of Nd^{3+} A-cation site. However, examination of the 4 different A'-cation sites in this framework, reveals they are far from ideal to accommodate K^+ with 2 being too small (BVS = 1.37, 1.41) and 2 being too large (BVS = 0.81, 0.85). This observation is consistent with the idea that the change in tilt pattern of the NdNb_2O_7 sheets from the large magnitude $a^-a^-c^+$ distortion of the Cs, Rb and Li phases, to the small magnitude $a^0b^+c^0/a^0-b^+c^0$ distortion observed in KNdNb_2O_7 occurs to better accommodate the K^+ cations. Together these features demonstrate that the A'-cations not only define the stacking pattern of the perovskite sheets (Cs, Rb = $(0, 0, z)$; K = $(0, \frac{1}{2}, z)$; Na, Li = $(\frac{1}{2}, \frac{1}{2}, z)$) but also have a large influence on the type and magnitude of the AB_2O_7 tilting distortions.

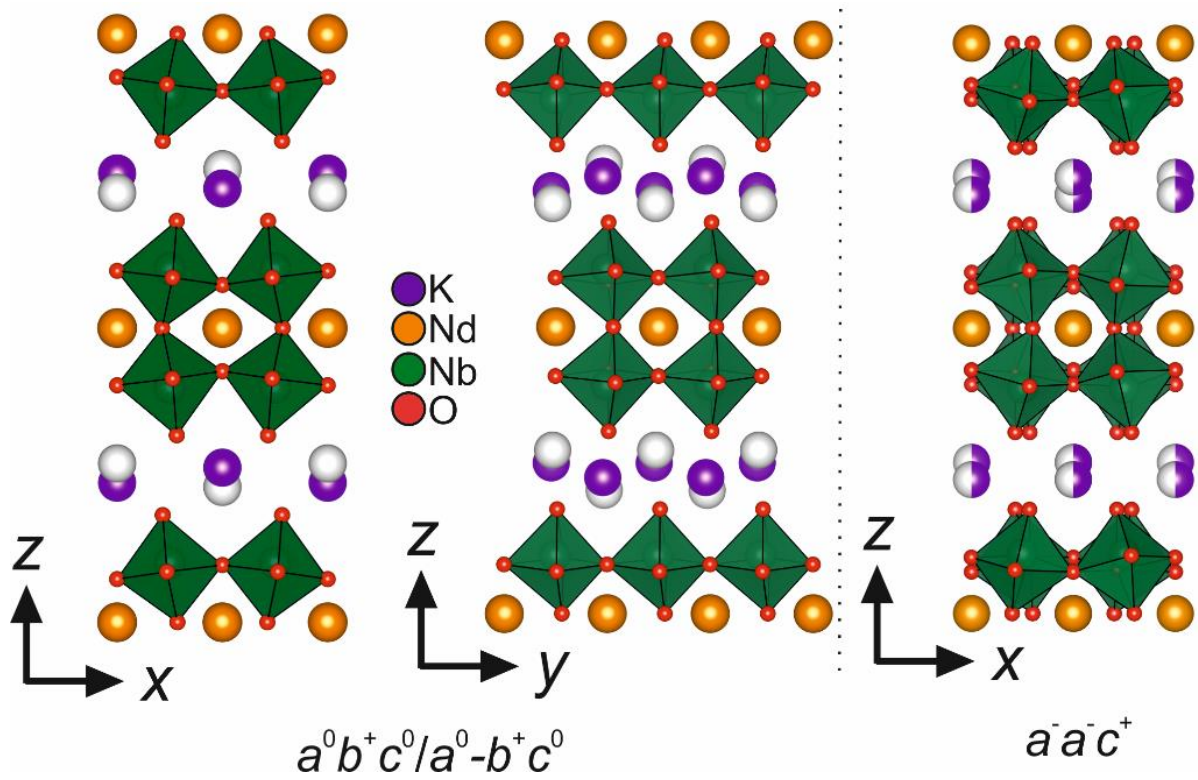


Figure 3.13. Observed $a^0 b^+ c^0 / a^0 - b^+ c^0$ distorted structure of KNdNb_2O_7 (left) and hypothetical $a^- a^- c^+$ distorted structure (right). Grey spheres indicate K-vacancy and half shading of the K-ions indicate a disordered 50% occupation in the $a^- a^- c^+$ distorted model.

This is an important observation because the tilting distortions exhibited by $A'\text{NdM}_2\text{O}_7$ phases can have a decisive influence on the physical properties of these materials. For example, the polar structures of CsNdM_2O_7 , RbNdM_2O_7 and LiNdM_2O_7 arise via a trilinear coupling mechanism in which a combination of two non-polar tilting-distortion modes (e.g. the M_2^+ and M_5^- modes of $\text{CsNdNb}_2\text{O}_7$) break the inversion symmetry of the lattice and couple to a third polar distortion mode (e.g. the Γ_5^- mode of $\text{CsNdNb}_2\text{O}_7$) resulting in the observed polar structures. The observation that only a single tilting distortion mode (T_1^+) accompanies the Γ_4^- polar distortion mode in KNdM_2O_7 phases rules out trilinear coupling as the origin of the polar structures of these phases. Instead, it is likely that the Γ point polar distortions of the KNdM_2O_7 phases are driven by a second-order Jahn-Teller distortion of the $\text{TaO}_6/\text{NbO}_6$ units, as is commonly observed for octahedrally coordinated d^0 transition metal cations, and consistent with the displacement of the Ta/Nb cations in Table 3.3 and Table 3.7.

3.4.3 Effect of M^{5+} cation on distortion of MO_6 octahedra

In Figure 3.14, a NdM_2O_7 sheet of $KNdM_2O_7$ structure is shown. We have used the $\angle O2^1-O3-O2^2$ bond angle to quantify the in-plane tilting magnitude. To do so we have manually moved the y co-ordinate of $O3$ to be the same as that of $O2$. For a no tilt system, this angle would be 180° . The more tilted the system, the larger the deviation from 180° . We have not used the $\angle M-O-M$ bond angle to measure tilting because M -cation is off-centered from the MO_6 octahedra.

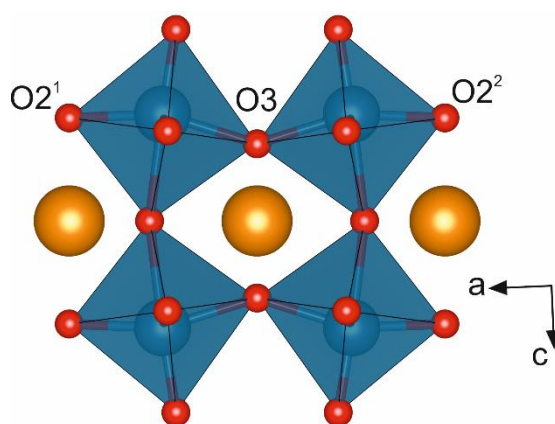


Figure 3.14. The in-plane tilt angle of NdM_2O_7 -sheet

The tilting angle is calculated to be 170.45° and 164.75° for $KNdTa_2O_7$ and $KNdNb_2O_7$ phases respectively. Although, both Nb^{5+} and Ta^{5+} cations are off-centered in the polar $Im2m$ structure; niobium in M -site results in larger tilting than that of tantalum. In addition, if we note the bond asymmetries in M -cation coordination for both these phases, we realize that one “short”, one “long” and four “normal” (compared to the average bond length) bonds are present in the M -cation coordination environment, which infers a local C_4 distortion has taken place. The “short” bond is even shorter in the niobium analogue, ($1.758 \text{ \AA}$ for the Nb-phase vs $1.801 \text{ \AA}$ for the Ta-phase) which means the C_4 distortion is more prominent in $KNdNb_2O_7$ than in $KNdTa_2O_7$. When a d^0 transition metal ion is off centred in an octahedral coordination of oxide ions, the metal d orbitals and oxygen $2p$ orbitals hybridize to lower the energy of the system. Oxygen $2p$ orbitals are closer to niobium $4d$ orbitals than tantalum $5d$ orbitals, so the hybridisation

between oxygen 2*p* orbitals and Nb 4*d* orbitals is expected to be stronger than that of Ta 5*d* orbitals. As a consequence, the C₄ distortion is stronger in the NbO₆ octahedra than in TaO₆.

3.4.4 *M*⁵⁺ cation off centering distortions of KNdM₂O₇ (*M* = Ta, Nb) phases

Analysis of the local NbO₆ and TaO₆ coordination polyhedra reveals that, as expected, the Nb/Ta cations are significantly displaced from the centers of the MO₆ units. The degree of off-centering can be quantified by considering the <*B*–O> bond lengths and the deviation from the linearity of the three trans ∠O–*B*–O bond angles. If we define the trans bond angles as θ₁ = ∠O₁–*B*–O₄, θ₂ = ∠O₂–*B*–O₅ and θ₃ = ∠O₃–*B*–O₆ as shown in Figure 3.15, the magnitude of out of center distortion⁷³ can be expressed as: (Δ*d*) = (|<*B* – O₁> – <*B* – O₄>| ÷ |cos θ₁|) + (|<*B* – O₂> – <*B* – O₅>| ÷ |cos θ₂|) + (|<*B* – O₃> – <*B* – O₆>| ÷ |cos θ₃|).

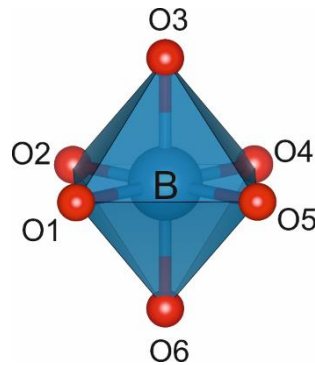


Figure 3.15. A regular BO₆ octahedra

A non-zero value will be obtained if the *B*-cation is off-centered. Using the *Im*2*m* structural models obtained from structure refinement against the neutron diffraction data, we obtain Δ*d* = 0.569 and 0.709 for KNdT_a2O₇ and KNdNb₂O₇ respectively. These values are larger than typically observed for Ta⁵⁺O₆ (Δ*d* = 0.38) and Nb⁵⁺O₆ (Δ*d* = 0.62), but follow the general trend that Nb > Ta. It should be noted that the majority of the off-centering of the *M*⁵⁺ cations is aligned along the *c*-axis, pointing “out” of the NdM₂O₇ sheets, and as a result, does not contribute to the polarization of the materials because pairs of MO₆ units are related by a mirror plane perpendicular to the *c*-axis.

3.5 Conclusion

KNdM_2O_7 ($M = \text{Ta}, \text{Nb}$) were synthesized by a 2-step cation exchange reaction from RbNdM_2O_7 via NaNdM_2O_7 . In these exchange reactions the structure changes from a $(0, 0, z)$ Dion-Jacobson framework of the Rb-phase to a $(0, \frac{1}{2}, z)$ stacked framework of the K-phase via the $(\frac{1}{2}, \frac{1}{2}, z)$ Ruddlesden-Popper framework of the Na-phase. Analysis of synchrotron X-ray and neutron diffraction data reveals that both the K-phases adopt a polar $Im2m$ structure with $a^0b^+c^0/a^0-b^+c^0$ tilting of MO_6 octahedra. The K^+ cations are ordered within the 6-coordinated trigonal prismatic sites in between the double perovskite layers. A competition between the requirement of bonding optimization of the K^+ and Nd^{3+} -cation sites is demonstrated for the KNdM_2O_7 ($M = \text{Ta}, \text{Nb}$) phases. The effect of the differing bonding requirements of the A- and A'-cations on the tilting distortions of layered perovskite phases is discussed for the structures of $A'\text{NdM}_2\text{O}_7$ ($A' = \text{Cs}, \text{Rb}, \text{Li}, \text{Na}, \text{K}; M = \text{Ta}, \text{Nb}$) compounds as a function of A'-cation size. The polarity in the RbNdM_2O_7 and LiNdM_2O_7 phases originates from a hybrid improper mechanism, where two non-polar distortion modes, described as octahedral rotation and tilting of MO_6 octahedra, couple to a 3rd polar mode to break inversion symmetry. On the other hand, in the KNdM_2O_7 phases, the polarity originates from an SOJT driven proper mechanism where d^0 electronic configuration of M^{5+} drives the mixing between 4d/5d orbitals of niobium/tantalum with 2p orbitals of oxygen. Another way of inducing noncentrosymmetry in crystal structures is to introduce a post transition metal cation with a “stereo chemically active” lone pair. Hence the obvious question would be what are the effects on the structural distortions of $A'\text{AM}_2\text{O}_7$ phases if Nd^{3+} is replaced by Bi^{3+} ; which has stereo-active $6s^2$ electronic configuration? This question will be answered in the following chapters where the structures of $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb}, \text{Li}, \text{Na}$ and K) phases will be discussed.

Chapter 4 – Synthesis and characterisation of $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb}, \text{Li}, \text{Na}$)

4.1 Introduction

The $n = 2$ Dion-Jacobson phase $\text{RbBiNb}_2\text{O}_7$ was previously reported⁷⁴ to adopt the same polar $P2_1am$ crystal structure of $\text{CsBiNb}_2\text{O}_7$ with $a^-a^-c^+$ tilting distortion.^{74–76} But recent theoretical and experimental investigation¹¹ reveals that the analogous $\text{RbNdNb}_2\text{O}_7$ phase adopts $I2cm$ structure with an $a^-a^-c^+/(a^-a^-c^+)$ tilting distortion, although the $\text{CsNdNb}_2\text{O}_7$ phase adopts the $P2_1am$ structure. In the Rb-phase, the sense of out of phase tilting in the xy -plane is inverted in the consecutive double perovskite block. The previous structure report⁷⁴ of $\text{RbBiNb}_2\text{O}_7$ was based on lab X-ray diffraction data which are unable to determine the correct positions of light oxide ions in presence of heavy metals. But structural distortions in these phases originate from small tilting of NbO_6 octahedra. Hence, we reinvestigated the structure of $\text{RbBiNb}_2\text{O}_7$ with the help of SHG, synchrotron X-ray and neutron diffraction data to determine if the similar inversion of the sense of the tilting is also present in the $\text{RbBiNb}_2\text{O}_7$ phase.

Further low-temperature cation exchange reactions of $\text{RbNdNb}_2\text{O}_7$ with LiNO_3 and NaNO_3 lead to the formation of the Ruddlesden-Popper phases $\text{LiNdNb}_2\text{O}_7$ and $\text{NaNdNb}_2\text{O}_7$ respectively.⁴² Different competing factors in these two phases lead to different crystal structures with different tilting distortions and different ordering schemes of the alkali metal ions. So, we decided to perform similar exchange reactions for $\text{RbBiNb}_2\text{O}_7$ to synthesize the corresponding Li and Na phases and determine their crystal structures. Synthesizing the series of compounds; $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb}, \text{Li}$ and Na) will enable us to compare these structures with the analogous structures of the Nd-phases, and thus to understand the effect of $6s^2$ electronic configuration of Bi^{3+} cation on structural distortions of $n = 2$ layered perovskites.

Results from this chapter are published as: **Mallick, S.**; Khalsa, G; Kaaret, J. Z.; Zhang, W.; Batuk, M.; Gibbs, A. S.; Hadermann, J.; Halasyamani, P. S.; Benedek, N. A.; Hayward, M. A. The influence of the $6s^2$ configuration of Bi^{3+} on the structures of $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb}, \text{Na}, \text{Li}$) layered perovskite oxides. *Dalton Trans.*, 2021, **50**, 15359 – 15369.

4.2 Synthesis

Polycrystalline samples of $\text{RbBiNb}_2\text{O}_7$ were prepared by a ceramic synthesis method from Bi_2O_3 (99.995%), Nb_2O_5 (99.9985%, dried at 900 °C) and Rb_2CO_3 (99.8%). Suitable stoichiometric ratios of Bi_2O_3 and Nb_2O_5 were ground together in an agate pestle and mortar and combined with 50 % excess of Rb_2CO_3 (to compensate for the loss due to volatilization at high temperature). These mixtures were placed in silica crucibles and heated at 600 °C in air for 12 h. The samples were then reground and heated at 1000 °C for 6 h then 12 h and 2 further periods of 4 h with regrinding between heating cycles. Finally, the powder samples were washed with distilled water to remove any excess rubidium oxide and then dried in air at 120 °C for 12 h. This heating regime was required to avoid the formation of BiNbO_4 .

$\text{LiBiNb}_2\text{O}_7$ and $\text{NaBiNb}_2\text{O}_7$ were synthesized by reacting $\text{RbBiNb}_2\text{O}_7$ with a 10 mole-equivalents of LiNO_3 (99.98 %) or NaNO_3 (>99%) respectively. These mixtures were ground together and loaded into silica crucibles and heated in air for two periods of 48 h at 360 °C. Between heating cycles, the samples were washed with distilled water, dried for 12 h at 120 °C in air, and mixed with a further 10 mole-equivalents of LiNO_3 or NaNO_3 . After the final heating step, all samples were washed with distilled water to remove the LiNO_3 and NaNO_3 and then dried for 12 h at 120 °C in air. Samples of $\text{NaBiNb}_2\text{O}_7$ were dried under flowing oxygen at 350 °C to eliminate all interlayer water and transferred to an argon-filled glovebox for storage.

4.3 Results

4.3.1 Optical SHG measurements

The particle-size dependent SHG measurements show that $\text{RbBiNb}_2\text{O}_7$, $\text{LiBiNb}_2\text{O}_7$ and $\text{NaBiNb}_2\text{O}_7$ are SHG active and their SHG activity increases with an increase in particle size (Figure 4.1). This indicates that all three phases adopt noncentrosymmetric crystal structures.

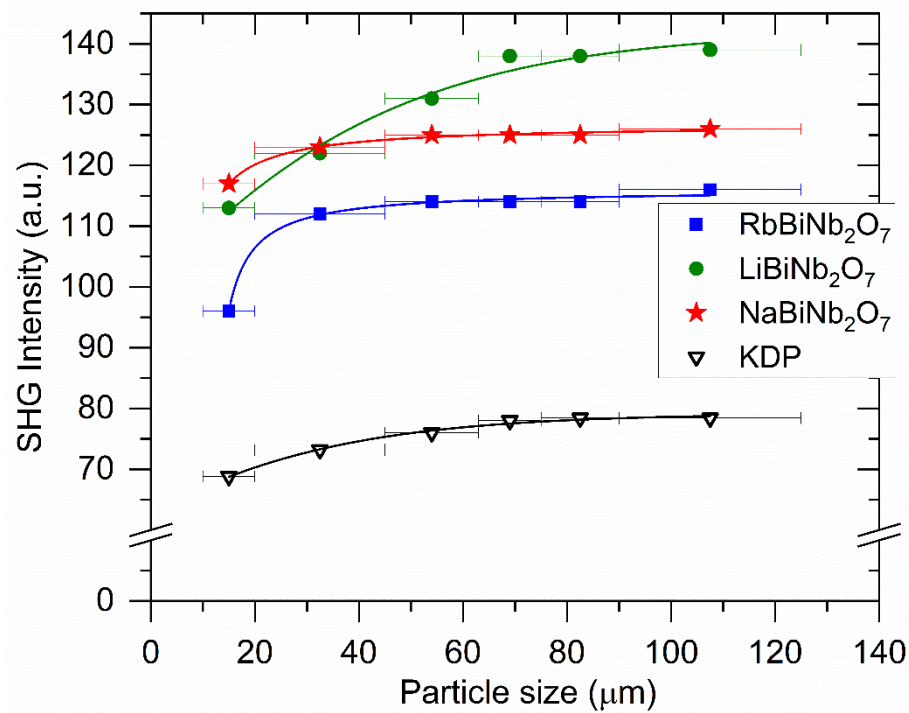


Figure 4.1. Plots of SHG activity of $\text{RbBiNb}_2\text{O}_7$, $\text{LiBiNb}_2\text{O}_7$ and $\text{NaBiNb}_2\text{O}_7$ as a function of particle size, compared to KH_2PO_4 (KDP) standard.

4.3.2 Structural characterisation of $\text{RbBiNb}_2\text{O}_7$

4.3.2.1 Synchrotron X-ray diffraction data

Previously $\text{RbBiNb}_2\text{O}_7$ has been reported to adopt an $n = 2$ Dion-Jacobson structure with $a^-a^-c^+$ tilting distortion, described in space group $P2_1am$.⁷⁴ High-resolution SXRD data collected from $\text{RbBiNb}_2\text{O}_7$ were initially indexed using the reported lattice parameters of $\text{RbBiNb}_2\text{O}_7$ ($a = 5.463 \text{ \AA}$, $b = 5.393 \text{ \AA}$, $c = 11.232 \text{ \AA}$) which is an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Dion-Jacobson aristotype unit cell. However, close inspection of the diffraction data reveals a series of superlattice peaks which correspond to the doubling of the c -lattice parameter as shown in Figure 4.2 indicating the unit cell is in fact an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx 2 \times c$ expansion of the aristotype Dion-Jacobson structure, with extinction conditions consistent with a body-centered unit cell.

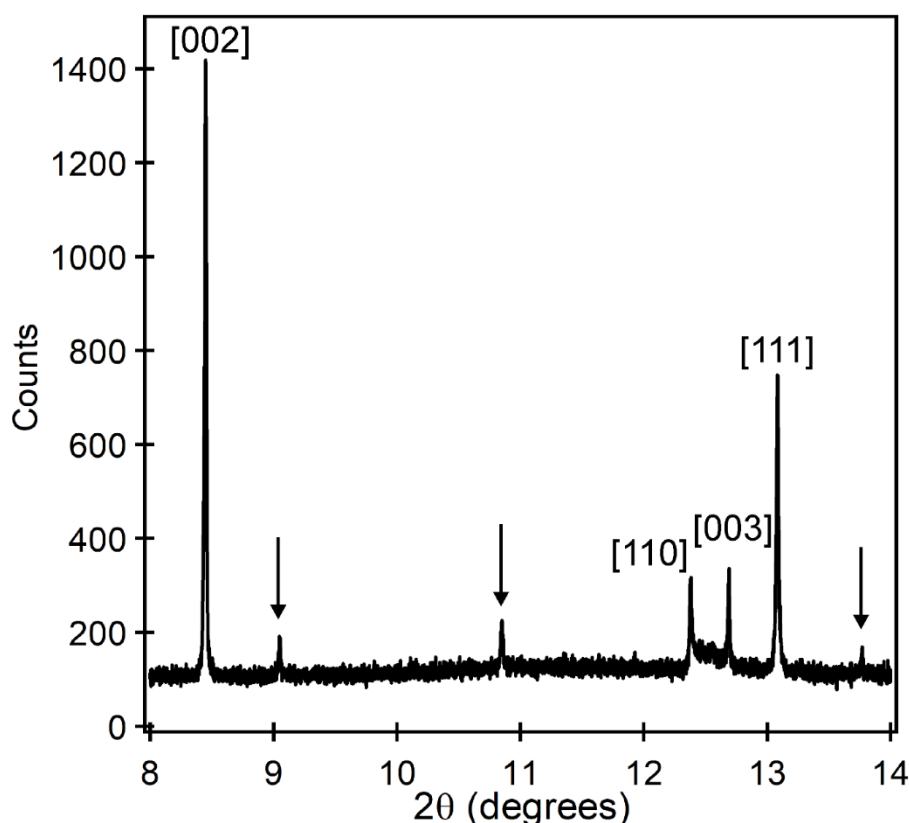


Figure 4.2. Synchrotron X-ray powder diffraction data collected from $\text{RbBiNb}_2\text{O}_7$ in the range $8 < 2\theta < 14$, indexed using the reported lattice parameters of $\text{RbBiNb}_2\text{O}_7$ ($a = 5.463 \text{ \AA}$, $b = 5.393 \text{ \AA}$, $c = 11.232 \text{ \AA}$). The black arrows denote peaks which require a doubling of the c lattice parameter.

Powder SHG measurements indicate $\text{RbBiNb}_2\text{O}_7$ exhibits SHG activity ~ 1.8 times that of KDP, as shown in Figure 4.1. In addition, $\text{RbBiNb}_2\text{O}_7$ is reported to exhibit ferroelectric behaviour.⁷⁴ Both of these observations indicate $\text{RbBiNb}_2\text{O}_7$ adopts a non-centrosymmetric structure. When combined with the diffraction data, and previous symmetry analysis of the $n = 2$ Dion-Jacobson framework,¹¹ these observations are consistent with the $a^-a^-c^+/(a^-a^-c^+)$ distorted structure previously reported for $\text{RbNdNb}_2\text{O}_7$.¹¹ A structural model was constructed for $\text{RbBiNb}_2\text{O}_7$ based on the $I2cm$ structure of $\text{RbNdNb}_2\text{O}_7$ and refined against the synchrotron X-ray diffraction data collected at room temperature. SXRD data collected from $\text{RbBiNb}_2\text{O}_7$ exhibit mild $(00l)$ preferred orientation, consistent with the layered structure of the material. This was modelled in the refinement using a 4th order spherical harmonic expression.⁷⁷ The

refinement proceeded smoothly to give a good fit to the data as shown in the refinement plot in Figure 4.3.

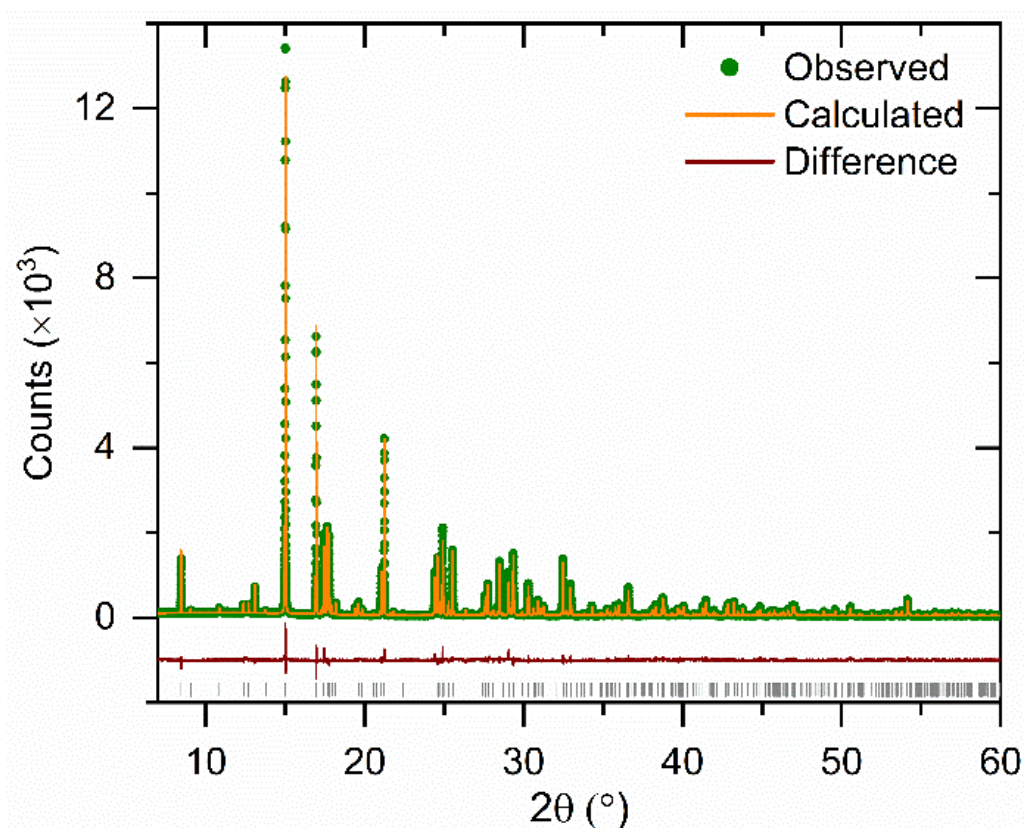


Figure 4.3. Observed, calculated and difference plots from the structural refinement of $\text{RbBiNb}_2\text{O}_7$ against synchrotron X-ray diffraction data collected at room temperature.

4.3.2.2 Neutron diffraction data

High-resolution neutron diffraction data collected from $\text{RbBiNb}_2\text{O}_7$ could be indexed using a body centred orthorhombic unit cell which is $\sqrt{2} \times \sqrt{2} \times 2$ geometric expansion of the aristotype unit cell of $n = 2$ Dion-Jacobson structure. The $I2cm$ model, isostructural to $\text{RbNdNb}_2\text{O}_7$ (which was refined against the synchrotron data), was refined against the neutron diffraction data collected at room temperature to give a good statistical fit confirming the $I2cm$ structure of $\text{RbBiNb}_2\text{O}_7$. The observed, calculated and difference plots for refinement in $I2cm$ model are shown in Figure 4.4. Full details of the refined parameters are shown in Table 4.1 with selected bond lengths from the refined structure of $\text{RbBiNb}_2\text{O}_7$ in Table 4.2.

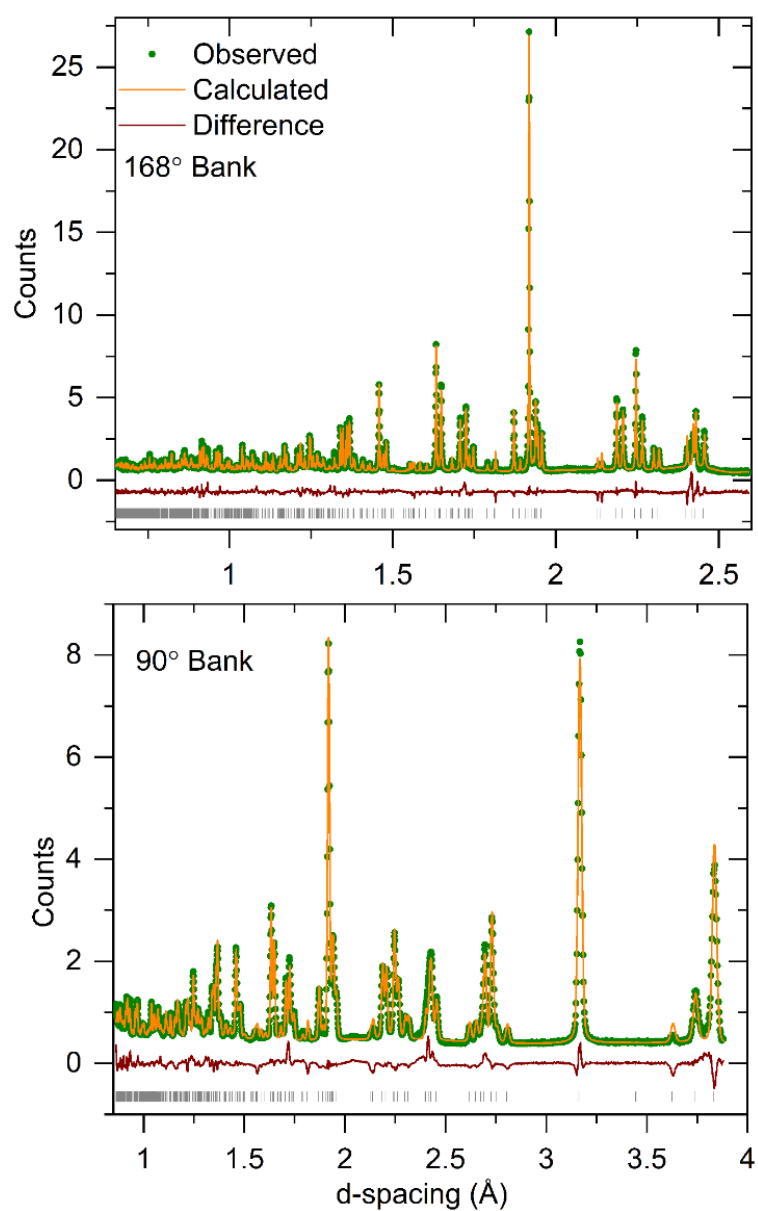


Figure 4.4. Observed, calculated and difference plot from the structure refinement of $\text{RbBiNb}_2\text{O}_7$ against the powder neutron diffraction data collected at room temperature.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
Rb1	4a	0.7363(9)	0	0	1	1.85(7)
Bi1	4b	0.6981(5)	0.0168(5)	$\frac{1}{4}$	1	1.03(7)
Nb1	8c	0.2473(6)	0.9952(6)	0.3574(1)	1	0.35(5)
O1	8c	0.9897(8)	0.7631(8)	0.3306(2)	1	1.99(10)
O2	8c	0.0616(6)	0.3003(8)	0.3451(2)	1	1.52(9)
O3	8c	0.7479(7)	0.5309(6)	0.4340(1)	1	1.02(7)
O4	4b	0.7813(11)	0.4303(9)	$\frac{1}{4}$	1	1.57(12)

RbBiNb₂O₇ – space group <i>I2cm</i> (#46) $a = 5.45245(8) \text{ \AA}$, $b = 5.38185(7) \text{ \AA}$, $c = 22.4229(3) \text{ \AA}$, volume = $657.98(2) \text{ \AA}^3$ Formula weight = $592.27 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Neutron Time of Flight Temperature: 298 K $R_p = 6.205 \%$, $wR_p = 7.474 \%$

Table 4.1. Parameters from the structural refinement of *I2cm* model of RbBiNb₂O₇ against neutron powder diffraction data collected at room temperature.

Cation	Anion	Bond length (Å)	BVS
Nb	O1 × 1	1.973(6)	+5.085
	O1 × 1	2.010(6)	
	O2 × 1	2.055(5)	
	O2 × 1	1.949(6)	
	O3 × 1	1.723(4)	
	O4 × 1	2.448(3)	
Bi	O1 × 2	2.613(5)	+2.943
	O1 × 2	2.767(5)	
	O2 × 2	3.287(5)	
	O2 × 2	2.464(5)	
	O4 × 1	2.290(7)	
	O4 × 1	3.189(6)	
	O4 × 1	2.271(6)	
	O4 × 1	3.193(7)	
Rb	O3 × 2	3.051(6)	+0.897
	O3 × 2	2.927(4)	
	O3 × 2	3.218(4)	
	O3 × 2	3.162(6)	

Table 4.2. Selected bond lengths and cation bond valence sums from the refined structure of RbBiNb₂O₇.

4.3.3 Structural characterisation of LiBiNb₂O₇

4.3.3.1 Synchrotron X-ray diffraction data

Synchrotron X-ray diffraction data collected from $\text{LiBiNb}_2\text{O}_7$ at room temperature can be indexed using an orthorhombic unit cell ($a = 5.456 \text{ \AA}$, $b = 5.341 \text{ \AA}$, $c = 20.819 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Ruddlesden-Popper aristotype unit cell, which is analogous to the reported structure of $\text{LiNdNb}_2\text{O}_7$.⁴² Powder SHG measurements indicate $\text{LiBiNb}_2\text{O}_7$ exhibits an SHG activity ~ 2 times that of KDP as shown in Figure 4.1 and thus adopts a non-centrosymmetric crystal structure. Symmetry analysis of the distortions of the $n = 2$ Ruddlesden-Popper framework^{42,78,79} indicates that there are four non-centrosymmetric candidate structures described in space groups $Bb2_1m$, $P2_1nm$, $B2cm$ and $P2cm$ respectively. Further examination of diffraction data allowed us to eliminate the $Bb2_1m$ structure based on extinction conditions, as shown in Figure 4.5.

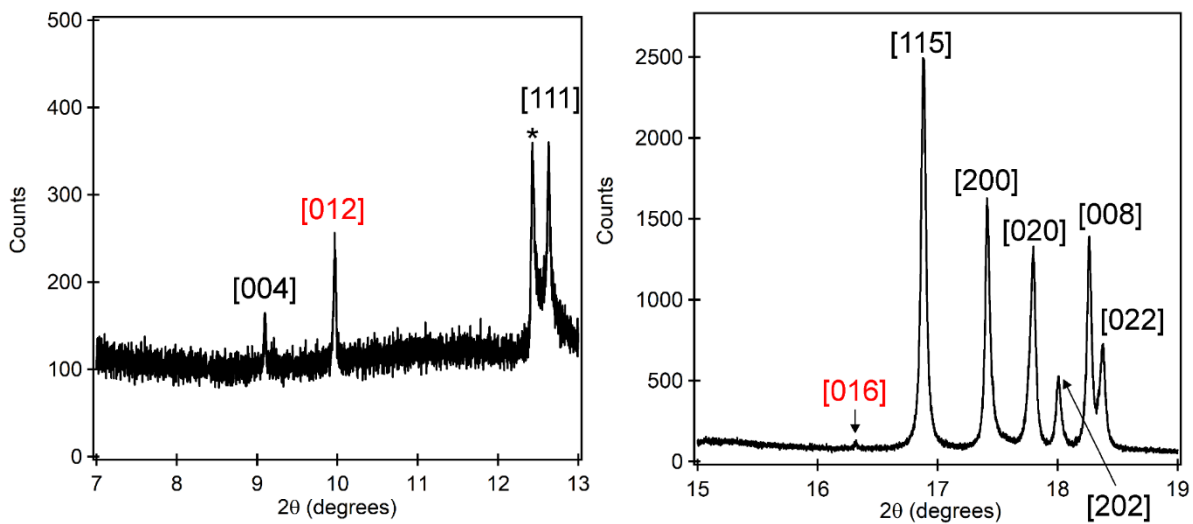


Figure 4.5. Synchrotron X-ray diffraction data collected from $\text{LiBiNb}_2\text{O}_7$. The presence of [012] and [016] peaks rules out the $Bb2_1m$ structural model. Peak marked with * is from a $(\text{Li/Rb})\text{NbO}_3$ impurity.

Structural models were constructed for $\text{LiBiNb}_2\text{O}_7$ based on the distortions described in space groups $P2_1nm$, $B2cm$ and $P2cm$ and these models were refined against the synchrotron X-ray data collected at room temperature to give equally good fitting for all three models. As an example, the observed, calculated and difference plots from the refinement of $B2cm$ model against the synchrotron X-ray diffraction data are shown in Figure 4.6.

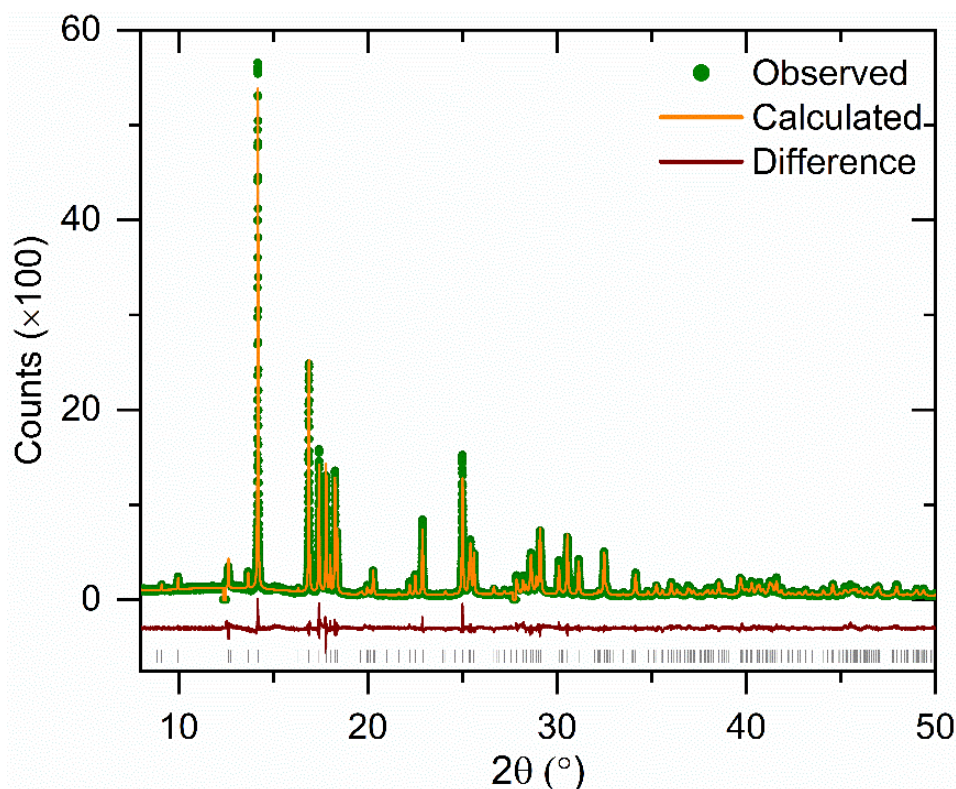


Figure 4.6. Observed, calculated and difference plots from the structure refinement of *B2cm* model of $\text{LiBiNb}_2\text{O}_7$ against the synchrotron X-ray diffraction data collected at room temperature.

4.3.3.2 Neutron diffraction data

High-resolution neutron diffraction data collected from $\text{LiBiNb}_2\text{O}_7$ could be indexed using a *B*-centred orthorhombic unit cell which is $\sqrt{2} \times \sqrt{2} \times 1$ geometric expansion of the aristotype unit cell of $n = 2$ Ruddlesden-Popper structure. Structural models based on the distortions described in space groups $P2_1nm$, *B2cm* and $P2cm$ were refined against the neutron powder diffraction data collected at room temperature. Refinement of $P2_1nm$ model results in a significantly worse fit to the data than either *B2cm* or $P2cm$ models as detailed in Table 4.3, and so this model was eliminated.

The Li^+ cations in cation-exchanged $\text{LiBiNb}_2\text{O}_7$ Ruddlesden-Popper phase occupy only half of the available pseudo-tetrahedral coordination sites in the framework, so can adopt either ordered or disordered arrangements. Refinement of lithium-ordered and disordered models against the powder neutron diffraction data revealed that ordered models give superior fits

compared to disordered models for both the $B2cm$ and $P2cm$ distorted structures. The refinement parameters shown in Table 4.3 indicate a slightly better fit for the unconstrained $P2cm$ model compared to the $B2cm$ model. However, examination of the unconstrained $P2cm$ model reveals that it has twice as many atoms in the asymmetric unit as the $B2cm$ model and that when refined against the neutron data, chemically equivalent atoms in the $P2cm$ model move to very different local environments. As a result, bond valence sums (BVS) calculated for pairs of chemically equivalent cations in the BiNb_2O_7 perovskite blocks are very different (Table 4.4) making the resulting structure chemically implausible. To address this situation, we added constraints to the $P2cm$ model to make the environments of the two niobium cations more similar. This more symmetric $P2cm_{\text{constrained}}$ model fits the data more poorly than the $B2cm$ model as shown in Table 4.3, confirming that $\text{LiBiNb}_2\text{O}_7$ adopts $a^-a^-c^+/(a^-a^-c^+)$ distorted $n = 2$ Ruddlesden-Popper structure, described in space group $B2cm$ analogous to that reported for $\text{LiNdNb}_2\text{O}_7$.⁴² The observed, calculated and difference plots for refinement in $B2cm$ model are shown in Figure 4.7. Full details of the refined parameters are shown in Table 4.5 with selected bond lengths from the refined structure of $\text{RbBiNb}_2\text{O}_7$ in Table 4.6.

Space group	Tilt system	Glazer tilt	#parameters	R _p (%)	wR _p (%)
$P2_1nm$	$\Phi_1\Phi_2\Psi_z/\Phi_2\Phi_1\Psi_z$	$a^-b^-c^+/b^-a^-c^+$	128	7.645	9.081
$B2cm$	$\Phi\Phi\Psi_z/-(\Phi\Phi\Psi_z)$	$a^-a^-c^+/(a^-a^-c^+)$	96	5.368	6.924
$P2cm$	$\Phi_1\Phi_2\Psi_z/-(\Phi_1\Phi_2)\Psi_z$	$a^-b^-c^+/(a^-b^-)c^+$	120	4.870	5.773
$P2cm_{\text{constrained}}$	$\Phi_1\Phi_2\Psi_z/-(\Phi_1\Phi_2)\Psi_z$	$a^-b^-c^+/(a^-b^-)c^+$	117	6.464	7.776

Table 4.3. Fitting statistics from the refinement of a series of structural models against the powder neutron diffraction data collected from $\text{LiBiNb}_2\text{O}_7$.

	$P2cm$	$P2cm_{\text{constrained}}$	$B2cm$
Li1	0.98	0.99	0.97
Li2	1.02	1.05	
Bi1	2.42	2.40	3.00
Bi2	3.53	3.18	
Nb1	4.55	5.03	5.03

Nb2	1.52	5.12	
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Table 4.4. Cation bond valence sums from the $P2cm$, constrained $P2cm$ and $B2cm$ structural models of $\text{LiBiNb}_2\text{O}_7$.

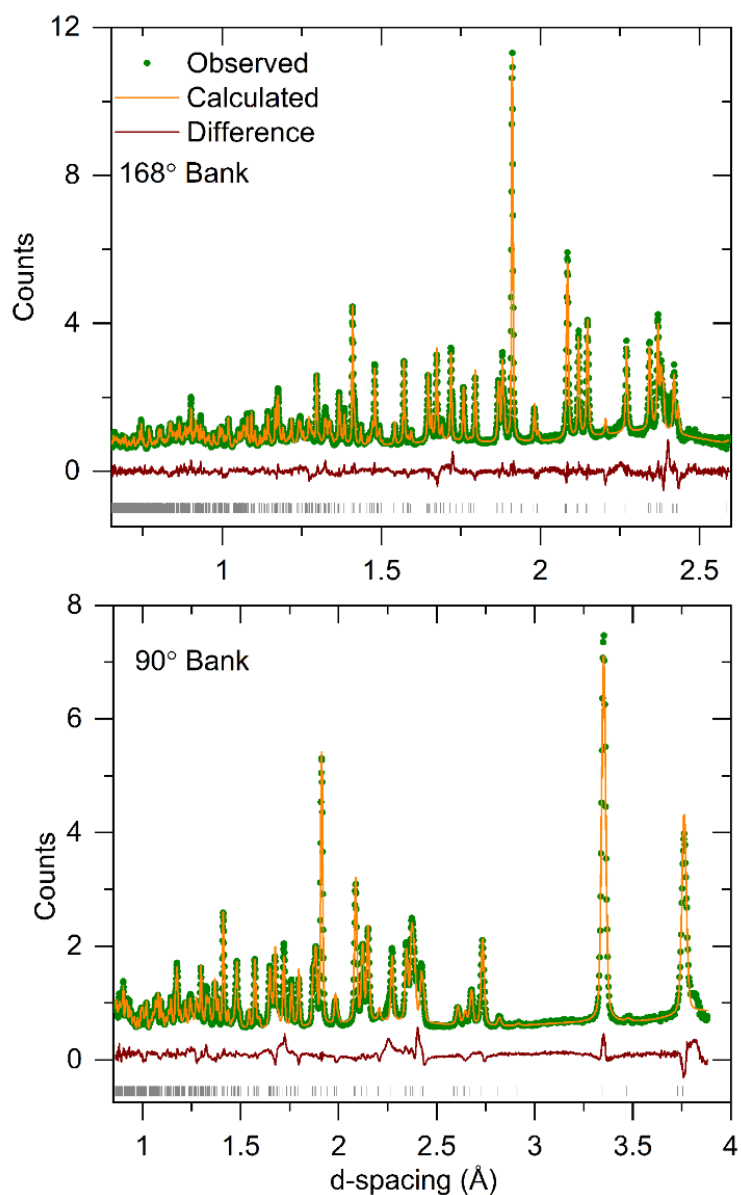


Figure 4.7. Observed, calculated and difference plots from the structural refinement of $B2cm$ model of $\text{LiBiNb}_2\text{O}_7$ against the powder neutron diffraction data collected at room temperature.

		x	y	z	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
Li1	4a	0.9993(52)	0	0	0.99(3)	3.69(4)
Bi1	4c	0.1893(4)	0.7348(6)	$\frac{1}{4}$	1	0.74(9)
Nb1	8d	0.2434(6)	0.7546(6)	0.6347(1)	1	0.30(6)
O1	4c	0.7520(14)	0.6789(7)	$\frac{1}{4}$	1	0.49(10)
O2	8d	0.0501(8)	0.5507(10)	0.3532(2)	1	1.42(10)

O3	8d	0.9878(9)	0.9888(10)	0.8328(2)	1	1.77(11)
O4	4d	0.2361(10)	0.8258(4)	0.5535(2)	1	0.65(7)
LiBiNb₂O₇ – space group <i>B2cm</i> (#39) $a = 5.4560(2) \text{ \AA}$, $b = 5.3415(1) \text{ \AA}$, $c = 20.8186(6) \text{ \AA}$, volume = 606.71(3) $\text{\AA}^3$ Formula weight = 513.726 g mol⁻¹, Z = 4 Radiation source: Neutron Time of Flight Temperature: 298 K $R_p = 5.37 \%$, $wR_p = 6.92 \%$						

Table 4.5. Parameters from the structural refinement of *B2cm* model of LiBiNb₂O₇ against neutron powder diffraction data collected at room temperature.

Cation	Anion	Bond length ($\text{\AA}$)	BVS
Nb	O1 $\times$ 1	2.435(3)	+5.032
	O2 $\times$ 1	1.958(6)	
	O2 $\times$ 1	2.012(6)	
	O3 $\times$ 1	1.992(6)	
	O3 $\times$ 1	2.028(6)	
	O4 $\times$ 1	1.733(5)	
Bi	O2 $\times$ 2	2.482(5)	+3.005
	O2 $\times$ 2	3.289(5)	
	O3 $\times$ 2	2.522(6)	
	O3 $\times$ 2	2.732(6)	
	O1 $\times$ 1	2.405(8)	
	O1 $\times$ 1	2.236(6)	
	O1 $\times$ 1	3.150(5)	
	O1 $\times$ 1	3.156(11)	
Li	O4 $\times$ 2	1.94(2)	+0.973
	O4 $\times$ 2	2.04(3)	

Table 4.6. Selected bond lengths and cation bond valence sums from the refined structure of LiBiNb₂O₇.

4.3.4 Structural characterisation of NaBiNb₂O₇

4.3.4.1 Synchrotron X-ray diffraction data

High-resolution synchrotron X-ray diffraction (SXRD) data collected from $\text{NaBiNb}_2\text{O}_7$ can be indexed using an orthorhombic unit cell ($a = 5.47 \text{ \AA}$, $b = 5.38 \text{ \AA}$, $c = 21.67 \text{ \AA}$) which is consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted aristotype unit cell of an $n = 2$ Ruddlesden-Popper structure. The extinction conditions observed in the SXRD data allow us to eliminate the majority of $n = 2$ Ruddlesden-Popper phases^{42,78,79} distorted by cooperative tilting on the NbO_6 units leaving 5 candidate structures described in space groups $Pbcm$, $Pnnm$, $Pnam$, $P2_1nm$ and $P2cm$. Structural models were constructed for $\text{NaBiNb}_2\text{O}_7$ based on the distortions described in space groups $Pbcm$, $Pnnm$, $Pnam$, $P2_1nm$ and $P2cm$, and these models were refined against the synchrotron X-ray data collected at room temperature to give equally good fitting for all models. As an example, the observed, calculated and difference plots from the refinement of $Pnam$ model against the synchrotron X-ray diffraction data are shown in Figure 4.8.

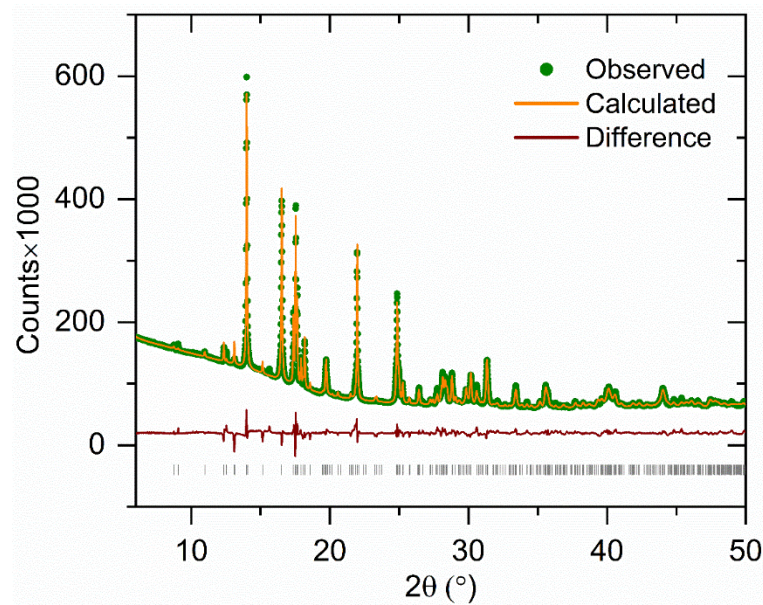


Figure 4.8. Observed, calculated and difference plots from the structural refinement of $Pnam$ model of $\text{NaBiNb}_2\text{O}_7$ against the synchrotron X-ray diffraction data collected at room temperature.

4.3.4.2 Neutron diffraction data

High-resolution neutron diffraction data collected from $\text{NaBiNb}_2\text{O}_7$ could be indexed using a primitive orthorhombic unit cell which is $\sqrt{2} \times \sqrt{2} \times 1$ geometric expansion of the aristotype

unit cell of $n = 2$ Ruddlesden-Popper structure. Structural models described in space groups $Pbcm$, $Pnnm$, $Pnam$, $P2_1nm$ and $P2cm$ were refined against the neutron powder data (NPD). The model described in space group $P2_1nm$ gave the best fit to the data as shown in Table 4.7. However, close inspection of the refined $P2_1nm$ model reveals that the resulting structure is very irregular, with chemically equivalent cations having very different local bonding environments, as evident from the bond valence sums of the metal cations (Table 4.8). To address this problem, constraints were added to the model to make the bond valence sums of chemically equivalent cations the same, resulting in a poor fit to the NPD data as noted in Table 4.7, so this model was discarded.

Space group	Tilt system	Glazer tilt	#parameters	R_p (%)	wR_p (%)
$Pbcm$ (#57)	$\Phi\Phi\Psi_z/-(\Phi\Phi)\Psi_z$	$a^-a^-c^+/(a^-a^-)c^+$	96	7.556	8.019
$Pnnm$ (#58)	$\Phi_1\Phi_20/\Phi_2\Phi_10$	$a^-b^-c^0/b^-a^-c^0$	98	7.848	8.114
$Pnam$ (#62)	$\Phi\Phi\Psi_z/\Phi\Phi-\Psi_z$	$a^-a^-c^+/a^-a^-c^+$	98	6.366	6.635
$P2_1nm$ (#31)	$\Phi_1\Phi_2\Psi_z/\Phi_2\Phi_1\Psi_z$	$a^-b^-c^+/b^-a^-c^+$	118	5.840	6.127
$P2_1nm_{constrained}$	$\Phi_1\Phi_2\Psi_z/\Phi_2\Phi_1\Psi_z$	$a^-b^-c^+/b^-a^-c^+$	105	7.405	7.700
$P2cm$ (#28)	$\Phi_1\Phi_2\Psi_z/-(\Phi_1\Phi_2)\Psi_z$	$a^-b^-c^+/(a^-b^-)c^+$	116	7.633	8.028

Table 4.7. Fitting statistics from the refinement of different models against the powder neutron diffraction data collected from $\text{NaBiNb}_2\text{O}_7$.

	$P2_1nm$	$P2_1nm_{constrained}$	$Pnam$
Bi1	2.138	2.671	2.948
Bi2	3.722	3.184	
Nb1	4.697	5.033	4.908
Nb2	5.513	4.900	

Table 4.8. Cation bond valence sum calculated for the $P2_1nm$, constrained $P2_1nm$ and $Pnam$ models of $\text{NaBiNb}_2\text{O}_7$.

The model described in space group $Pnam$ gives the best fit to the data of the remaining models as shown in Table 4.7, and yields a chemically reasonable structure. However, this model is centrosymmetric (incompatible with observed SHG activity), suggesting that it describes the tilting distortion of the NbO_6 units accurately, but the ‘true’ structure of $\text{NaBiNb}_2\text{O}_7$ is subject

to a further distortion which breaks the inversion symmetry of this *Pnam* model. Thus, we considered the inclusion of Γ -point distortion modes in the *Pnam* model with the help of the ISODISTORT software.⁶⁶ This symmetry analysis yields four candidate non-centrosymmetric models described in space groups *P2₁2₁2₁*, *Pn2₁m*, *P2₁am* and *Pna2₁*. Fitting statistics from the refinement of these four non-centrosymmetric models are comparable to one another as shown in Table 4.9. We, therefore, examined the refined structures to see if they were chemically reasonable.

Space group	Distortion mode	#parameters	R _p (%)	wR _p (%)	Na ordering pattern
<i>Pnam</i> (#62)		98	6.37	6.63	Disordered
<i>Pn2₁m</i> (#31)	Γ_2^-	119	6.50	5.56	Checkerboard
<i>Pna2₁</i> (#33)	Γ_4^-	112	6.05	6.29	Stripes
<i>P2₁am</i> (#26)	Γ_3^-	114	5.23	5.37	Stripes
<i>P2₁2₁2₁</i> (#19)	Γ_1^-	111	6.13	6.35	Checkerboard

Table 4.9. Fitting statistics from the structural refinement, against NPD data, of a series of different models obtained by the addition of Γ -point distortion modes to the *Pnam* structural model of NaBiNb₂O₇.

***Pn2₁m* model:** There are 2 sites for Na, Bi and Nb in the *Pn2₁m* model. The Na site occupancies were refined within the constraint of the total composition being NaBiNb₂O₇, to establish if the Na⁺ cations were ordered over the two sites. After refinement, the occupancy of one site reached 0.68 and the other 0.32. As the Na ordering is not significant we continued further analysis with this level of ordering. Examining the refined models, it can be seen in Table 4.10 that the two Bi sites have very different bond valence sum values, and the fitting statistics for this model are the poorest of the 4 considered, so this structure was discarded.

***Pna2₁* model:** There are 2 sites for Na and Nb and one site for Bi in this model. The Na site occupancies were refined within the constraint of the total composition being NaBiNb₂O₇, to establish if the Na⁺ cations were ordered over the two sites. The occupancy of one site moves to 0.81 and the other site to 0.19, indicating the Na⁺ cations are ordered. The site with 0.81

occupancy was fixed as fully occupied which did not alter the fitting statistics significantly. In the final refined structure, we observe that the two chemically equivalent Nb sites have very different local bonding environments which result in significantly different bond valence sum values (Table 4.10) which make the structure chemically implausible and thus the model was discarded.

***P2₁am* model:** There are two sites for Na, Nb and Bi in this model. The Na site occupancies were refined within the constraint of the total composition being NaBiNb₂O₇, to establish if the Na⁺ cations were ordered over the two sites. The occupancy of one site moves to 0.88 and the other site to 0.12, indicating the Na⁺ cations are ordered. The site with 0.88 occupancy was fixed to be fully occupied which did not alter the fitting statistics significantly. Table 4.10 reveals that the bond valence sums of chemically equivalent Bi and Nb cations are significantly different from one another in the final refined structure. Close inspection reveals that the Bi1 and Nb1 sites belong to one Nb₂O₇ layer and Bi2 and Nb2 belong to another Nb₂O₇ layer. This allows the structure to have a very irregular local bonding environment for these chemically equivalent cations. From the Cartesian coordinates and bond valence sum values of the two Bi sites, it is clear that they are uneven and if this were the true structure we would be able to distinguish them in high-resolution X-ray powder diffraction given the strong X-ray scattering power of bismuth. Indeed, we observe that the calculated X-ray powder diffraction pattern of this *P2₁am* structure yields calculated intensities that are not observed in the experimental X-ray powder diffraction pattern as shown in Figure 4.10. For these reasons, the *P2₁am* model was discarded.

***P2₁2₁2₁* model:** There are two independent sites for Na and Nb and one site for Bi in this model. The Na site occupancies were refined within the constraint of the total composition being NaBiNb₂O₇, to establish if the Na⁺ cations were ordered over the two sites. The occupancy of one site moves to 0.88 and the other site to 0.12, indicating the Na⁺ cations are ordered. The

site with occupancy 0.88 was fixed to be completely occupied which did not alter the fitting statistics significantly. Bond valence sums of the chemically equivalent cations in the refined structure (Table 4.10) are similar to one another and close to their ideal value. Furthermore, the $P2_12_12_1$ model allows the ‘checkerboard’ ordering of Na, which minimizes the Na-Na repulsion as evident from the large Na-Na distance (3.77 Å) compared to a stripe order Na-arrangement (Na-Na distance 2.74 Å) in $P2_1am$ model as shown in Figure 4.9. For these reasons, the $P2_12_12_1$ model is thought to be the best description of the structure of $\text{NaBiNb}_2\text{O}_7$. In the final cycles of refinement, the occupancy of the Na cation site was allowed to deviate from full occupancy to yield a value of 0.81(4), without any significant changes to any other structural parameters. The observed, calculated and difference plots for refinement in $P2_12_12_1$ model are shown in Figure 4.11. Full details of the refined parameters are shown in Table 4.11 with selected bond lengths from the refined structure of $\text{RbBiNb}_2\text{O}_7$ in Table 4.12.

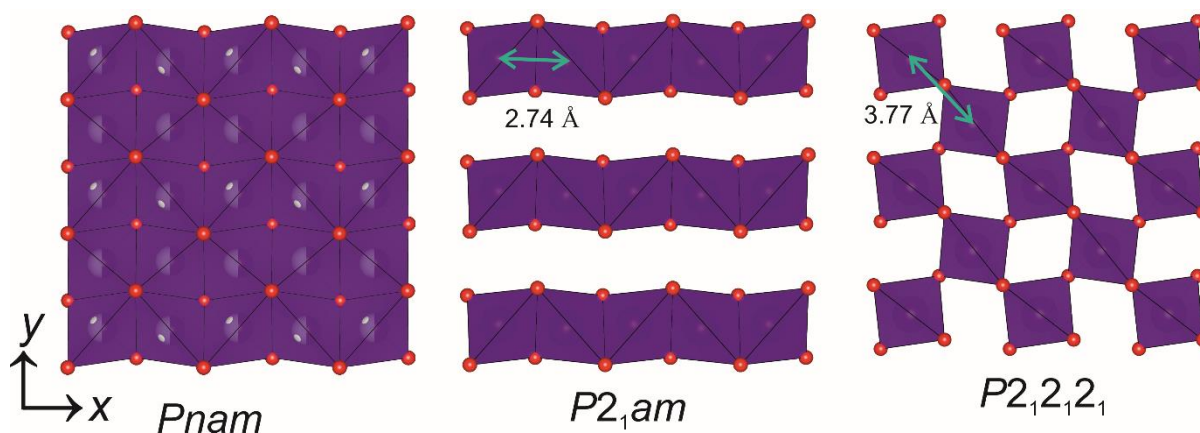


Figure 4.9. Disordered, ordered and checkerboard ordered arrangements of Na atoms in $Pnam$, $P2_1am$ and $P2_12_12_1$ structures respectively.

$Pnam$				
	x	y	z	BVS
Na	0.9984(22)	0.2568(27)	0.4908(8)	+1.037
Bi	0.6917(6)	0.0237(7)	0.25	+2.948
Nb	0.7538(5)	0.0139(5)	0.8583(1)	+4.908
$P2_12_12_1$				
Na	0.991(2)	0.995(3)	0.5047(9)	+0.989

Bi	0.6936(6)	0.2716(7)	0.2510(8)	+2.960
Nb1	0.7481(12)	0.2610(20)	0.8630(4)	+4.863
Nb2	0.2420(11)	0.2330(20)	0.1439(4)	+5.092
<i>Pn2₁m</i>				
Na1	0.7197(23)	0.6986(25)	0.2603(7)	+1.183
Na2	0.4945(65)	0.5650(37)	0.6947(15)	+1.105
Bi1	0.4891(21)	0.9247(15)	0.0000	+2.723
Bi2	0.9216(13)	0.4949(16)	0.0000	+3.196
Nb1	0.5152(13)	0.9474(10)	0.6117(3)	+5.112
Nb2	0.0007(13)	0.4839(8)	0.3953(3)	+5.081
<i>P2₁am</i>				
Na	0.9761(21)	0.4855(20)	0.2502(6)	+1.010
Bi1	0.3110(14)	0.7135(13)	0.0000	+3.650
Bi2	0.8075(14)	0.7737(13)	0.0000	+2.481
Nb1	0.2328(10)	0.7412(11)	0.6135(2)	+4.871
Nb2	0.7486(9)	0.7655(11)	0.1033(2)	+5.183
<i>Pna2₁</i>				
Na	0.4957(25)	0.7522(31)	0.0026(10)	+0.859
Bi	0.6870(6)	0.9816(7)	0.7621(6)	+2.950
Nb1	0.7553(17)	0.9794(10)	0.1470(2)	+5.472
Nb2	0.2549(18)	0.5168(14)	0.3651(2)	+4.683

Table 4.10. Fractional coordinates and cation bond valence sums from the structural refinement of a series of distorted non-centrosymmetric models against the powder neutron diffraction data collected from NaBiNb₂O₇.

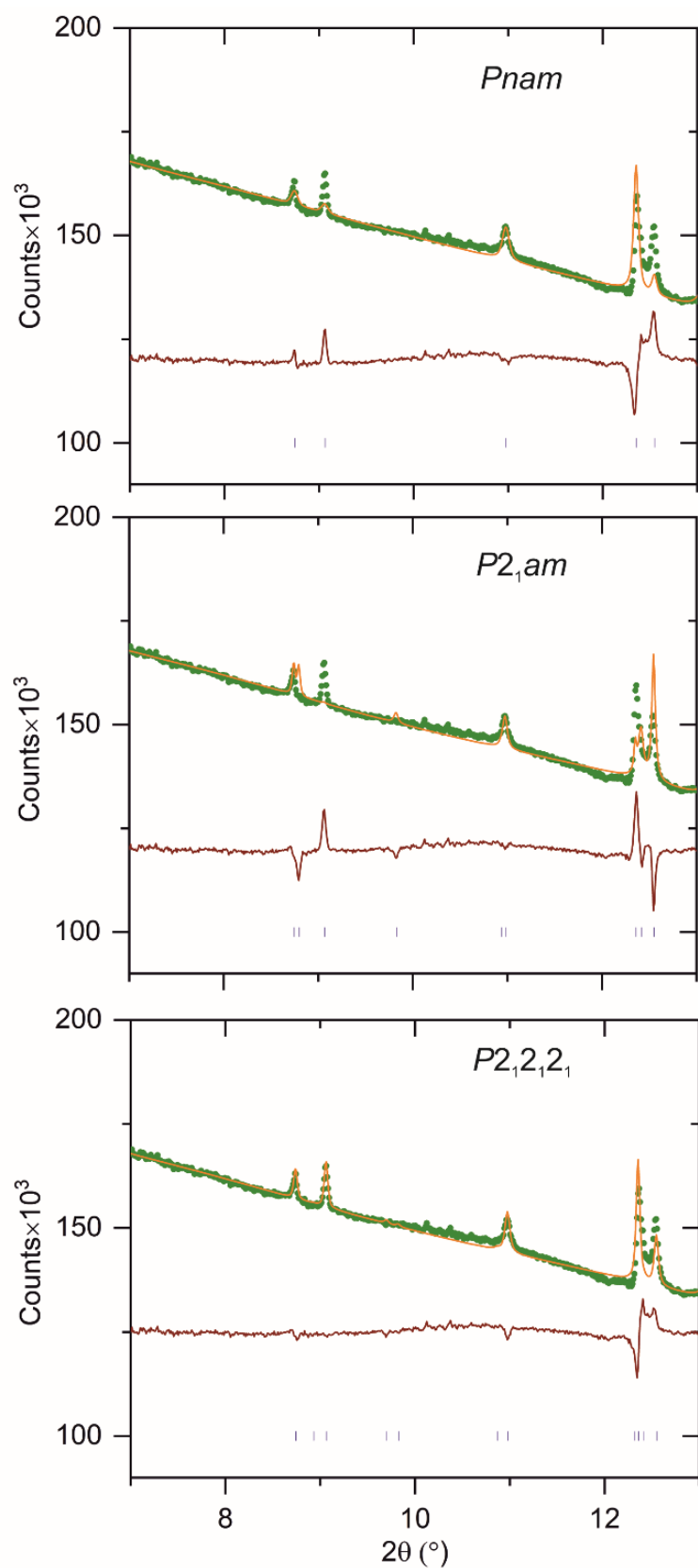


Figure 4.10. Observed, calculated and difference plots from the structural refinement of $Pnam$, $P2_1am$ and $P2_12_12_1$ symmetry models against synchrotron X-ray diffraction data collected from $\text{NaBiNb}_2\text{O}_7$, showing the poor fits obtained by the $Pnam$, $P2_1am$ models.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	B _{iso} (Å ²)
Na	4 <i>a</i>	0.991(2)	0.995(3)	0.5047(9)	0.81(4)	0.62(41)
Bi	4 <i>a</i>	0.6936(6)	0.2716(7)	0.2510(8)	1	1.80(11)
Nb1	4 <i>a</i>	0.7481(12)	0.2610(20)	0.8630(4)	1	0.05*
Nb2	4 <i>a</i>	0.2420(11)	0.2330(20)	0.1439(4)	1	0.05*
O1	4 <i>a</i>	0.7620(15)	0.6788(9)	0.2495(14)	1	2.31(14)
O2	4 <i>a</i>	0.997(2)	0.501(2)	0.8400(6)	1	1.81(14)
O3	4 <i>a</i>	0.980(2)	0.014(2)	0.1702(6)	1	1.81(14)
O4	4 <i>a</i>	0.454(2)	0.034(2)	0.8488(7)	1	1.12(11)
O5	4 <i>a</i>	0.5580(20)	0.4460(20)	0.1571(7)	1	1.12(11)
O6	4 <i>a</i>	0.7229(14)	0.279(2)	0.9437(6)	1	0.53(10)
O7	4 <i>a</i>	0.2295(14)	0.2046(19)	0.0620(6)	1	0.53(10)
NaBiNb₂O₇ – space group <i>P</i>2₁2₁2₁ (#19) <i>a</i> = 5.4711(2) Å, <i>b</i> = 5.3841(2) Å, <i>c</i> = 21.6750(8) Å, volume = 638.48(4) Å³ Formula weight = 529.78 g mol⁻¹, <i>Z</i> = 4 Radiation source: Neutron Time of Flight Temperature: 298 K <i>R</i>_p = 6.13 %, <i>wR</i>_p = 6.35 %						

Table 4.11. Parameters from the structural refinement of *P*2₁2₁2₁ model against the neutron powder diffraction data collected from NaBiNb₂O₇ at 298 K.

Cation	Anion	Bond length (Å)	BVS
Nb1	O1 × 1	2.48(4)	+4.8630
	O2 × 1	1.942(15)	
	O3 × 1	1.983(17)	
	O4 × 1	2.044(14)	
	O5 × 1	2.047(15)	
	O6 × 1	1.757(16)	
Nb2	O1 × 1	2.36(4)	+5.092
	O2 × 1	1.929(14)	
	O3 × 1	1.942(16)	
	O4 × 1	1.950(15)	
	O5 × 1	2.094(14)	

	O7 × 1	1.783(16)	
Bi	O1 × 1	3.121(9)	+2.960
	O1 × 1	2.224(7)	
	O1 × 1	3.214(7)	
	O1 × 1	2.376(9)	
	O2 × 1	2.957(17)	
	O2 × 1	2.665(18)	
	O3 × 1	2.729(19)	
	O3 × 1	2.578(19)	
	O4 × 1	3.224(18)	
	O4 × 1	2.50(3)	
	O5 × 1	3.202(17)	
	O5 × 1	2.36(3)	
Na	O6 × 1	2.383(19)	+0.989
	O6 × 1	2.244(19)	
	O7 × 1	2.37(2)	
	O7 × 1	2.30(2)	

Table 4.12. Selected bond lengths from the refined structure of NaBiNb₂O₇.

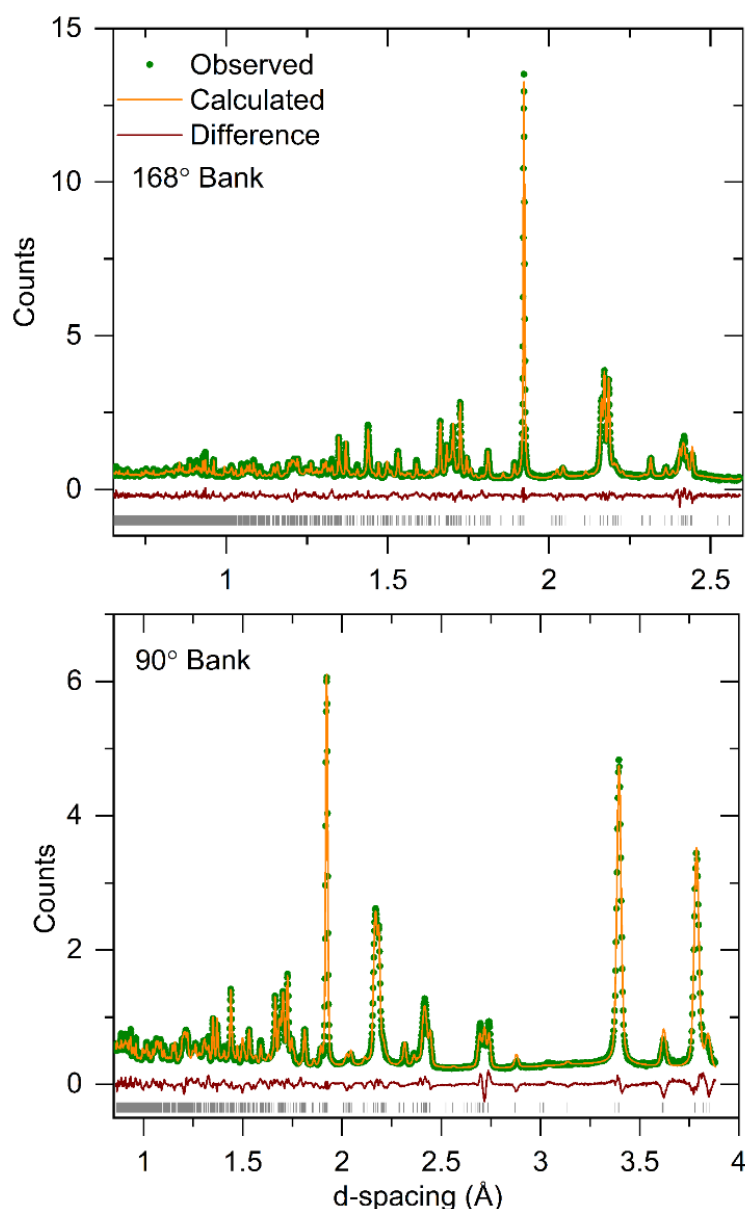


Figure 4.11. Observed, calculated and difference plots from the structural refinement of $P2_12_12_1$ model of $\text{NaBiNb}_2\text{O}_7$ against the neutron powder diffraction data collected at room temperature.

4.3.4.3 Microstructural characterisation of $\text{NaBiNb}_2\text{O}_7$

Synchrotron X-ray diffraction and neutron diffraction patterns collected from $\text{NaBiNb}_2\text{O}_7$ exhibit strongly hkl -dependent peak widths. Figure 4.12 shows a small section ($16 < 2\theta/^\circ < 24$) of the SXRD data collected from $\text{LiBiNb}_2\text{O}_7$ and $\text{NaBiNb}_2\text{O}_7$, with the central panel plotting the full-width at half-maximum (FWHM) of each of the observed peaks as a function of 2θ . The widths of the peaks in the $\text{LiBiNb}_2\text{O}_7$ diffraction pattern are relatively uniform ranging from 0.0508° to 0.0705° across this angular range. In contrast, the widths of the peaks in the

NaBiNb₂O₇ data range from 0.0617° to 0.1331°, with three peaks ([115], [117] and [0010]) being significantly broader than the others.

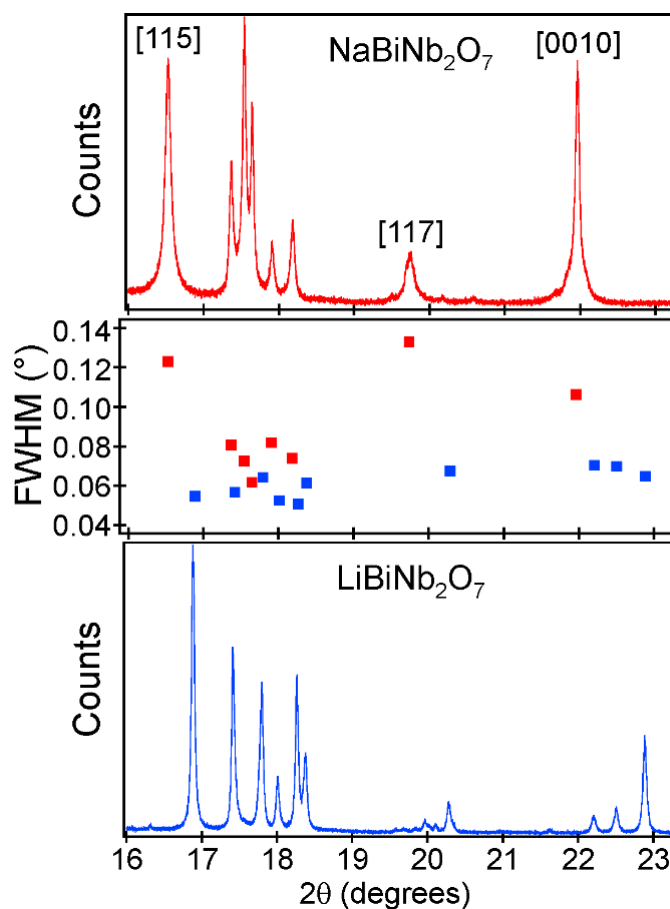


Figure 4.12. SXR data collected from NaBiNb₂O₇ (top) and LiBiNb₂O₇ (bottom) in the range $16 < 2\theta/^\circ < 20$. The central panel plots the FWHM of the diffraction peaks of NaBiNb₂O₇ (red) and LiBiNb₂O₇ (blue) as a function of 2θ .

During the structural refinement of NaBiNb₂O₇ this variation in peak width, which is also observed in the NPD data, was modelled using an anisotropic line-shape broadening function described by Stephens⁸⁰ implemented in the structural model. The inclusion of Stephen's anisotropic broadening improved the refinement parameters significantly as shown in Figure 4.13. In addition, the diffraction data collected from NaBiNb₂O₇ exhibited strong (00l) preferred orientation which was modelled using a 4th order spherical harmonic expression,⁷⁷ which made a significant improvement to the fitting as shown in Figure 4.13.

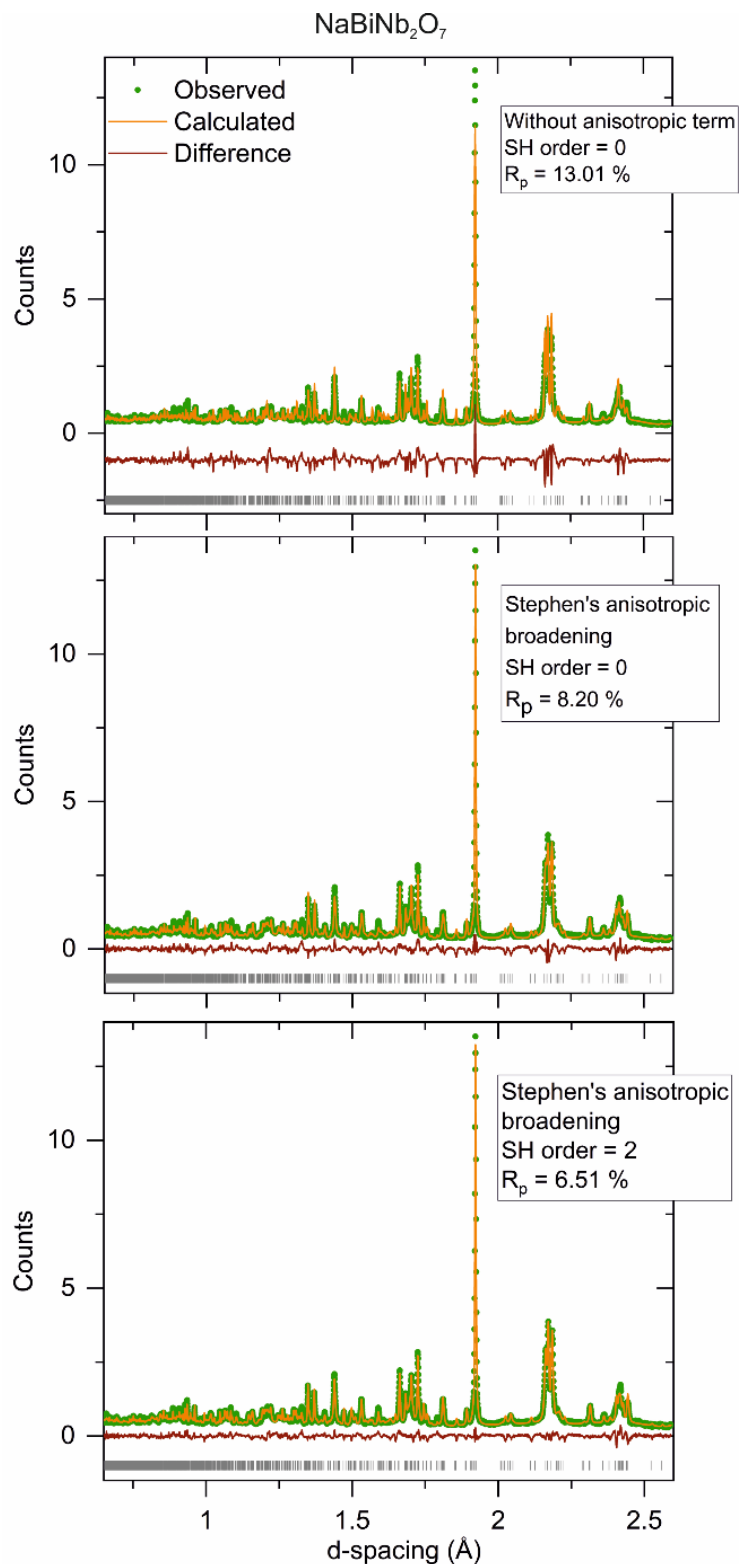


Figure 4.13. Fit to NPD data collected from $\text{NaBiNb}_2\text{O}_7$ (top) without accounting for preferred orientation or anisotropic peak broadening; (middle) accounting for anisotropic broadening only; (bottom) accounting for both anisotropic peak broadening and preferred orientation.

We were interested in determining the origin of this broadening phenomenon so undertook a microstructural study of the material. HAADF-STEM images collected from the NaBiNb₂O₇ sample revealed extensive intergrowths of other phases derived from RbBiNb₂O₇. Figure 4.14 shows a HAADF-STEM image in which layers of NaBiNb₂O₇ are intergrown with an Aurivillius type phase (thought to be Na_{0.5}Bi_{2.5}Nb₂O₉)^{81,82} and a perovskite phase, thought to be NaNbO₃.

Annealing samples of NaBiNb₂O₇ in air at 600 °C leads to decomposition to form NaNbO₃, and the Aurivillius phases Na_{0.5}Bi_{2.5}Nb₂O₉, Na_{2.5}Bi_{2.5}Nb₄O₁₅, Na_{3.5}Bi_{2.5}Nb₅O₁₈.

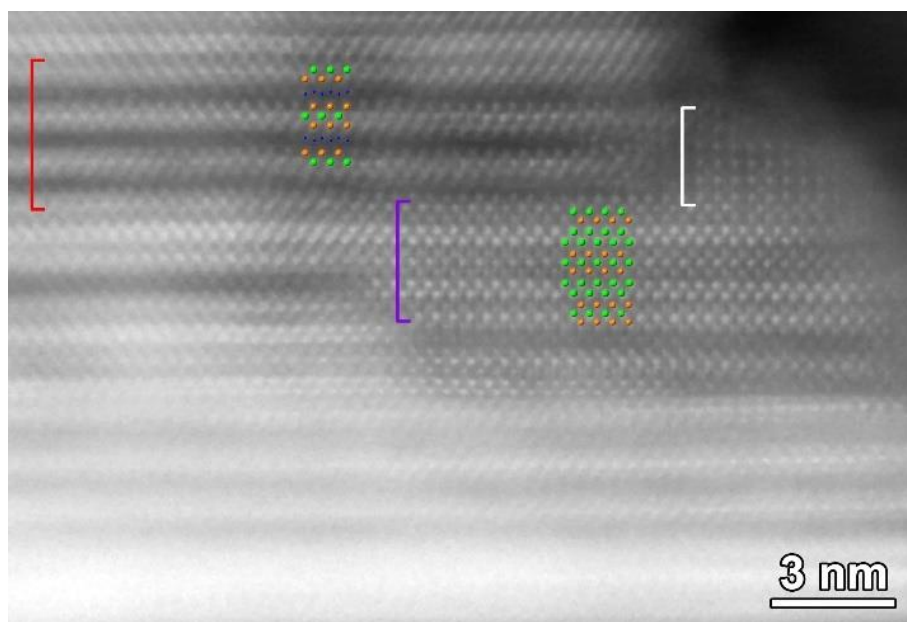


Figure 4.14. HAADF-STEM image of the layered crystal. Red bracket: [100] of target phase NaBiNb₂O₇. Violet bracket: [110] of Aurivillius type structure Bi_{2.5}Na_{0.5}Nb₂O₉: (*A*2₁*am*, *a* = 5.49 Å, *b* = 5.46 Å, *c* = 24.92 Å). White: perovskite-type blocks. The models are inserted: green – Bi, orange – Nb, blue – Na.

4.4 Discussion

RbBiNb₂O₇ adopts an *n* = 2 Dion-Jacobson structure with an $a^-a^-c^+/(a^-a^-c^+)$ tilting distortion described in polar, *I*2*cm* space group; analogous to that of RbNdNb₂O₇.¹¹ In contrast, the CsBiNb₂O₇ phase adopts *P*2₁*am* structure^{74–76} with $a^-a^-c^+/a^-a^-c^+$ tilting distortion. Different structural distortions of the Cs and Rb phases in *A'*ANb₂O₇ (*A'* = Cs, Rb; *A* = Nd, Bi) series could be explained by a competition between the optimization of bonding in the *A'*-cation site

and minimizing the O–O Coulombic repulsion. The larger Cs^+ cation has more degrees of freedom to displace in the $P2_1am$ structure which optimizes the bonding of Cs^+ ion in CsO_8 polyhedra but exhibits a stronger apical O–O repulsion. Smaller Rb^+ in the $I2cm$ structure minimizes the O–O repulsion between the apical oxide ions but forces the Rb^+ cation to stay in a high symmetry site; which compromises the bonding of RbO_8 polyhedra as indicated by non-optimal BVS of 0.897.

The reaction of $\text{RbBiNb}_2\text{O}_7$ with LiNO_3 and NaNO_3 yields the pseudo-Ruddlesden-Popper phases $\text{LiBiNb}_2\text{O}_7$ and $\text{NaBiNb}_2\text{O}_7$ respectively. The Li^+ and Na^+ cations in these structures reside in tetrahedral coordination sites in-between the BiNb_2O_7 double perovskite sheets. There are two tetrahedral coordination sites per formula unit in the pseudo-Ruddlesden-Popper structure. The Li^+ and Na^+ cations occupy half of these sites in ordered arrangements. The Li^+ cations in $\text{LiBiNb}_2\text{O}_7$ adopt a striped order arrangement but the Na^+ cations in $\text{NaBiNb}_2\text{O}_7$ adopt a chequerboard pattern as shown in Figure 4.15. These ordering arrangements are analogous to the ordering of Li^+ and Na^+ cations in the respective Nd-compounds. The differing cation ordering patterns adopted by Li^+ and Na^+ cations in the $A'\text{ANb}_2\text{O}_7$ ($A = \text{Nd}, \text{Bi}$) phases could be attributed to a competition between minimizing the repulsion between the A' -cations and optimization of the bonding of the $\text{Nd}^{3+}/\text{Bi}^{3+}$ A-cations, with stripe and chequerboard order being the optimum solution of the Li^+ and Na^+ cations respectively.

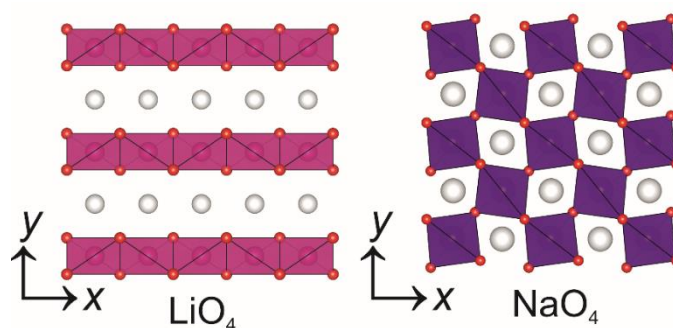


Figure 4.15. “Stripe” and “chequerboard” ordering of LiO_4 and NaO_4 tetrahedra respectively.

The cation exchange reaction of $\text{RbBiNb}_2\text{O}_7$ with LiNO_3 proceeds in a purely topochemical manner to yield $\text{LiBiNb}_2\text{O}_7$ similar to the reaction between $\text{LiNdNb}_2\text{O}_7$ and LiNO_3 .⁴² In

contrast, the exchange reaction between $\text{RbBiNb}_2\text{O}_7$ and NaNO_3 is accompanied by some non-topochemical processes as indicated by the formation of some NaNbO_3 and $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ intergrown into the main $\text{NaBiNb}_2\text{O}_7$ phase which can be seen in the microscopy image in Figure 4.14. This partial decomposition of the $A'\text{BiNb}_2\text{O}_7$ framework to thermodynamic phases on Na exchange is not observed in the analogous reaction between $\text{RbNdNb}_2\text{O}_7$ and NaNO_3 .⁴² This suggests that the replacement of Nd^{3+} by Bi^{3+} lowers the activation barriers for non-topochemical processes in the RbANb_2O_7 system.

The $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb}, \text{Li}, \text{Na}$) phases have the same basic structural framework to the corresponding $A'\text{NdNb}_2\text{O}_7$ phases. Synthesis of these three compounds with both Bi and Nd analogues allows us to investigate the effect of $6s^2$ electronic configuration of Bi^{3+} cation on the structural distortions of $A'\text{ANb}_2\text{O}_7$ layered perovskite phases.

4.4.1 $\text{RbBiNb}_2\text{O}_7$ vs $\text{RbNdNb}_2\text{O}_7$

The co-operative rotation and tilting of BO_6 octahedra in ABO_3 perovskites and related layered perovskite phases arise from a mismatch between the size of A'/A -site cation and B -site cation. When a small cation is placed in the 12 co-ordinate A -site of ABO_3 perovskite; cooperative tilting of BO_6 octahedra optimizes the bonding of A -site cation by shortening the $\langle A-O \rangle$ bond length without changing the $\langle B-O \rangle$ bond length. This size mismatch can be quantified by the Goldschmidt tolerance factor, which is defined as $t = \langle A-O \rangle / (\sqrt{2} \times \langle B-O \rangle)$.³ The smaller the tolerance factor (t), the larger is the mismatch between the sizes of A'/A -cation and B -cation; hence larger is the structural distortion. Now, the tolerance factor of a compound can be calculated from the tabulated values of ionic radii or by extracting the average $\langle A-O \rangle$ and $\langle B-O \rangle$ bond lengths from an experimental crystal structure. Table 4.13 lists the tolerance factors for $\text{RbBiNb}_2\text{O}_7$ and $\text{RbNdNb}_2\text{O}_7$ calculated by both methods. The tolerance factors of $\text{RbBiNb}_2\text{O}_7$ calculated by both methods are similar and they are larger than the tolerance factors calculated for $\text{RbNdNb}_2\text{O}_7$. So, we would expect that $\text{RbNdNb}_2\text{O}_7$ will have a more

distorted structure than $\text{RbBiNb}_2\text{O}_7$ if Bi^{3+} acts as a purely spherical cation. We can also analyse the structures of RbANb_2O_7 ($A = \text{Nd, Bi}$) phases in terms of the distortion modes which need to be applied to get the distorted structure from the aristotype $P4/mmm$ symmetry structure. The $I2cm$ structure of RbANb_2O_7 can be obtained by sequentially applying two tilting distortion modes (A_5^- and A_2^+) and a Γ_5^- polar distortion mode as shown in Figure 4.16. The A_5^- and A_2^+ irreducible representations describe the $a^-a^-c^0/-(a^-a^-c^0)$ and the $a^0a^0c^+/-(a^0a^0c^+)$ tilting distortions respectively. Hence the atomic displacement which takes place as a result of symmetry lowering from the aristotype $P4/mmm$ structure to the distorted $I2cm$ structure can be deconvoluted into contributions from the above three distortion modes with the help of ISODISTORT software. Table 4.14 shows that the magnitude of A_5^- distortion mode and the a^-a^- tilting angle of NbO_6 octahedra are smaller in the Bi-phase compared to the Nd-phase; which is in line with the larger tolerance factor of $\text{RbBiNb}_2\text{O}_7$ than $\text{RbNdNb}_2\text{O}_7$. The magnitude of A_2^+ distortion mode and the c^+ tilting angle are essentially the same for both phases. The magnitude of Γ_5^- polar distortion mode, as well as the Γ_5^- instability, is significantly larger for $\text{RbBiNb}_2\text{O}_7$ than $\text{RbNdNb}_2\text{O}_7$ phase as shown in Table 4.14. This is surprising because the Γ_5^- mode arises as a result of coupling between the A_5^- and A_2^+ distortion modes via the trilinear coupling mechanism. So, we can expect that the larger combined amplitude of A_5^- and A_2^+ distortion modes in the $\text{RbNdNb}_2\text{O}_7$ phase will result in a structure with a larger polar distortion. However, close inspection of the atom displacements associated with the Γ_5^- mode reveals that the Bi^{3+} contributes more than 25% of the total magnitude of Γ_5^- distortion mode (Table 4.16) in the $\text{RbBiNb}_2\text{O}_7$ structure. On the other hand, the Nd^{3+} contributes only 4% towards the total atom displacement (Table 4.15) resulted because of the Γ_5^- polar distortion mode in the $\text{RbNdNb}_2\text{O}_7$ structure. This suggests while the coupling of A_5^- and A_2^+ modes establishes the $I2cm$ symmetry thus a non-zero amplitude of Γ_5^- distortion mode; the $6s^2$ electronic configuration of Bi^{3+} enhances the Bi^{3+} polar displacement

via a SOJT mechanism which results in a larger polar distortion thus a stronger SHG activity in the RbBiNb₂O₇ phase compared to the RbNdNb₂O₇ phase.

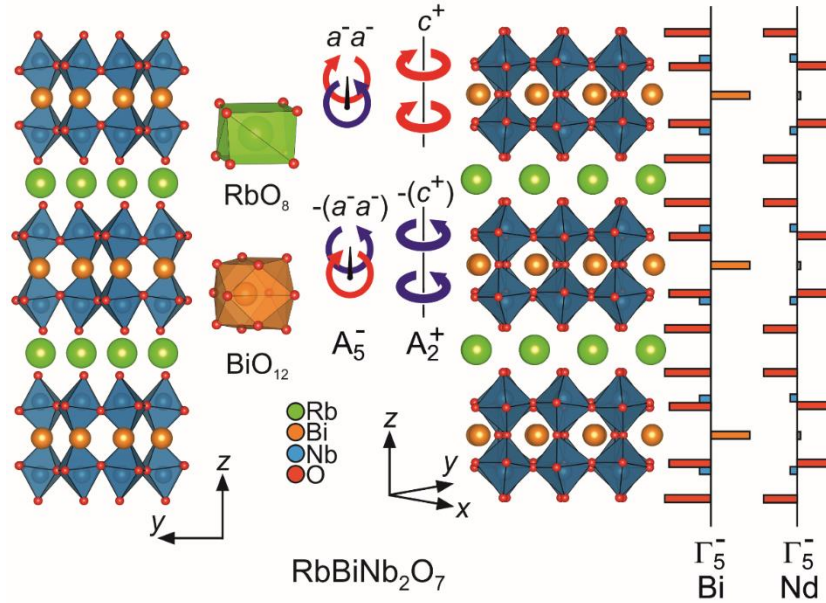


Figure 4.16. Structural distortions of RbBiNb₂O₇. The distortion modes relate the experimental structure to the *P4/mmm* aristotype structure. Solid bars represent the direction and magnitude of displacements due to the Γ_5^- polar distortion mode.

	Tolerance factor	
	ionic radii	bond lengths
RbNdNb ₂ O ₇	0.925	0.958
RbBiNb ₂ O ₇	0.964	0.965

Table 4.13. Tolerance factors of RbANb₂O₇ (A = Nd, Bi)

	$A_5^- a^- a^- c^0 / -(a^- a^- c^0)$			$A_2^+ a^0 a^0 c^+ / -(a^0 a^0 c^+)$			Polar Γ_5^-	
	a^- tilt angle (°)	Mode magnitude	Force constant (eV/Å ²)	c^+ tilt angle (°)	Mode magnitude	Force constant (eV/Å ²)	Mode magnitude	Force constant (eV/Å ²)
RbNdNb ₂ O ₇	7.49	0.785	-2.347	7.57	0.510	-0.486	0.432	-0.866
RbBiNb ₂ O ₇	5.85	0.560	-3.101	7.70	0.518	-2.080	0.582	-2.984

Table 4.14. Distortion mode magnitudes extracted from the refined structures of RbANb₂O₇ (A = Nd, Bi). A negative value of force constant indicates an energy lowering distortion.

RbNdNb ₂ O ₇			
Distortion mode	A_s	A_p	$d_{\max}$ (Å)
[0,0,0] Γ_1^+ [Nb1:h:dsp] A1(a)	0.06720	0.04752	0.03360

[0,0,0] Γ_1^+ [O1:i:dsp] A1(a)	0.24133	0.17065	0.08532
[0,0,0] Γ_1^+ [O2:h:dsp] A1(a)	0.11508	0.08137	0.05754
[0,0,0] Γ_1^+ all	0.27568	0.19494	
[0,0,0] Γ_5^- [Rb1:b:dsp] Eu(a)	0.0000	0.0000	0.0000
[0,0,0] Γ_5^- [Nd1:a:dsp] Eu(a)	0.01537	0.01087	0.01087
[0,0,0] Γ_5^- [Nb1:h:dsp] E(a)	-0.07282	-0.05149	0.03641
[0,0,0] Γ_5^- [O1:i:dsp] B2(a)	0.53204	0.37621	0.18810
[0,0,0] Γ_5^- [O1:i:dsp] B1(a)	0.12119	0.08569	0.04285
[0,0,0] Γ_5^- [O2:h:dsp] E(a)	-0.08043	-0.05687	0.04022
[0,0,0] Γ_5^- [O3:c:dsp] Eu(a)	-0.25286	-0.17880	0.17880
[0,0,0] Γ_5^- all	0.61131	0.43226	
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_2^+ [O1:i:dsp] B2(a)	-0.72225	-0.51071	0.25535
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_2^+ all	0.72225	0.51071	
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_3^+ [O1:i:dsp] B1(a)	-0.10054	-0.07109	0.03555
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_3^+ all	0.10054	0.07109	
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_5^- [Nd1:a:dsp] Eu(a)	-0.00769	-0.00544	0.00544
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_5^- [Nb1:h:dsp] E(a)	0.00978	0.00692	0.00489
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_5^- [O1:i:dsp] A1(a)	-0.76748	-0.54269	0.27135
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_5^- [O2:h:dsp] E(a)	-0.57280	-0.40503	0.28640
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_5^- [O3:c:dsp] Eu(a)	0.56182	0.39727	0.39727
$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ A_5^- all	1.1104	0.78515	

Table 4.15. Distortion mode amplitudes extracted from the refined structure of RbNdNb₂O₇ (space group *I2cm*) compared to the *P4/mmm* symmetry aristotype structure.

RbBiNb ₂ O ₇			
Distortion mode	A _s	A _p	d _{max} (Å)
[0,0,0] Γ_1^+ [Nb1:h:dsp] A1(a)	0.25562	0.18075	0.12781
[0,0,0] Γ_1^+ [O1:i:dsp] A1(a)	0.31711	0.22423	0.11212
[0,0,0] Γ_1^+ [O2:h:dsp] A1(a)	0.19732	0.13953	0.09866
[0,0,0] Γ_1^+ all	0.45259	0.32003	

[0,0,0] Γ_5^- [Rb1:b:dsp] Eu(a)	0.0000	0.0000	0.0000
[0,0,0] Γ_5^- [Bi1:a:dsp] Eu(a)	-0.29270	-0.20697	0.20697
[0,0,0] Γ_5^- [Nb1:h:dsp] E(a)	0.11920	0.08429	0.05960
[0,0,0] Γ_5^- [O1:i:dsp] B2(a)	0.62795	0.44403	0.22201
[0,0,0] Γ_5^- [O1:i:dsp] B1(a)	0.22485	0.15899	0.07950
[0,0,0] Γ_5^- [O2:h:dsp] E(a)	0.12570	0.08888	0.06285
[0,0,0] Γ_5^- [O3:c:dsp] Eu(a)	0.34480	0.24381	0.24381
[0,0,0] Γ_5^- all	0.82429	0.58286	
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_2^+ [O1:i:dsp] B2(a)	-0.73305	-0.51834	0.25917
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_2^+ all	0.73305	0.51834	
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_3^+ [O1:i:dsp] B1(a)	-0.04605	-0.03256	0.01628
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_3^+ all	0.04605	0.03256	
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_5^- [Bi1:a:dsp] Eu(a)	0.12872	0.09102	0.09102
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_5^- [Nb1:h:dsp] E(a)	-0.05201	-0.03678	0.02601
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_5^- [O1:i:dsp] A1(a)	-0.45980	-0.32513	0.16256
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_5^- [O2:h:dsp] E(a)	-0.33483	-0.23676	0.16742
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_5^- [O3:c:dsp] Eu(a)	0.53406	0.37764	0.37764
[$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$] A_5^- all	0.79248	0.56037	

Table 4.16. Distortion mode amplitudes extracted from the refined structure of RbBiNb₂O₇ (space group *I2cm*) compared to the *P4/mmm* symmetry aristotype structure.

4.4.2 LiBiNb₂O₇ vs LiNdNb₂O₇

We can perform a similar distortion mode analysis for the LiANb₂O₇ (A = Nd, Bi) phases. The *B2cm* structure of the Li-phases can be obtained from the aristotype *I4/mmm* structure by sequentially applying two tilting distortion modes (X_4^- and X_2^+) and a Γ_5^- polar distortion mode as shown in Figure 4.17. The X_4^- and X_2^+ irreducible representations describe the $a^-a^-c^0/-(a^-a^-c^0)$ and the $a^0a^0c^+/(a^0a^0c^+)$ tilting distortions respectively. Hence the atomic displacement which takes place as a result of symmetry lowering from the aristotype *I4/mmm* structure to

the distorted $B2cm$ structure can be deconvoluted into contributions from the above three distortion modes with the help of ISODISTORT software. Table 4.18 shows that the magnitude of X_4^- distortion mode as well as the a^-a^- tilting angle of NbO_6 octahedra is smaller in the Bi-phase compared to the Nd-phase; which is in line with the larger tolerance factor of $LiBiNb_2O_7$ than $LiNdNb_2O_7$ as listed in Table 4.17. The c^+ tilt angles in both the Li compounds are essentially the same. A large Li^+ displacement is observed as a result of the X_2^+ distortion mode in the Nd-phase which means the magnitude of X_2^+ distortion mode is significantly larger in the $LiNdNb_2O_7$ phase than $LiBiNb_2O_7$ phase as shown in Table 4.19. The magnitude of polar distortion mode is larger in the Nd-phase (Table 4.19) than in the Bi-phase (Table 4.20) which is consistent with a larger magnitude of X_3^- and X_2^+ distortion modes in the Nd-phase. But close inspection of the displacement of atoms as a result of Γ_5^- polar displacement in these two Li-phases shows that the Bi^{3+} accounts for 45% of the total magnitude of Γ_5^- in $LiBiNb_2O_7$; whereas the contribution of Nd^{3+} is less than 4% towards the total magnitude of Γ_5^- distortion mode in $LiNdNb_2O_7$. This suggests the $6s^2$ electronic configuration of Bi^{3+} enhances its polar displacement.

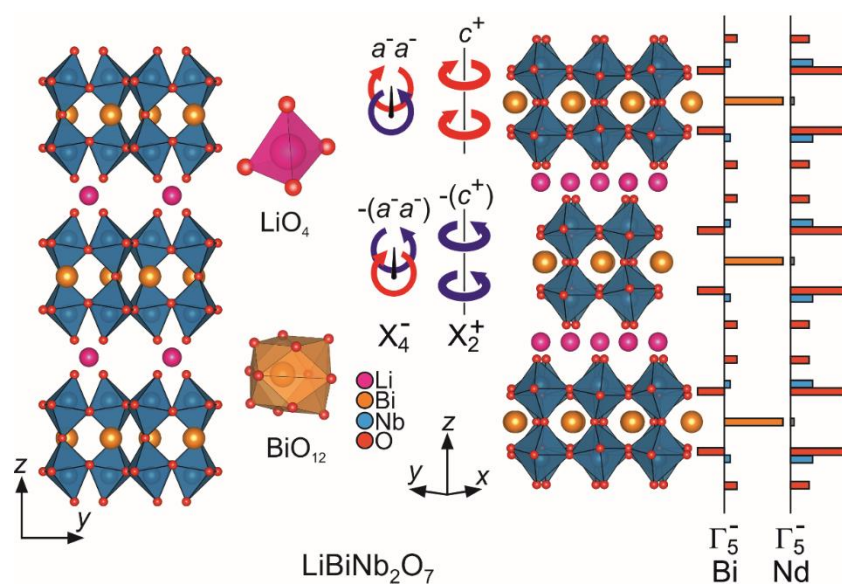


Figure 4.17. Structural distortions of $LiBiNb_2O_7$. The distortion modes relate the experimental structure to the $I4/mmm$ aristotype structure. Solid bars represent the direction and magnitude of displacements due to the Γ_5^- polar distortion mode.

	Tolerance factor	
	ionic radii	bond lengths
LiNdNb ₂ O ₇	0.925	0.956
LiBiNb ₂ O ₇	0.964	0.957

Table 4.17. Tolerance factors of LiANb₂O₇ (A = Nd, Bi)

	$X_4^- a^- a^- c^0 / -(a^- a^- c^0)$		$X_2^+ a^0 a^0 c^+ / -(a^0 a^0 c^+)$		Polar Γ_5^-
	a^- tilt angle (°)	Mode magnitude	c^+ tilt angle (°)	Mode magnitude	Mode magnitude
LiNdNb ₂ O ₇	9.62	0.957	6.98	0.565	0.629
LiBiNb ₂ O ₇	8.06	0.819	7.10	0.474	0.456

Table 4.18. Distortion mode magnitudes extracted from the refined structures of LiANb₂O₇ (A = Nd, Bi). A negative value of force constant indicates an energy lowering distortion

LiNdNb ₂ O ₇			
Distortion mode	A _s	A _p	d _{max} (Å)
[0,0,0] Γ_1^+ [Nb1:e:dsp] A1(a)	-0.44990	-0.31813	0.22495
[0,0,0] Γ_1^+ [O2:g:dsp] A1(a)	-0.46851	-0.33129	0.16564
[0,0,0] Γ_1^+ [O3:e:dsp] A1(a)	0.67894	0.48008	0.33947
[0,0,0] Γ_1^+ all	0.93961	0.66441	
[0,0,0] Γ_5^- [Li1:d:dsp] E(a)	0	0	0
[0,0,0] Γ_5^- [Nd1:a:dsp] Eu(a)	0.03605	0.02549	0.02549
[0,0,0] Γ_5^- [Nb1:e:dsp] E(a)	0.24514	0.17334	0.12257
[0,0,0] Γ_5^- [O1:b:dsp] Eu(a)	0.21859	0.15457	0.15457
[0,0,0] Γ_5^- [O2:g:dsp] B2(a)	0.70126	0.49587	0.24793
[0,0,0] Γ_5^- [O2:g:dsp] B1(a)	0.38670	0.27344	0.13672
[0,0,0] Γ_5^- [O3:e:dsp] E(a)	0.20718	0.14650	0.10359
[0,0,0] Γ_5^- all	0.89073	0.62984	
[½,½,0] X_2^+ [Li1:d:dsp] E(a)	0.44473	0.31447	0.22236
[½,½,0] X_2^+ [O2:g:dsp] B2(a)	-0.66438	-0.46979	0.23489
[½,½,0] X_2^+ [O2:g:dsp] B1(a)	0.01573	0.01112	0.00556

$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+$ all	0.79965	0.56543	
$[\frac{1}{2}, \frac{1}{2}, 0] X_4^-$ [Nd1:a:dsp] Eu(a)	0.01534	0.01085	0.01085
$[\frac{1}{2}, \frac{1}{2}, 0] X_4^-$ [Nb1:e:dsp] E(a)	-0.01952	-0.01380	0.00976
$[\frac{1}{2}, \frac{1}{2}, 0] X_4^-$ [O1:b:dsp] Eu(a)	0.52233	0.36934	0.36934
$[\frac{1}{2}, \frac{1}{2}, 0] X_4^-$ [O2:g:dsp] A1(a)	0.79821	0.56442	0.28221
$[\frac{1}{2}, \frac{1}{2}, 0] X_4^-$ [O3:e:dsp] E(a)	-0.96105	-0.67956	0.48052
$[\frac{1}{2}, \frac{1}{2}, 0] X_4^-$ all	1.3543	0.95765	

Table 4.19. Distortion mode amplitudes extracted from the refined structure of $\text{LiNdNb}_2\text{O}_7$ (space group $B2cm$) compared to the $I4/mmm$ symmetry aristotype structure

$\text{LiBiNb}_2\text{O}_7$			
Distortion mode	A_s	A_p	$d_{\max}$ (Å)
$[0,0,0] \Gamma_1^+$ [Nb1:e:dsp] A1(a)	-0.63705	-0.45046	0.31853
$[0,0,0] \Gamma_1^+$ [O2:g:dsp] A1(a)	-0.41219	-0.29146	0.14573
$[0,0,0] \Gamma_1^+$ [O3:e:dsp] A1(a)	0.56210	0.39746	0.28105
$[0,0,0] \Gamma_1^+$ all	0.94429	0.66772	
$[0,0,0] \Gamma_5^-$ [Li1:d:dsp] E(a)	0.0000	0.0000	0.0000
$[0,0,0] \Gamma_5^-$ [Bi1:a:dsp] Eu(a)	-0.46107	-0.32603	0.32603
$[0,0,0] \Gamma_5^-$ [Nb1:e:dsp] E(a)	-0.06753	-0.04775	0.03377
$[0,0,0] \Gamma_5^-$ [O1:b:dsp] Eu(a)	0.01795	0.01269	0.01269
$[0,0,0] \Gamma_5^-$ [O2:g:dsp] B2(a)	0.42192	0.29834	0.14917
$[0,0,0] \Gamma_5^-$ [O2:g:dsp] B1(a)	-0.00486	-0.00344	0.00172
$[0,0,0] \Gamma_5^-$ [O3:e:dsp] E(a)	-0.14640	-0.10352	0.07320
$[0,0,0] \Gamma_5^-$ all	0.64571	0.45659	
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+$ [Li1:d:dsp] E(a)	-0.00378	-0.00267	0.00189
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+$ [O2:g:dsp] B2(a)	-0.67097	-0.47445	0.23722
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+$ [O2:g:dsp] B1(a)	0.00216	0.00153	0.00076
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+$ all	0.67098	0.47446	
$[\frac{1}{2}, \frac{1}{2}, 0] X_4^-$ [Bi1:a:dsp] Eu(a)	0.11613	0.08212	0.08212

$[\frac{1}{2}, \frac{1}{2}, 0]$ X_4^- [Nb1:e:dsp] E(a)	-0.04970	-0.03514	0.02485
$[\frac{1}{2}, \frac{1}{2}, 0]$ X_4^- [O1:b:dsp] Eu(a)	0.54320	0.38410	0.38410
$[\frac{1}{2}, \frac{1}{2}, 0]$ X_4^- [O2:g:dsp] A1(a)	0.60062	0.42470	0.21235
$[\frac{1}{2}, \frac{1}{2}, 0]$ X_4^- [O3:e:dsp] E(a)	-0.81899	-0.57911	0.40950
$[\frac{1}{2}, \frac{1}{2}, 0]$ X_4^- all	1.1587	0.81930	

Table 4.20. Distortion mode amplitudes extracted from the refined structure of $\text{LiBiNb}_2\text{O}_7$ (space group $B2cm$) compared to the $I4/mmm$ symmetry aristotype structure.

4.4.3 $\text{NaBiNb}_2\text{O}_7$ vs $\text{NaNdNb}_2\text{O}_7$

$\text{NaBiNb}_2\text{O}_7$ adopts an $a^-a^-c^+/a^-a^-(-c^+)$ tilting distortion which can be described in the $P2_12_12_1$ space group, which is noncentrosymmetric but non-polar. On the other hand, the Nd analogue of the Na-phase adopts a centrosymmetric $P4_2/mnm$ structure with an $a^-b^0c^0/b^0a^-c^0$ tilting distortion. Thus, replacing Nd^{3+} with Bi^{3+} in NaNb_2O_7 structure leads to a more distorted structure although the tolerance factor of the Bi-phase is larger than that of the Nd-phase as shown in Table 4.21. Similar to the Rb and Li phases, we can perform symmetry mode analysis of the distorted Na phase with respect to the $I4/mmm$ aristotype structure. Deconvolution of the $P2_12_12_1$ structure of $\text{NaBiNb}_2\text{O}_7$ reveals that 7 distortion modes are allowed when symmetry is lowered from $I4/mmm$ as shown in Table 4.22. But only three of them have significant amplitudes: the X_3^- distortion mode which describes as the $a^-a^-c^0/a^-a^-c^0$ tilting distortion; the X_2^+ distortion mode which describes the $a^0a^0c^+/a^0a^0(-c^+)$ tilting distortion and the M_5^- anti-polar distortion mode which displaces the cations along X -axis in such a way that the polarity of one BiNb_2O_7 layer is cancelled out by the polarity of the next layer as shown in Figure 4.18. Close inspection of the atom displacements as a result of M_5^- reveals that Bi^{3+} accounts for more than 50% of the total magnitude of M_5^- antipolar distortion as shown in Table 4.22. This implies that the asymmetric nature of $6s^2 \text{Bi}^{3+}$ cation has a significant role in the more distorted structure adopted by $\text{NaBiNb}_2\text{O}_7$ compared to $\text{NaNdNb}_2\text{O}_7$.

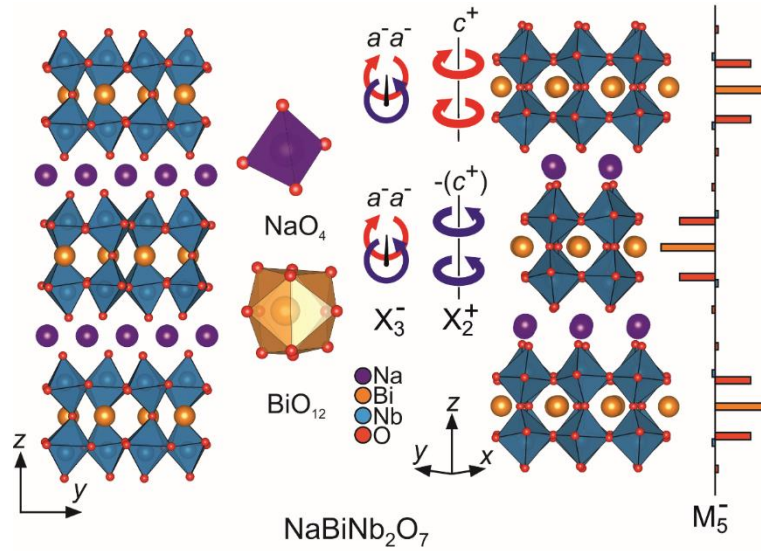


Figure 4.18. Structural distortions of $\text{NaBiNb}_2\text{O}_7$. The distortion modes relate the experimental structure to the $I4/mmm$ aristotype structure. Solid bars represent the direction and magnitude of displacements due to the M_5^- anti-polar distortion mode.

	Tolerance factor		a^- tilt	c^+ tilt
	ionic radii	bond length	angle ($^\circ$)	angle ($^\circ$)
$\text{NaNdNb}_2\text{O}_7$	0.925	0.956	10.09	0.00
$\text{NaBiNb}_2\text{O}_7$	0.964	0.966	4.84	6.40

Table 4.21. Tolerance factor and tilt angles of NaNb_2O_7 ($A = \text{Nd, Bi}$)

$\text{NaBiNb}_2\text{O}_7$			
Distortion mode	A_s	A_p	$d_{\max}$ ($\text{\AA}$)
$[0,0,0] \Gamma_1^+ [\text{Nb1:e:dsp}] A1(a)$	-0.58470	-0.29235	0.20672
$[0,0,0] \Gamma_1^+ [\text{O2:g:dsp}] A1(a)$	-0.83339	-0.41669	0.20835
$[0,0,0] \Gamma_1^+ [\text{O3:e:dsp}] A1(a)$	1.1725	0.58623	0.41453
$[0,0,0] \Gamma_1^+$ all	1.5528	0.77638	
$[0,0,0] \Gamma_4^- [\text{O2:g:dsp}] A1(a)$	-0.34851	-0.17425	0.087130
$[0,0,0] \Gamma_4^-$ all	0.34851	0.17425	
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+ [\text{Na1:d:dsp}] E(a)$	-0.06896	-0.03448	0.02438
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+ [\text{O2:g:dsp}] B2(a)$	-0.85046	-0.42523	0.21262
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+ [\text{O2:g:dsp}] B1(a)$	0.07662	0.03831	0.01916
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^+$ all	0.85668	0.42834	

$[\frac{1}{2}, \frac{1}{2}, 0] X_3^+ [\text{Na1:d:dsp}] B2(a)$	0.14388	0.07194	0.05087
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^+ [\text{Nb1:e:dsp}] E(a)$	0.07585	0.03793	0.02682
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^+ [\text{O2:g:dsp}] A1(a)$	0.09308	0.04654	0.02327
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^+ [\text{O3:e:dsp}] E(a)$	0.36470	0.18235	0.12894
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^+ \text{ all}$	0.41003	0.20502	
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^- [\text{Na1:d:dsp}] E(a)$	0.06896	0.03448	0.02438
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^- [\text{Bi1:a:dsp}] A2u(a)$	0.04329	0.02165	0.02165
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^- [\text{Nb1:e:dsp}] A1(a)$	0.21123	0.10562	0.07468
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^- [\text{O1:b:dsp}] A2u(a)$	0.02165	0.01082	0.01083
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^- [\text{O2:g:dsp}] B2(a)$	0.26816	0.13408	0.06704
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^- [\text{O3:e:dsp}] A1(a)$	0.17449	0.08725	0.06169
$[\frac{1}{2}, \frac{1}{2}, 0] X_2^- \text{ all}$	0.39252	0.19626	
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^- [\text{Na1:d:dsp}] B2(a)$	-0.14388	-0.07194	0.05087
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^- [\text{Bi1:a:dsp}] Eu(a)$	-0.23405	-0.11703	0.11703
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^- [\text{Nb1:e:dsp}] E(a)$	-0.21453	-0.10726	0.07585
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^- [\text{O1:b:dsp}] Eu(a)$	0.77148	0.38574	0.38574
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^- [\text{O2:g:dsp}] A1(a)$	0.47406	0.23703	0.11852
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^- [\text{O3:e:dsp}] E(a)$	-0.56697	-0.28348	0.20045
$[\frac{1}{2}, \frac{1}{2}, 0] X_3^- \text{ all}$	1.1238	0.56189	
$[1, 1, 1] M_5^+ [\text{Na1:d:dsp}] E(a)$	-0.03831	-0.01915	0.01354
$[1, 1, 1] M_5^+ [\text{Nb1:e:dsp}] E(a)$	0.04597	0.02298	0.01625
$[1, 1, 1] M_5^+ [\text{O2:g:dsp}] B2(a)$	0.02299	0.01150	0.00575
$[1, 1, 1] M_5^+ [\text{O2:g:dsp}] B1(a)$	0.06129	0.03064	0.01532
$[1, 1, 1] M_5^+ [\text{O3:e:dsp}] E(a)$	0.12259	0.06130	0.04334
$[1, 1, 1] M_5^+ \text{ all}$	0.15131	0.07565	
$[1, 1, 1] M_5^- [\text{Na1:d:dsp}] E(a)$	-0.03831	-0.01915	0.01354
$[1, 1, 1] M_5^- [\text{Bi1:a:dsp}] Eu(a)$	-0.61112	-0.30556	0.30556

[1,1,1] M ₅ ⁻ [Nb1:e:dsp] E(a)	0.04674	0.02337	0.01653
[1,1,1] M ₅ ⁻ [O1:b:dsp] Eu(a)	-0.13003	-0.06502	0.06502
[1,1,1] M ₅ ⁻ [O2:g:dsp] B2(a)	-0.62061	-0.3103	0.15515
[1,1,1] M ₅ ⁻ [O2:g:dsp] B1(a)	0.04597	0.02298	0.01149
[1,1,1] M ₅ ⁻ [O3:e:dsp] E(a)	-0.05057	-0.02528	0.01788
[1,1,1] M ₅ ⁻ all	0.88536	0.44268	

Table 4.22. Distortion mode amplitudes extracted from the refined structure of NaBiNb₂O₇ (space group *P*₂₁₂₁) compared to the *I*4/*mmm* symmetry aristotype structure.

4.4.4 AO₁₂ polyhedra in *A'*ANb₂O₇

Close examination of the structures of RbANb₂O₇ and LiANb₂O₇ reveals that the A³⁺ cations in both structures reside on a 12 coordinate site with *..m* point symmetry. These low symmetry coordinate sites are compatible with the asymmetric nature of the 6s² Bi³⁺ ion. Thus, no change in structure is observed when Nd³⁺ is replaced by Bi³⁺. So, we conclude that the presence of Bi³⁺ enhances the polarity of these two phases, but it is not the primary driver for the polar structures adopted. On the other hand, the Nd³⁺ in the *P*₄₂/*mmn* structure of NaNdNb₂O₇ resides on a 4*f* site with *m.2m* point symmetry. This high symmetry (*x, x, 0*) crystallographic site is not compatible with the expected asymmetric coordination geometry of Bi³⁺ cation. Hence on substituting Nd³⁺ by Bi³⁺, the NbO₆ octahedra tilt in such a way that the Bi³⁺ cation symmetry is lowered to *..m* in the *Pnam* model without Na-ordering which eventually becomes a general position in Na-ordered *P*₂₁₂₁ structure. In general, in all three analogous structures, BiO₁₂ polyhedra are more distorted than the corresponding NdO₁₂ polyhedra as indicated by the calculated distortion index⁸³ of AO₁₂ polyhedra listed in Table 4.23. The distortion index is a measure of asymmetry in polyhedral coordination which is defined as:

$$D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{av}|}{l_{av}}$$

where l_{av} is the average bond length, l_i is the i^{th} bond length and n is the total number of bonds in the considered polyhedral (in this case $n = 12$)

	RbANb ₂ O ₇	LiANb ₂ O ₇	NaANb ₂ O ₇
$D(\text{NdO}_{12})$	0.096	0.094	0.076
$D(\text{BiO}_{12})$	0.114	0.112	0.114

Table 4.23. Calculated distortion index of $A'\text{ANb}_2\text{O}_7$ ($A' = \text{Rb, Li, Na}$; $A = \text{Nd, Bi}$) phases.

4.5 Conclusion

RbBiNb₂O₇ was synthesized by high-temperature ceramic synthesis, and LiBiNb₂O₇ and NaBiNb₂O₇ were synthesized by low-temperature cation exchange reactions from RbBiNb₂O₇. In these exchange reactions the structure changes from a (0, 0, z) Dion-Jacobson framework of the Rb-phase to the (½, ½, z) Ruddlesden-Popper framework of the Li- and Na-phase. Analysis of synchrotron X-ray and neutron diffraction data reveals that the RbBiNb₂O₇ and LiBiNb₂O₇ phases adopt polar $I2cm$ and $B2cm$ structures respectively with $a^-a^-c^+/- (a^-a^-c^+)$ tilting distortion of the NbO₆ octahedra which are isostructural to the corresponding Nd-phases. Distortion mode analysis shows that the polarity in the Rb and Li-phase originates from a hybrid improper mechanism but the presence of 6s² Bi³⁺ cation enhances the polarity in these phases. NaBiNb₂O₇ adopts a noncentrosymmetric $P2_12_12_1$ structure with $a^-a^-c^+/a^-a^-(-c^+)$ tilting distortion but unlike the Rb or Li phase; in the NaBiNb₂O₇ phase the inversion symmetry is broken as a result of the stereo active 6s² Bi³⁺ cation via SOJT mechanism. Li⁺ and Na⁺ ions are ordered in “stripe” and “chequerboard” arrangement respectively in tetrahedral coordination sites of LiBiNb₂O₇ and NaBiNb₂O₇.

In this chapter the structures and tilting distortions of $A'\text{BiNb}_2\text{O}_7$ phases are discussed, where the A' sites are alkali metals Rb, Li or Na, and compared them to the analogous Nd-phases. In the next chapter, the structure of another related layered perovskite phase KBiNb₂O₇ will be discussed.

Chapter 5 – Synthesis and characterisation of KBiNb_2O_7

5.1 Introduction

In chapter 4, the room temperature crystal structure of $n = 2$ Dion-Jacobson phase $\text{RbBiNb}_2\text{O}_7$ has been described by a polar $I2cm$ space group with an $a^-a^-c^+/- (a^-a^-c^+)$ tilting distortion. Further low-temperature cation exchange reactions of $\text{RbBiNb}_2\text{O}_7$ with LiNO_3 and NaNO_3 lead to the formation of the Ruddlesden-Popper phases $\text{LiBiNb}_2\text{O}_7$ and $\text{NaBiNb}_2\text{O}_7$ respectively. The crystal structure of the Li-phase is described in a polar $B2cm$ space group with $a^-a^-c^+/- (a^-a^-c^+)$ tilting distortion, but the structure of the $\text{NaBiNb}_2\text{O}_7$ phase can be explained in a noncentrosymmetric but non-polar $P2_12_12_1$ space group with an $a^-a^-c^+/a^-a^-(-c^+)$ tilting distortion. Polarity in the Rb- and the Li-phases originate from a hybrid improper mechanism whereas the noncentrosymmetry in the Na-phase originates from a SOJT driven proper mechanism.

KNdNb_2O_7 adopts a $(0, \frac{1}{2}, z)$ stacked framework of the NdNb_2O_7 double perovskite layers as discussed in chapter 3.⁸⁴ The crystal structure of this phase can be described in a polar $Im2m$ space group with an $a^0b^+c^0/a^0-b^+c^0$ tilting of NbO_6 octahedra. In the KNdNb_2O_7 phase, the polarity originates from an SOJT driven proper mechanism where the d^0 electronic configuration of Nb^{5+} drives the mixing between $4d$ orbitals of niobium with $2p$ orbitals of oxygen.

The $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb}, \text{Li}, \text{Na}, \text{K}$) phases have the same basic structural framework as the corresponding $A'\text{NdNb}_2\text{O}_7$ phases. Synthesis of the KANb_2O_7 compounds with both Bi and Nd analogues allows the investigation of the effect of $6s^2$ electronic configuration of Bi^{3+} cation on the structural distortions of KANb_2O_7 layered perovskite phases.

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5.2 Synthesis

Samples of KBiNb_2O_7 were synthesized by first synthesizing the $\text{RbBiNb}_2\text{O}_7$ phase and then converting that to $\text{LiBiNb}_2\text{O}_7$ phase via Li-for-Rb cation exchange reaction, and finally converting the Li-phase to the KBiNb_2O_7 via K-for-Li cation exchange reaction. The synthesis of polycrystalline $\text{RbBiNb}_2\text{O}_7$ and the cation exchange to $\text{LiBiNb}_2\text{O}_7$ is described in the synthesis section of chapter 4. KBiNb_2O_7 was synthesized by reacting $\text{LiBiNb}_2\text{O}_7$ with 10 mole-equivalents of KNO_3 (99.995%) in open-ended silica tubes at 400 °C in air, for two periods of 48 h. Between heating cycles, samples were washed with distilled water, dried for 12 h at 120 °C in air and mixed with a further 10 mole-equivalents of KNO_3 . After the final heating step, all samples were washed with distilled water to remove the excess KNO_3 and then dried for 12 h at 120 °C in air.

5.3 Results

5.3.1 Low-temperature cation exchange reaction

High-temperature solid-state synthesis of KBiNb_2O_7 was not successful. When the stoichiometric combination of K_2CO_3 , Bi_2O_3 and Nb_2O_5 were heated at 1100 °C, the major product obtained is $\text{K}_2\text{BiNb}_5\text{O}_{15}$ indicating that KBiNb_2O_7 is not the thermodynamically most stable product of the combination of these reagents and hence cannot be prepared by a high-temperature procedure. So, we have synthesized the K-phase in a low-temperature 2-step cation exchange pathway. $\text{RbBiNb}_2\text{O}_7$ was first converted to $\text{LiBiNb}_2\text{O}_7$ and finally, the Li-phase was converted to KBiNb_2O_7 . A single-step cation exchange reaction to synthesize the KBiNb_2O_7 phase from $\text{RbBiNb}_2\text{O}_7$ by treatment with KNO_3 was not successful.

5.3.2 Optical SHG measurement

Particle-size dependent SHG measurement shows that KBiNb_2O_7 is SHG active and the activity increases with an increase in particle size before reaching a plateau (Figure 5.1). This indicates that KBiNb_2O_7 adopts a noncentrosymmetric crystal structure at room temperature.

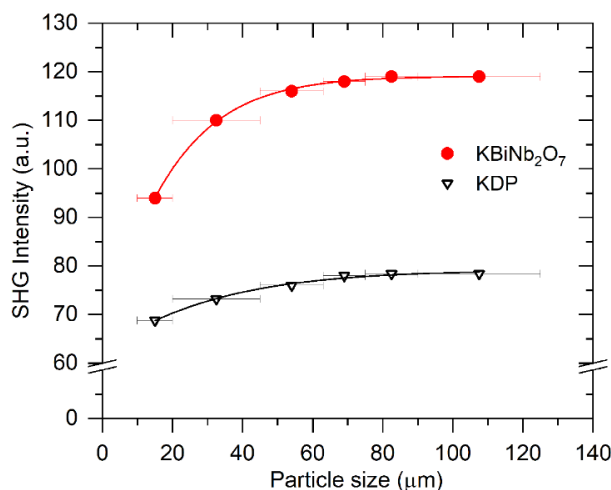


Figure 5.1. The plot of SHG activity of KBiNb₂O₇ as a function of particle size, compared to KH₂PO₄ (KDP) standard.

5.3.3 Characterisation of KBiNb₂O₇

5.3.3.1 Synchrotron X-ray diffraction data

High resolution synchrotron X-ray diffraction data (SXRDX) collected from KBiNb₂O₇ could be indexed using a monoclinic unit cell ($a = 3.847 \text{ \AA}$, $b = 3.840 \text{ \AA}$, $c = 22.193 \text{ \AA}$, $\gamma = 90.80^\circ$). This unit cell is consistent with the aristotype unit cell of a $(0, \frac{1}{2}, z)$ stacked $n = 2$ layered perovskite.^{71,72,85} However, on close inspection a series of small diffraction peaks were observed as shown in Figure 5.5, which could be indexed using an expanded unit cell ($a = 7.694 \text{ \AA}$, $b = 3.840 \text{ \AA}$, $c = 22.193 \text{ \AA}$, $\gamma = 90.80^\circ$) which is an $a' \approx 2a$, $b' \approx b$, $c' \approx c$ geometric expansion of the aristotype unit cell. Extinction conditions of the diffraction pattern were consistent with an A-centred unit cell. Particle-size dependent SHG data (Figure 5.1) reveal that KBiNb₂O₇ has an SHG activity approximately 1.5 times that of KDP, and thus has a non-centrosymmetric crystal structure.

Combining the information above, we can deduce that KBiNb₂O₇ adopts a crystal structure described in an A-centred, non-centrosymmetric monoclinic space group. This gives 3 candidates: *A11a* (#9), *A11m* (#8) and *A112* (#5) with unit cell settings chosen to preserve the z -axis as the stacking direction. Structural models were constructed in these three space groups and refined against the synchrotron X-ray diffraction data collected at room temperature. The

diffraction data show a strong hkl -dependent peak shape as shown in Figure 5.2, which arises from stacking faults in the material, which is discussed later in the chapter. At this stage of the structural refinement, no attempt was made to include stacking faults in the structural model. Fitting parameters obtained from the structure refinement of three polar space group models against the synchrotron X-ray data were comparable. As an example, the observed, calculated and difference plots from the structure refinement of $A11m$ model against the synchrotron X-ray diffraction data are shown in Figure 5.3.

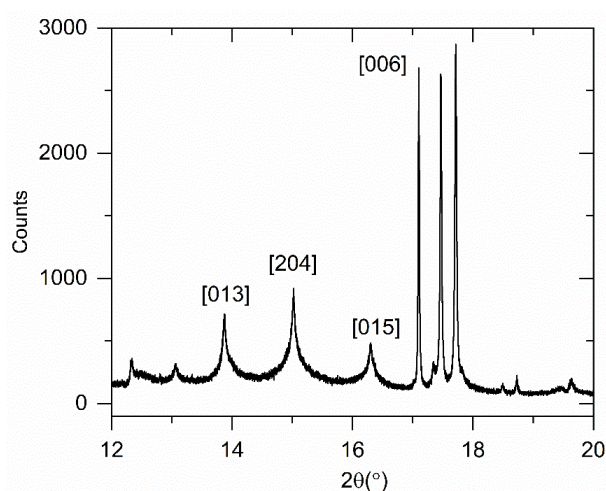


Figure 5.2. A section of the SXRD data collected from KBiNb_2O_7 which exhibits a strongly hkl -dependent peak width, indicative of stacking faults.

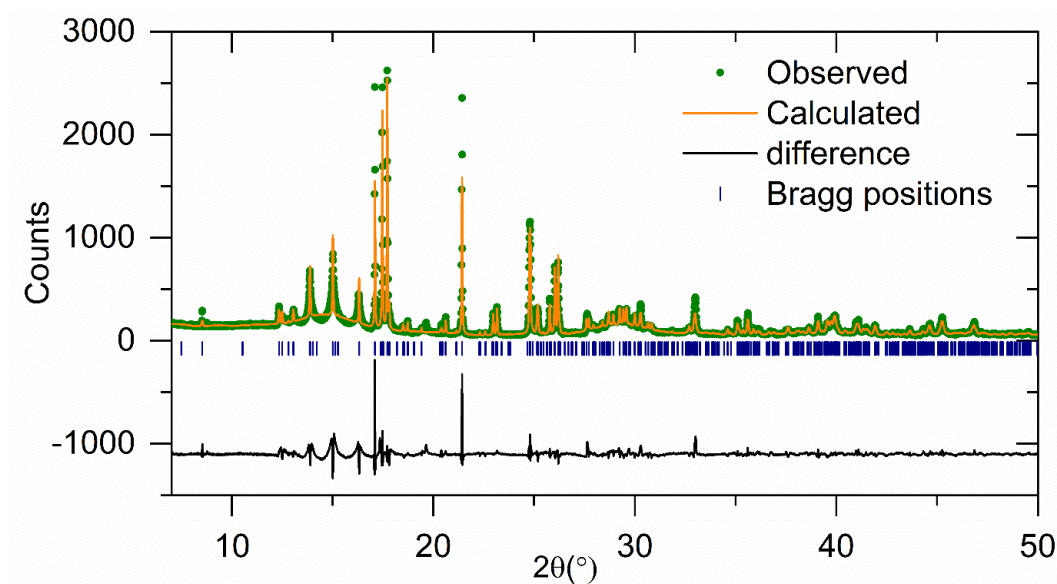


Figure 5.3. Observed, calculated and difference plots from the structure refinement of the $A11m$ model of KBiNb_2O_7 against the SXRD data collected at room temperature.

5.3.3.2 Electron diffraction data

Electron diffraction (ED) and imaging data presented in this chapter were collected by Maria Batuk and Prof. Joke Hadermann at the University of Antwerp. ED patterns were acquired from an FEI Tecnai transmission electron microscope operated at 200 kV. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were acquired using a probe aberration-corrected FEI Titan 80-300 “cubed” microscope operated at 300 kV. The electron diffraction patterns collected from the KBiNb_2O_7 sample are shown in Figure 5.4. The diffuse streaks along the c^* -axis indicate the presence of stacking faults in the crystal. the presence of the $[10l]$ reflections in Figure 5.4(a) and the $[1-1l]$ reflections in Figure 5.4(b) justifies the necessity to use $a' \approx 2a$ lattice parameter consistent with the lattice parameters obtained from SXRD and neutron diffraction data (shown later). The reflection conditions obtained from the ED patterns are as follows hkl : $k+l=2n$; $h0l$: $l=2n$; $0kl$: $k+l=2n$; $h00$; $0k0$: $k=2n$; $00l$: $l=2n$. These reflection conditions are consistent with an A -centred unit cell.

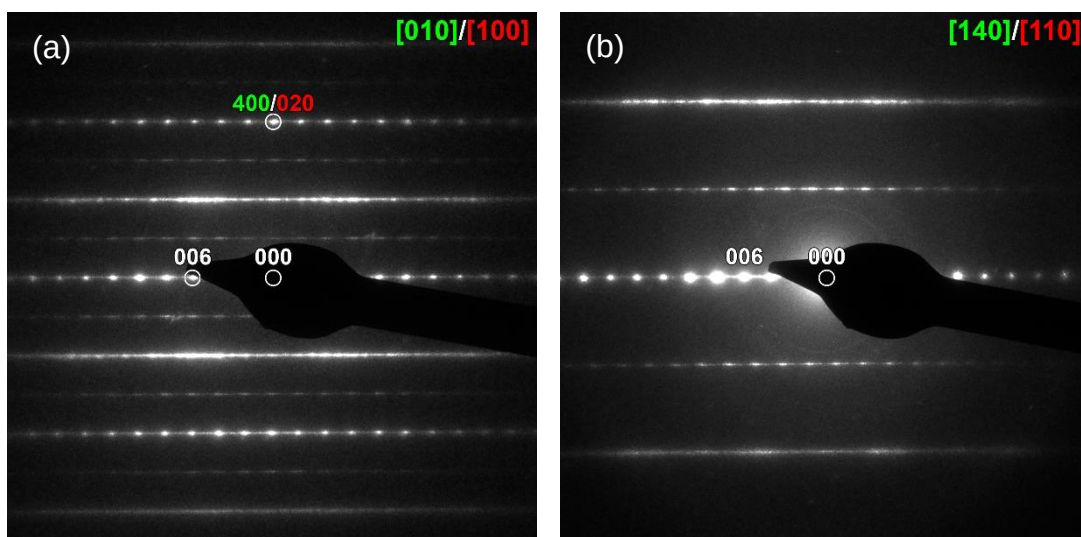


Figure 5.4. Experimental electron diffraction patterns of the KBiNb_2O_7 sample. Patterns in (a) and (b) are intergrowths of two zones indicated in red and green. Indices for the zone is given in the corresponding colour.

5.3.3.3 Neutron diffraction data

High-resolution neutron diffraction data collected from KBiNb_2O_7 could be initially indexed using a unit cell which is consistent with the aristotype unit cell of a $(0, \frac{1}{2}, z)$ stacked $n = 2$ layered perovskites. However, on close inspection, a series of small diffraction peaks were observed as shown in Figure 5.5 which could be indexed using an expanded unit cell ($a = 7.694 \text{ \AA}$, $b = 3.840 \text{ \AA}$, $c = 22.193 \text{ \AA}$, $\gamma = 90.80^\circ$) which is an $a' \approx 2a$, $b' \approx b$, $c' \approx c$ geometric expansion of the aristotype unit cell. The extinction conditions are consistent with an A -centred unit cell. Combining the information above, three noncentrosymmetric models were constructed in $A11a$, $A11m$ and $A112$ space groups and refined against the neutron diffraction data. The diffraction pattern shows a strong hkl -dependent peak shape especially in the high d -spacing of 90° bank. They originate from the stacking faults in the structure as discussed later in the chapter. No attempt was made to include a stacking fault model in the neutron data to account for variable peak width; instead, we have used spherical harmonics of 6th order⁷⁷ to get a better fitting. This made significant improvement of the refinement statistics although relatively poor fitting is still observed at high d -spacing of 90° bank as shown in Figure 5.6. The fitting parameters obtained from the structure refinement of these three models against the neutron diffraction data are listed in Table 5.1.

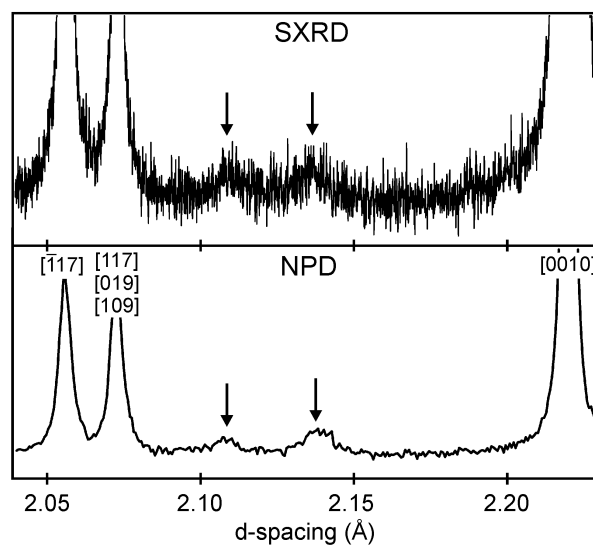


Figure 5.5. Selected regions of SXRD (top) and NPD (bottom) data collected from KBiNb_2O_7 at room temperature, indexed using the small $a = 3.847 \text{ \AA}$, $b = 3.840 \text{ \AA}$, $c = 22.193 \text{ \AA}$, $\gamma = 90.80^\circ$ -unit cell. Arrows indicate the peaks which require the doubling of a lattice parameter.

Space group	no of parameters	R _p (%)	wR _p (%)
<i>A11a</i>	126	7.69	8.50
<i>A11m</i>	128	7.54	8.43
<i>A112</i>	102	8.72	10.24

Table 5.1. Fitting parameters from the structural refinement of different A-centred, monoclinic structural models of KBiNb₂O₇ against the NPD data collected at room temperature.

A comparison of fitting statistics reveals that the *A112* model fits the data poorly ($wR_p = 10.2$) and yields a chemically implausible structure for KBiNb₂O₇, so this model was rejected. The fitting parameters from the refinement of *A11m* ($wR_p = 8.43$) and *A11a* ($wR_p = 8.50$) symmetry models are comparable as shown in Table 5.1. There are twice as many K-sites in the structures that are required to satisfy the KBiNb₂O₇ stoichiometry, so the K⁺ ions can be arranged in either ordered or disordered configurations. Occupancies of the K-sites were refined within the constraint of the total occupancy being one, to check if the K⁺ ions are ordered. The refined occupancies of both the K sites were close to 0.5, which excludes any possibility of a K-ordered structure.

There are two Bi sites in the *A11m* model where the atom is allowed to move in *x* and *y* coordinates but the *z* coordinates are fixed at 0. On the other hand, there is only one Bi site in the *A11a* space group model which is a general position that means the Bi atom is free to move in *x*, *y* and *z*, all three coordinates. But the refinement of the *A11a* model shows that the *z*-coordinate of the bismuth site stays at zero within errors after refinement as shown in Table 5.2. There are two equivalent oxygen sites (O1 and O2) in the *A11m* structure for only one oxygen in *A11a*. Again, the *z*-coordinates of O1 and O2 in *A11m* are fixed while O1 in *A11a* is a general position. Similar to the Bi site, the O1 site in the *A11a* model also stays at zero within errors after structure refinement as shown in Table 5.2. This is consistent with the presence of a mirror plane perpendicular to the *z*-axis at this position.

Bi and O both are highly sensitive with respect to neutron diffraction (coh b for O is 5.803 and coh b for Bi is 8.532), so even small displacements from the general position of these atoms should be detectable with the help of neutrons. As both Bi and O1 practically stay at $z = 0$ within error, despite being in general positions; suggests that the atoms are indeed at $z = 0$, which is the case for the $A11m$ structure model. Hence, the $A11m$ space group model was considered to be a better symmetry description of the KBiNb_2O_7 phase than the $A11a$ structure model.

Refined structures were also examined to see if they were chemically reasonable. An analysis of the bond valence sums (BVS)⁶⁵ revealed the $A11m$ model yielded more chemically realistic values for the K^+ , Nb^{5+} and Bi^{3+} cations (Table 5.2) than the $A11a$ model. These observations indicate that the $A11m$ model is a better choice for the room temperature structure of KBiNb_2O_7 than the $A11a$ symmetry model. Full details of the refined $A11m$ model of KBiNb_2O_7 are given in Table 5.3, with selected bond lengths in Table 5.4. The observed, calculated and difference plots from the structure refinement of KBiNb_2O_7 are shown in Figure 5.6.

Atom	x	y	z	BVS
<i>A11a</i>				
Bi1	0.988(3)	0.006(6)	0.9994(12)	+2.47
Nb1	0.210(3)	0.023(6)	0.3892(5)	+5.96
Nb2	0.703(2)	0.059(5)	0.3911(4)	+4.24
O1	0.759(2)	0.543(4)	0.9995(8)	
<i>A11m</i>				
Bi1	0.0204(1)	0.066(4)	0	+2.58
Bi2	0.5205(1)	0.932(4)	0	+2.61
Nb1	0.251(1)	0.001(1)	0.3958(1)	+5.22
Nb2	0.750(1)	0.999(1)	0.3957(1)	+5.12
O1	0.214(1)	0.524(4)	0	
O2	0.713(1)	0.475(4)	0	

Table 5.2. Atomic coordinates and bond valence sums of selected atoms after structural refinements of the models described in $A11a$ and $A11m$ space groups.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	B _{iso} (Å ²)
K1	4 <i>b</i>	0.003(3)	0.967(6)	0.1963(6)	½	3.2(1)
K2	4 <i>b</i>	0.501(3)	0.966(5)	0.1965(5)	½	3.2(1)
Bi1	2 <i>a</i>	0.0204(1)	0.066(4)	0	1	6.3(4)
Bi2	2 <i>a</i>	0.5205(1)	0.932(4)	0	1	6.3(4)
Nb1	4 <i>b</i>	0.251(1)	0.001(1)	0.3958(1)	1	4.2(1)
Nb2	4 <i>b</i>	0.750(1)	0.999(1)	0.3957(1)	1	4.2(1)
O1	2 <i>a</i>	0.214(1)	0.524(4)	0	1	5.3(2)
O2	2 <i>a</i>	0.713(1)	0.475(4)	0	1	5.3(2)
O3	4 <i>b</i>	0.001(1)	0.962(5)	0.4130(6)	1	6.8(3)
O4	4 <i>b</i>	0.499(1)	0.038(5)	0.4132(5)	1	6.8(3)
O5	4 <i>b</i>	0.275(1)	0.009(4)	0.3160(3)	1	5.9(2)
O6	4 <i>b</i>	0.774(1)	0.008(4)	0.3159(3)	1	5.9(2)
O7	4 <i>b</i>	0.2907(9)	0.993(1)	0.0889(2)	1	4.3(2)
O8	4 <i>b</i>	0.7905(9)	0.994(1)	0.0888(2)	1	4.3(2)
KBiNb₂O₇ – space group A11<i>m</i> (#8) <i>a</i> = 7.6735(3) Å, <i>b</i> = 3.8437(2) Å, <i>c</i> = 22.1699(9) Å, <i>γ</i> = 90.806(1), volume = 653.83(5) Å³ Formula weight = 545.89 g mol⁻¹, <i>Z</i> = 4 Radiation source: Neutron Time of Flight Temperature: 298 K R_p = 7.54 %, wR_p = 8.43 %						

Table 5.3. Parameters from the structural refinement of KBiNb₂O₇ against NPD data collected at room temperature.

Cation	Anion	Bond length (Å)	BVS
Nb(1)	O(1)	2.329(3)	Nb+5.22
	O(3)	1.960(11)	
	O(4)	1.945(11)	
	O(5)	1.779(7)	
	O(7)	1.941(6)	
	O(7)	2.009(6)	
Nb(2)	O(2)	2.331(3)	Nb+5.12
	O(3)	1.971(11)	

	O(4)	1.973(11)	
	O(5)	1.779(7)	
	O(8)	1.954(6)	
	O(8)	2.000(6)	
Bi(1)	O(1)	2.292(20)	Bi+2.58
	O(1)	2.574(20)	
	O(2)	2.853(18)	
	O(2)	3.252(19)	
	O(3) × 2	2.463(18)	
	O(3) × 2	3.020(21)	
	O(7) × 2	2.878(12)	
	O(8) × 2	2.655(11)	
Bi(2)	O(1)	2.804(18)	Bi+2.61
	O(1)	3.296(19)	
	O(2)	2.311(20)	
	O(2)	2.540(20)	
	O(4) × 2	2.453(18)	
	O(4) × 2	3.028(20)	
	O(7) × 2	2.657(11)	
	O(8) × 2	2.866(12)	
K(1)	O(3)	3.081(24)	K+1.27
	O(3)	3.105(24)	
	O(5)	2.763(26)	
	O(5)	2.941(26)	
	O(5)	3.379(19)	
	O(6)	2.487(26)	
	O(6)	2.755(26)	
	O(6)	3.186(18)	
	O(7)	3.248(19)	
	O(8)	2.890(18)	
K(2)	O(4)	2.936(20)	K+1.30
	O(4)	3.279(22)	

	O(5)	2.467(24)	
	O(5)	2.746(25)	
	O(5)	3.172(17)	
	O(6)	2.769(25)	
	O(6)	2.946(24)	
	O(6)	3.378(18)	
	O(7)	2.883(17)	
	O(8)	3.262(19)	

Table 5.4. Selected bond lengths from the refined structure of KBiNb_2O_7

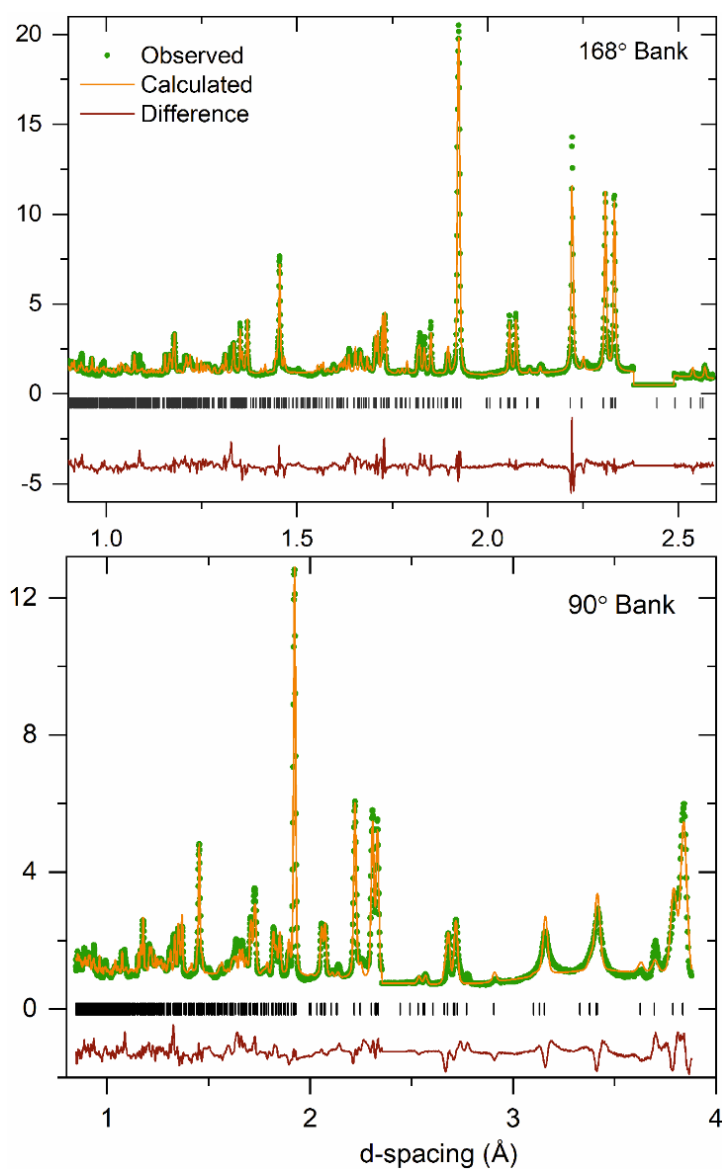


Figure 5.6. Observed, calculated and difference plots from the structural refinement of KBiNb_2O_7 against NPD data collected at room temperature. Excluded regions remove contributions from an unknown (possibly BiNbO_4) impurity.

5.3.4 Stacking fault characterisation of KBiNb_2O_7

Very strong hkl -dependent peak broadening observed in the SXRD and NPD data, and extensive streaking parallel to the c^* direction in the ED data suggest that the KBiNb_2O_7 sample exhibits some variety of stacking fault disorder. To investigate the nature of stacking fault disorder, a series of HAAD-STEM images were collected.

The aristotype $n = 2$, $(0, \frac{1}{2}, z)$ layered perovskite structure adopted by the KBiNb_2O_7 phase can be considered as a hybrid of the $(0,0, z)$ stacked Dion-Jacobson framework and the $(\frac{1}{2}, \frac{1}{2}, z)$ stacked Ruddlesden-Popper framework. HAADF-STEM images collected from KBiNb_2O_7 show that the BiNb_2O_7 perovskite sheets in KBiNb_2O_7 adopt an evenly spaced stacking sequence. However, close inspection shows that the stacking exhibits frequent ‘faults’ in which the $(0, \frac{1}{2}, z)$ stacking changes to a $(\frac{1}{2}, 0, z)$ and *vice versa*, as shown in Figure 5.7. This type of stacking fault corresponds to a switching of the x - and y -axes in the aristotype structure, and from the HAAD-STEM images, these faults appear to be prevalent throughout the KBiNb_2O_7 sample measured.

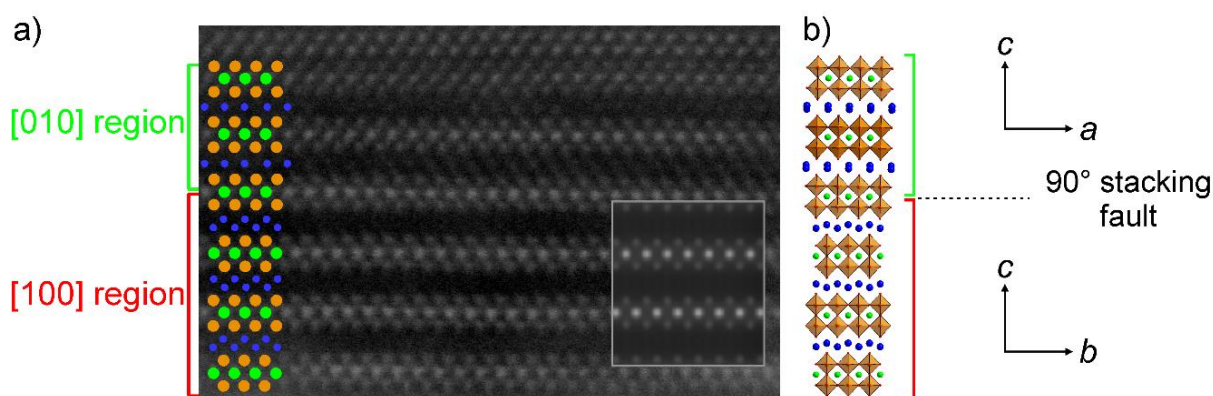


Figure 5.7. a) HAADF-STEM image collected from KBiNb_2O_7 . The green bracket shows the stacking of BiNb_2O_7 sheets corresponding to the $[010]$ zone. The red bracket shows stacking corresponding to the $[100]$ zone. Superimposed spheres correspond to Bi (green), Nb (orange) and K (blue) atoms. Inset shows simulated $[100]$ image of KBiNb_2O_7 . b) Representation of the 90° stacking fault in KBiNb_2O_7 .

In order to account for the strongly hkl -dependent peak widths observed in the diffraction patterns collected from KBiNb_2O_7 and to quantify the frequency of the ‘axis-switch’ stacking

faults, we have performed a series of Rietveld refinements that include a stacking fault model as implemented in the Topas (V6) software.^{61,86}

A model describing a $\text{K}_2\text{BiNb}_2\text{O}_7$ block (labelled layer A) was constructed based on the atomic coordinates of the $A11m$ model obtained from refinement against neutron diffraction data (Table 5.3). To facilitate the calculation, the area of the ab -plane of the model layer was half that of the refined $A11m$ model, and described by lattice parameters $a' = a/2$, $b' = b$, with the alternating displacement of the Bi cations parallel to the y -axis (which leads to the original doubling the a lattice parameter) neglected in the model. Thus, the model block contains 1 bismuth, 2 niobium, 2 potassium and 7 oxygen atom sites, with the locations of the atoms described using the $P1$ space group (i.e. no symmetry). A second model $\text{K}_2\text{BiNb}_2\text{O}_7$ block (labelled layer B) was constructed by taking the model of layer A and switching the x - and y -coordinates (i.e. rotating the model by 90° around the z -axis).

Supercells were then constructed by stacking the model layers into large arrays. As shown in Figure 5.8, if layer A is stacked on itself repeatedly, such that there is a $(0, \frac{1}{2}, c/2)$ shift in the origin of the blocks between adjacent layers, then a ‘perfect’ unfaulted structure for KBiNb_2O_7 is described. Likewise, if layer B is stacked on itself repeatedly, such that there is a $(\frac{1}{2}, 0, c/2)$ shift in the origin of the blocks between adjacent layers, then a ‘perfect’ unfaulted structure for KBiNb_2O_7 is described, with the x and y -axes exchanged compared to the all-layer-A stack. However, if an A layer is followed by a B layer (Figure 5.8) such that there is a $(0, \frac{1}{2}, c/2)$ shift in the origin of the blocks between adjacent layers, or a B layer is followed by an A layer with a $(\frac{1}{2}, 0, c/2)$ shift in the origin of the blocks between adjacent layers then the x and y -axes of the stack will be switched. Thus, by intermixing blocks of layer A and layer B, arrays containing ‘axis-switch’ faults can be constructed.

Stacking faults were introduced into models using the parameter “ P ” which takes values between 0 and 1. The value of P describes the probability that an A layer will be followed by

another A layer stacked in a $(0, \frac{1}{2}, c/2)$ manner, and $1-P$ describes the probability that an A layer will be followed by a B layer stacked in a $(0, \frac{1}{2}, c/2)$ manner. Similarly, P also describes the probability that a B layer will be followed by another B layer stacked in a $(\frac{1}{2}, 0, c/2)$ manner, and $1-P$ describes the probability that a B layer will be followed by an A layer stacked in a $(0, \frac{1}{2}, c/2)$ manner. Thus, it can be seen that the concentration of axis-switch faults is equant to $1-P$, a value which we more clearly described as FF , the fault frequency.

Stacking fault models with supercells of finite size were constructed by stacking $N_v = 1000$ KBiNb_2O_7 blocks. To more accurately represent the probabilistic nature of stacking faults, an average intensity from $N_{str} = 100$ crystals was calculated. The peak shape parameters for refinement were fixed after the first refinement with $P = 1$. A series of models with different values of P were refined against the SXRD data, whilst keeping the atomic coordinates of the model static, to find the value of FF which best fitted the data. The introduction of this fault description led to a great improvement in the fit to the data as shown in Figure 5.9. As shown in Figure 5.10, the best fit to the SXRD data was obtained with a value of $FF = 0.09$, which corresponds to a 9% chance of a stacking fault occurring between any particular pair of perovskite double sheets. This faulting probability appears to be in line with the number of faults observed in the HAADF-STEM images.

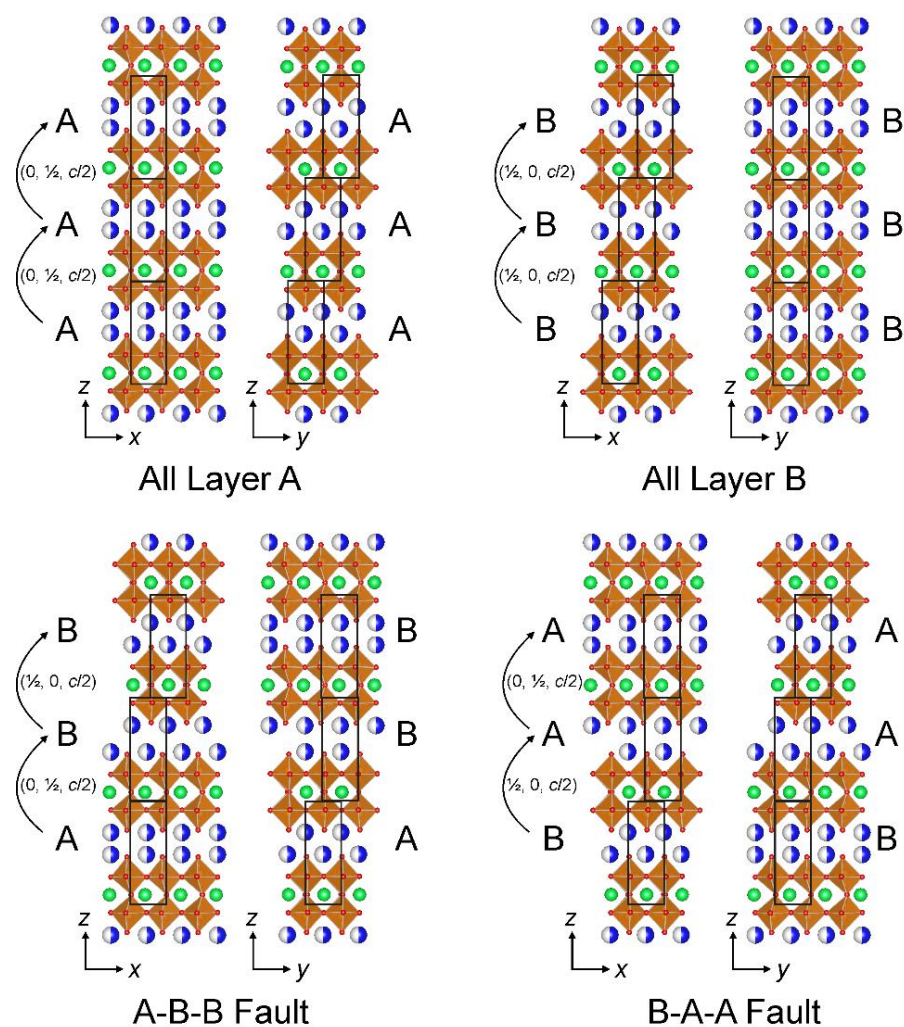


Figure 5.8. Schematic diagram showing the stacking of A-layers and B-layers to yield ‘perfect’, unfaulted structures, and the combination of A-layers and B-layers to produce stacks with ‘axis-switch’ faults. Black rectangles indicate the boundaries of a single block.

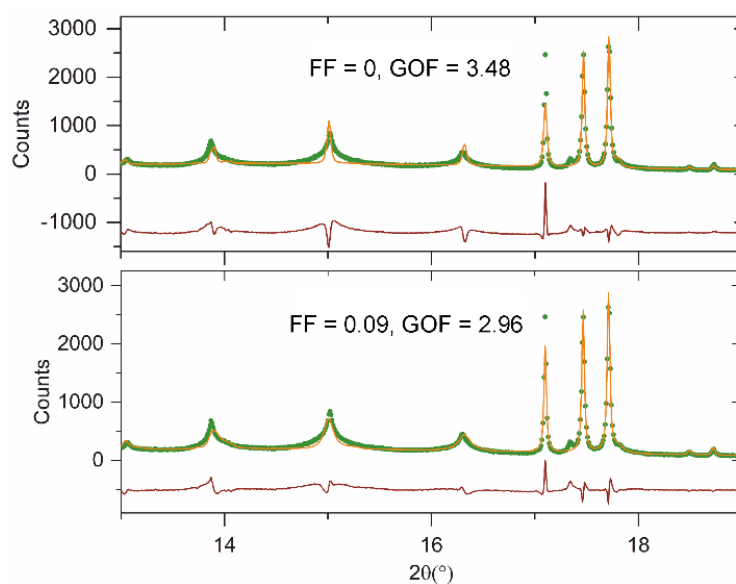


Figure 5.9. Observed calculated and difference plots from the structural refinement of KBiNb_2O_7 (bottom) with and (top) without 90° stacking fault description.

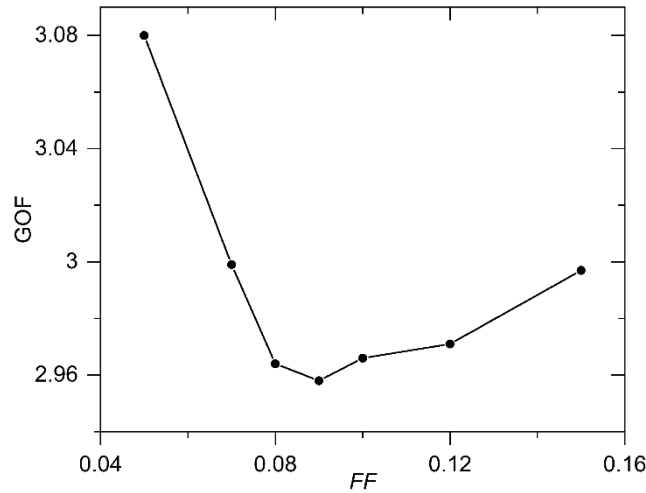


Figure 5.10. Plot of Goodness of fit (GOF) parameter against Fault Frequency (FF) as determined by fitting the synchrotron X-ray diffraction data.

5.4 Discussion

The size of the interlayer A' -cations defines the stacking pattern of the ANb_2O_7 double perovskite sheets in $A'ANb_2O_7$ ($A' = Cs, Rb, Li, Na, K$; $A = Nd, Bi$) layered phases. When the large Cs^+/Rb^+ cations are exchanged for much smaller Na^+/Li^+ cations; the $(0, 0, z)$ stacking of Dion-Jacobson phases are changed to the $(\frac{1}{2}, \frac{1}{2}, z)$ stacking of Ruddlesden-Popper phase. This change in stacking pattern is accompanied by a change in coordination number of the A' -cation; from 8-coordinate sites in the Dion-Jacobson framework to 4-coordinate sites in the Ruddlesden-Popper framework. The intermediate ionic radius of K^+ cation drives the ANb_2O_7 sheets to adopt a $(0, \frac{1}{2}, z)$ stacking. Although the stacking pattern of $KNdNb_2O_7$ and $KBiNb_2O_7$ are the same; the K^+ ions in the Nd-phase occupy a 6-coordinated trigonal-prismatic site but the K^+ ions in the Bi-phase occupy 10-coordinate sites as shown in Figure 5.12.

The $Im2m$ polar structure of $KNdNb_2O_7$ can be derived from the aristotype $Ammm$ structure of $n = 2$ $(0, \frac{1}{2}, z)$ stacked framework by sequential application of two distortion modes: The T_1^+ mode, which describes the $a^0b^+c^0/a^0-b^+c^0$ rotation of NbO_6 octahedra and a Γ_4^- polar distortion. The cooperative rotation of NbO_6 octahedra along the b -axis requires the a -lattice parameter to be doubled with respect to its aristotype structure. The $A11m$ structure of $KBiNb_2O_7$ does not

consist of any rotation or tilting of NbO_6 octahedra, although the a -lattice parameter is twice that of the aristotype structure. Deconvolution of the $A11m$ structure of KBiNb_2O_7 reveals that seven distortion modes are allowed on descending in symmetry from the aristotype $Ammm$ structure, as shown in Table 5.6. But only three of them have significant amplitudes. These are two polar distortion modes which represent as Γ_2^- and Γ_3^- , and another distortion mode which transforms as Z_3^- . Z_3^- irreducible representation displaces the atoms in the Bi1 and Bi2 sites in an opposite direction along the y -axis which leads to a zigzag arrangement of the Bi^{3+} cations. The zig-zag arrangement of Bi^{3+} is accompanied by another zig-zag arrangement of a pair of oxygen sites: O3 and O4, again, as a result of the Z_3^- distortion mode. In this case, the O3 and O4 move in an opposite direction to Bi1 and Bi2 respectively as shown in Figure 5.11 and as indicated by the opposite sign of Z_3^- distortion mode magnitudes for the Bi-sites and O-sites in Table 5.6.

Cooperative tilting and rotation of BO_6 octahedra in ABO_3 perovskites and related layered phases originate as a result of size mismatch between the A - and B -site cations, as cooperative tilting of BO_6 octahedra can shorten the A -O bond length without changing the B -O bond length. In ABO_3 perovskite structure, the size mismatch between the A -site and B -site cations can be quantified using the structural tolerance factor $t = \langle A-O \rangle / \sqrt{2} \langle B-O \rangle$, where a small value of t indicates a large mismatch between A - and B -site cations hence will result in a more tilted structure. The tolerance factor of a compound can either be calculated from the tabulated values of the ionic radii of A and B -cations or by extracting the average A -O and B -O bond lengths from the experimental crystal structures. Table 5.5 shows that the tolerance factor of the KNdNb_2O_7 phase is smaller than the KBiNb_2O_7 phase as calculated using both methods, indicating that the Nd-phase will have a more distorted structure than the Bi-one. This is somewhat true provided that the KNdNb_2O_7 phase exhibits $a^0b^+c^0/a^0-b^+c^0$ rotation of NbO_6 octahedra whereas the NbO_6 octahedra of the Bi-phase do not have any tilting or rotation. As

the cooperative rotation of BO_6 octahedra occurs to optimize the A-O bonding in the ABO_3 perovskite structure, evidently the bond valence sums of Nd sites (2.894 and 2.996) in the $KNdNb_2O_7$ structure are close to the ideal value of 3, whereas the bond valence sums of the Bi sites in the $KBiNb_2O_7$ structure have non-ideal values of 2.58 and 2.61. We must note that the idea of bond valence sum originates from the structures of the thermodynamically stable phases, hence the atomic sites in a topochemically prepared kinetic phase such as $KBiNb_2O_7$ do not necessarily have to satisfy an optimal bond valence sum value.

Close examination of the structures of $RbANb_2O_7$ and $LiANb_2O_7$ reveals that the A^{3+} cations in both structures reside on a 12 coordinate site with $..m$ point symmetry. These low symmetry coordinate sites are compatible with the asymmetric nature of the $6s^2 Bi^{3+}$ ion. Thus, no change in structure is observed when Nd^{3+} is replaced by Bi^{3+} . On the other hand, the Nd^{3+} in the $P4_2/mnm$ structure of $NaNdNb_2O_7$ resides on a $4f$ site with $m.2m$ point symmetry. This high symmetry $(x, x, 0)$ crystallographic site is not compatible with the expected asymmetric coordination geometry of Bi^{3+} cation. Hence on substituting Nd^{3+} by Bi^{3+} , the NbO_6 octahedra tilt in such a way that the Bi^{3+} cation symmetry is lowered to a general position in the Na-ordered $P2_12_12_1$ structure. Similarly, the Nd^{3+} cations in the $Im2m$ structure of the $KNdNb_2O_7$ phase reside on $2a$ and $2b$ sites with $mm2$ point symmetry. This high symmetry $((0, y, 0)$ and $(0.5, y, 0))$ crystallographic sites are not compatible with the asymmetric coordination of Bi^{3+} . Hence, on substituting the Nd^{3+} by Bi^{3+} the site symmetry lowers to $m(x, y, 0)$ in the $A11m$ structure of $KBiNb_2O_7$.

If we consider the distortion in the AO_{12} polyhedra of the $KANb_2O_7$ phases ($A = Nd, Bi$), the BiO_{12} polyhedra are more distorted than the NdO_{12} polyhedra as indicated by a larger distortion index (D)⁸³ and quadratic elongation ($\langle \lambda \rangle$)⁸⁷ of the BiO_{12} polyhedra than the NdO_{12} polyhedra ($D_{Bi} = 0.085$, $D_{Nd} = 0.058$, $\langle \lambda_{Bi} \rangle = 1.047$, $\langle \lambda_{Nd} \rangle = 1.033$); which could be attributed to the non-spherical nature of $6s^2$ electronic configuration of the Bi^{3+} cation. A significant fraction of the

polar distortion modes: Γ_2^- and Γ_3^- are contributed by the displacement of Bi^{3+} ions as shown in Table 5.6. On the other hand, Nd^{3+} has almost no contribution towards the polar distortion in the $Im2m$ structure of KNdNb_2O_7 as shown in Table 5.7, indicating $6s^2$ electronic configuration of Bi^{3+} cation drives the polarity in the $A11m$ structure of KBiNb_2O_7 .

The presence of $(\frac{1}{2}, 0, z)$ stacked layers in a majorly $(0, \frac{1}{2}, z)$ stacked structure as faults indicates that both types of stacking are energetically accessible at room temperature, which could be a consequence of the absence of any kind of NbO_6 octahedral rotation to preferentially stabilize one kind of stacking of the BiNb_2O_7 double-layer perovskite sheets over the other. As a result of this 90° twinning, the difference between b and a' ($= a/2$) lattice parameters is significantly smaller in the KBiNb_2O_7 phase than the same difference in the Nd-phase (0.007 in the KBiNb_2O_7 phase against 0.0163 in the KNdNb_2O_7 phase). This is because the axis switch stacking fault along with large orthorhombicity in the lattice parameters will introduce a large strain in the structure.

	Tolerance factor	
	Ionic radii	Bond length
KNdNb_2O_7	0.925	0.964
KBiNb_2O_7	0.964	0.973

Table 5.5. Tolerance factor of KNdNb_2O_7 and KBiNb_2O_7 from ionic radii and bond length.

KBiNb_2O_7			
Distortion mode	A_s	A_p	$d_{\max}$ (Å)
$[0,0,0] \Gamma_1^+ [\text{K1:i:dsp}]A1(a)$	-1.70496	-1.20559	0.85248
$[0,0,0] \Gamma_1^+ [\text{Nb1:j:dsp}]A1(a)$	0.00666	0.00471	0.00333
$[0,0,0] \Gamma_1^+ [\text{O2:i:dsp}]A1(a)$	-0.05772	-0.04081	0.02886
$[0,0,0] \Gamma_1^+ [\text{O3:j:dsp}]A1(a)$	-0.07326	-0.05180	0.03663
$[0,0,0] \Gamma_1^+ [\text{O4:j:dsp}]A1(a)$	-0.00222	-0.00157	0.00111
$[0,0,0] \Gamma_1^+ \text{ all}$	1.70752	1.20740	
$[0,0,0] \Gamma_2^- [\text{K1:i:dsp}]B1(a)$	0.00000	0.00000	0.00000

[0,0,0] Γ_2^- [Bi1:a:dsp]B1u(a)	0.20091	0.14206	0.14206
[0,0,0] Γ_2^- [Nb1:j:dsp]B1(a)	-0.02310	-0.01633	0.01155
[0,0,0] Γ_2^- [O1:c:dsp]B1u(a)	-0.41924	-0.29645	0.29645
[0,0,0] Γ_2^- [O2:i:dsp]B1(a)	-0.03080	-0.02178	0.01540
[0,0,0] Γ_2^- [O3:j:dsp]B1(a)	0.34650	0.24501	0.17325
[0,0,0] Γ_2^- [O4:j:dsp]B1(a)	0.59444	0.42033	0.29722
[0,0,0] Γ_2^- all	0.83128	0.58781	
[0,0,0] Γ_3^- [K1:i:dsp]B2(a)	0.00000	0.00000	0.00000
[0,0,0] Γ_3^- [Bi1:a:dsp]B3u(a)	0.17879	0.12642	0.12642
[0,0,0] Γ_3^- [Nb1:j:dsp]B2(a)	0.26063	0.18429	0.13031
[0,0,0] Γ_3^- [O1:c:dsp]B3u(a)	0.18154	0.12837	0.12837
[0,0,0] Γ_3^- [O2:i:dsp]B2(a)	0.26063	0.18429	0.13031
[0,0,0] Γ_3^- [O3:j:dsp]B2(a)	0.32676	0.23105	0.16338
[0,0,0] Γ_3^- [O4:j:dsp]B2(a)	0.21006	0.14853	0.10503
[0,0,0] Γ_3^- all	0.59302	0.41933	
[1/2,0,0] Z_1^+ [K1:i:dsp]A1(a)	0.00444	0.00314	0.00222
[1/2,0,0] Z_1^+ [Nb1:j:dsp]B1(a)	-0.00770	-0.00544	0.00385
[1/2,0,0] Z_1^+ [O1:c:dsp]B1u(a)	-0.00544	-0.00385	0.00385
[1/2,0,0] Z_1^+ [O2:i:dsp]A1(a)	0.00444	0.00314	0.00222
[1/2,0,0] Z_1^+ [O3:j:dsp]B1(a)	-0.00770	-0.00544	0.00385
[1/2,0,0] Z_1^+ [O4:j:dsp]B1(a)	-0.00154	-0.00109	0.00077
[1/2,0,0] Z_1^+ all	0.01378	0.00975	
[1/2,0,0] Z_4^+ [Nb1:j:dsp]B2(a)	-0.00778	-0.00550	0.00389
[1/2,0,0] Z_4^+ [O1:c:dsp]B3u(a)	-0.13478	-0.09530	0.09530
[1/2,0,0] Z_4^+ [O3:j:dsp]B2(a)	-0.00389	-0.00275	0.00194
[1/2,0,0] Z_4^+ [O4:j:dsp]B2(a)	0.00389	0.00275	0.00194
[1/2,0,0] Z_4^+ all	0.13512	0.09554	

[1/2,0,0] Z_2^- [K1:i:dsp]B1(a)	-0.01540	-0.01089	0.00770
[1/2,0,0] Z_2^- [Bi1:a:dsp]B1u(a)	0.00054	0.00038	0.00038
[1/2,0,0] Z_2^- [Nb1:j:dsp]A1(a)	-0.00222	-0.00157	0.00111
[1/2,0,0] Z_2^- [O2:i:dsp]B1(a)	-0.01540	-0.01089	0.00770
[1/2,0,0] Z_2^- [O3:j:dsp]A1(a)	-0.00222	-0.00157	0.00111
[1/2,0,0] Z_2^- [O4:j:dsp]A1(a)	-0.00222	-0.00157	0.00111
[1/2,0,0] Z_2^- all	0.02212	0.01564	
[1/2,0,0] Z_3^- [K1:i:dsp]B2(a)	-0.00389	-0.00275	0.00194
[1/2,0,0] Z_3^- [Bi1:a:dsp]B3u(a)	-0.36859	-0.26063	0.26063
[1/2,0,0] Z_3^- [O2:i:dsp]B2(a)	0.29564	0.20905	0.14782
[1/2,0,0] Z_3^- all	0.47252	0.33412	

Table 5.6. Distortion mode amplitudes extracted from the refined structure of KBiNb_2O_7 (space group $A11m$) compared to the $Ammm$ symmetry aristotype structure.

KNdNb_2O_7			
Distortion mode	A_s	A_p	$d_{\max}$ (Å)
[0,0,0] Γ_1^+ [K1:i:dsp]A1(a)	0.09916	0.07012	0.04958
[0,0,0] Γ_1^+ [Nb1:j:dsp]A1(a)	0.12502	0.08840	0.06251
[0,0,0] Γ_1^+ [O2:i:dsp]A1(a)	-0.00216	-0.00153	0.00108
[0,0,0] Γ_1^+ [O3:j:dsp]A1(a)	0.01724	0.01219	0.00862
[0,0,0] Γ_1^+ [O4:j:dsp]A1(a)	-0.14227	-0.10060	0.07114
[0,0,0] Γ_1^+ all	0.21449	0.15167	
[0,0,0] Γ_3^- [K1:i:dsp]B2(a)	0.00000	0.00000	0.00000
[0,0,0] Γ_3^- [Nd1:a:dsp]B3u(a)	0.04106	0.02903	0.02903
[0,0,0] Γ_3^- [Nb1:j:dsp]B2(a)	0.14709	0.10401	0.07355
[0,0,0] Γ_3^- [O1:c:dsp]B3u(a)	0.48940	0.34606	0.34606
[0,0,0] Γ_3^- [O2:i:dsp]B2(a)	0.48115	0.34022	0.24058
[0,0,0] Γ_3^- [O3:j:dsp]B2(a)	0.28722	0.20310	0.14361
[0,0,0] Γ_3^- [O4:j:dsp]B2(a)	0.28645	0.20255	0.14323

[0,0,0] Γ_3^- all	0.81172	0.57397	
[1/2,1,0] T_1^+ [K1:i:dsp]A1(a)	0.00000	0.00000	0.00000
[1/2,1,0] T_1^+ [Nb1:j:dsp]B1(a)	-0.02313	-0.01636	0.01156
[1/2,1,0] T_1^+ [O1:c:dsp]B1u(a)	0.39467	0.27907	0.27907
[1/2,1,0] T_1^+ [O2:i:dsp]A1(a)	-0.53243	-0.37648	0.26622
[1/2,1,0] T_1^+ [O3:j:dsp]B1(a)	0.52423	0.37069	0.26211
[1/2,1,0] T_1^+ [O4:j:dsp]B1(a)	-0.18040	-0.12756	0.09020
[1/2,1,0] T_1^+ all	0.86437	0.61120	
[1/2,1,0] T_3^- [K1:i:dsp]B2(a)	0.03097	0.02190	0.01549
[1/2,1,0] T_3^- [Nd1:a:dsp]B3u(a)	0.00274	0.00194	0.00194
[1/2,1,0] T_3^- [O2:i:dsp]B2(a)	0.31858	0.22527	0.15929
[1/2,1,0] T_3^- all	0.32009	0.22634	

Table 5.7. Distortion mode amplitudes extracted from the refined structure of KNdNb_2O_7 (space group $Im2m$) compared to the $Ammm$ symmetry aristotype structure.

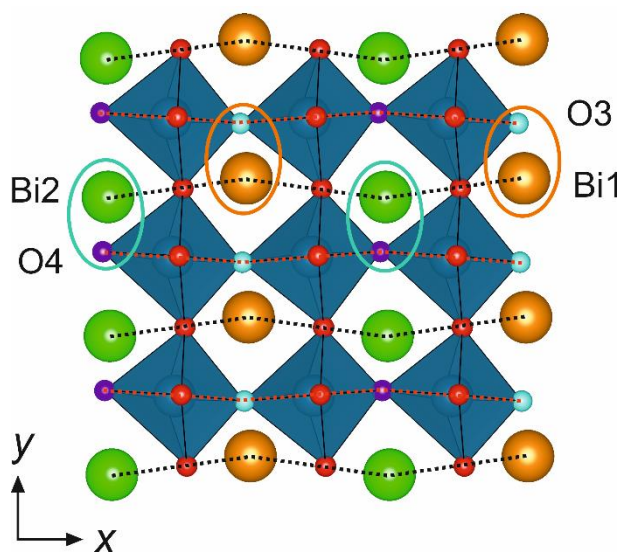


Figure 5.11. The zig-zag pattern of Bi1 and Bi2, which is accompanied by the zig-zag pattern of O3 and O4.

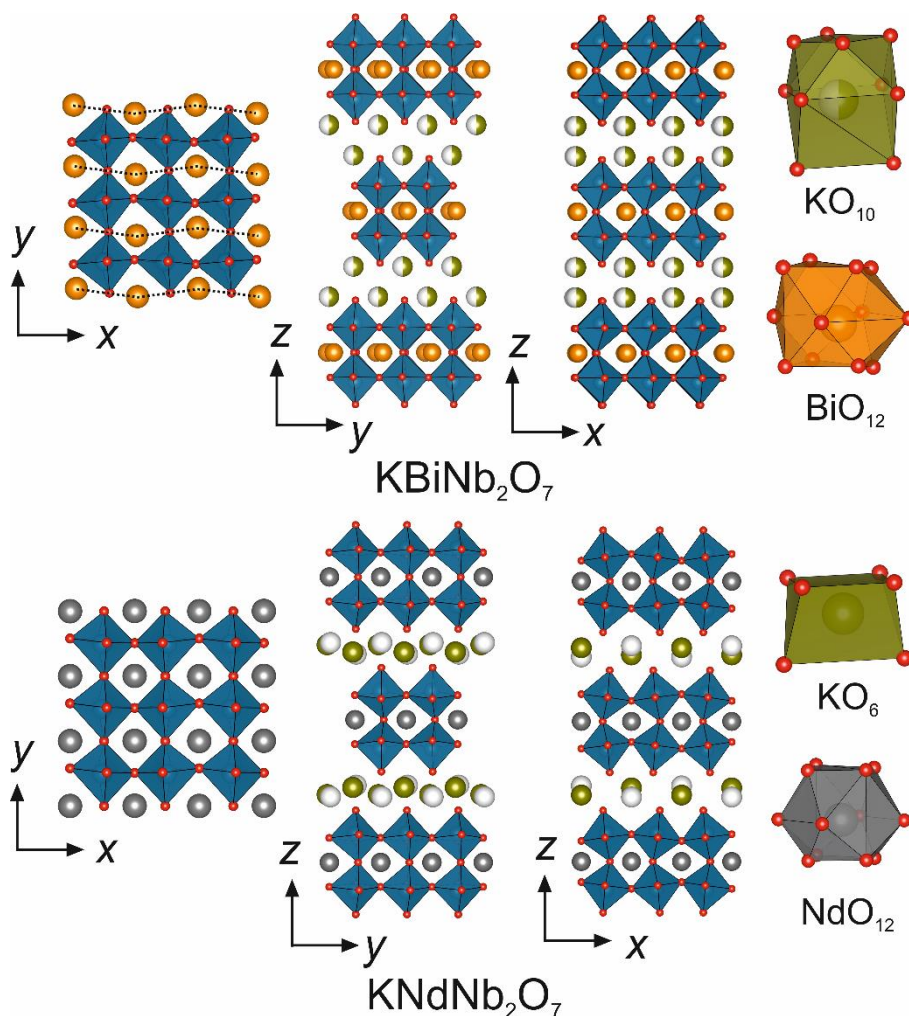


Figure 5.12. Structures, and A- and A'-site coordination environments of KBiNb_2O_7 and KNdNb_2O_7 .

5.5 Conclusion

Polycrystalline KBiNb_2O_7 was synthesized by a 2-step cation exchange reaction from $\text{RbBiNb}_2\text{O}_7$ via $\text{LiBiNb}_2\text{O}_7$. In this exchange reaction, the structure changes from a $(0, 0, z)$ Dion-Jacobson framework of the Rb-phase to a $(0, \frac{1}{2}, z)$ stacked framework of the K-phase via the $(\frac{1}{2}, \frac{1}{2}, z)$ Ruddlesden-Popper framework of the Li-phase. The K^+ cations are disordered within the 10-coordinate sites in between the double perovskite layers. Analysis of synchrotron X-ray and neutron powder diffraction data along with the support from SHG and electron diffraction data reveal that the KBiNb_2O_7 adopts a polar $A11m$ structure without any octahedral tilting of NbO_6 octahedra. A zig-zag pattern of Bi^{3+} cations in the xy -plane results in the doubling of the a -cell parameter. The $6s^2$ electronic configuration of Bi^{3+} cation results in an

asymmetric coordination environment in BiO_{12} polyhedra, which is also responsible for the polarity in the KBiNb_2O_7 phase. The KBiNb_2O_7 sample exhibits frequent ‘faults’ in which the $(0, \frac{1}{2}, z)$ stacking changes to a $(\frac{1}{2}, 0, z)$ and *vice versa*, which results in strong *hkl*-dependent peak broadening in the diffraction data.

The cation exchange reaction of $\text{RbBiNb}_2\text{O}_7$ with LiNO_3 proceeds in a purely topochemical manner to yield $\text{LiBiNb}_2\text{O}_7$ as discussed in chapter 4. But the reaction of $\text{RbBiNb}_2\text{O}_7$ with NaNO_3 is accompanied by some non-topochemical processes as indicated by the formation of NaNbO_3 and $\text{Na}_{2.5}\text{Bi}_{0.5}\text{Nb}_2\text{O}_7$ intergrown into the main $\text{NaBiNb}_2\text{O}_7$. On the other hand, the cation exchange reactions of $\text{RbNdNb}_2\text{O}_7$ with LiNO_3 , NaNO_3 and KNO_3 proceed in a purely topochemical manner as discussed in chapter 3. This indicates that replacing Nd^{3+} in the A-site of $\text{RbNdNb}_2\text{O}_7$ by Bi^{3+} lowers the activation energy barrier for non-topochemical processes. The inaccessibility of the KBiNb_2O_7 phase by direct exchange of $\text{RbBiNb}_2\text{O}_7$ and the formation of extensive faults in the structure, again, support the hypothesis that the $\text{RbBiNb}_2\text{O}_7$ phase is susceptible to thermodynamic reactions when treated with $A'\text{NO}_3$ ($A' = \text{Li}, \text{Na}, \text{K}$).

Further cation exchange reactions were performed on $\text{RbBiNb}_2\text{O}_7$ and $\text{LiBiNb}_2\text{O}_7$ by reacting with transition metal chlorides (MnCl_2 , CoCl_2 and CuCl_2) to incorporate magnetic ions in between the distorted double perovskite sheets of BiNb_2O_7 . In all cases, BiOCl was obtained as the major product instead of the exchanged $(\text{MCl})\text{BiNb}_2\text{O}_7$ phases, indicating that $\text{Rb/LiBiNb}_2\text{O}_7$ decomposes at the reaction temperature to give a non-topochemical phase BiOCl , assisting the hypothesis that the Bi^{3+} in the A-site of $A'\text{Nb}_2\text{O}_7$ phases lowers the activation energy barrier towards thermodynamic products.

Chapter 6 – Synthesis, characterisation and phase transition behaviour of $n = 2$ Ruddlesden-Popper phases with interlayer Li^+ cations

6.1 Introduction

The room temperature and low-temperature structures of $\text{Li}_2\text{SrNb}_2\text{O}_7$ are controversial. A study from Uppuluri *et al.* reported a structural transition from a polar $A2_1am$ phase at room temperature to an antipolar $Pnam$ phase at low temperature.⁸⁸ In contrast, Nagai *et al.* reported the phase transition from nonpolar $Amam$ structure at room temperature to polar $Pna2_1$ structure at low temperature.⁸⁹ $\text{Li}_2\text{SrTa}_2\text{O}_7$ and $\text{Li}_2\text{CaTa}_2\text{O}_7$ are reported to have the polar $A2_1am$ and $Pna2_1$ structures respectively at room temperature.^{90–92} In this chapter, the structure and the low-temperature phase transition behaviour of the solid solutions with composition $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ are investigated. In addition, the reinvestigation of the structure and phase transition behaviour of the $\text{Li}_2\text{SrNb}_2\text{O}_7$ and $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ ⁹³ phases are presented.

6.2 Synthesis

6.2.1 $\text{Li}_2\text{CaTa}_2\text{O}_7$

Polycrystalline samples of $\text{Li}_2\text{CaTa}_2\text{O}_7$ were prepared by a ceramic synthesis method from Ta_2O_5 (99.9985%, dried at 900 °C), CaCO_3 (99.8%) and Li_2CO_3 (99.998%). Stoichiometric ratios of Ta_2O_5 and CaCO_3 were ground together in an agate pestle and mortar and combined with a 3 % excess of Li_2CO_3 (to compensate for the weight loss due to volatilization at high temperature). These mixtures were placed in an alumina crucible and heated at 800 °C in the air for 12 h. The mixtures were reground and pressed into 13 mm pellets and heated at 1200 °C for two periods of 2 h. The samples were reground between heating cycles, placed in an alumina crucible and directly put in a furnace which was kept at 1200 °C.

6.2.2 $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$

Polycrystalline samples of $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ ($x = 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.75$) were prepared by a ceramic synthesis method from Ta_2O_5 (99.995%, dried at 900 °C), SrCO_3 (99.8%), CaCO_3 (99.98%) and Li_2CO_3 (99.998%). Stoichiometric ratios of Ta_2O_5 , CaCO_3 and SrCO_3 were ground together in an agate pestle and mortar and combined with a 5 % excess of Li_2CO_3 (to compensate for the weight loss due to volatilization at high temperature). These mixtures were placed in an alumina crucible and heated at 800 °C in the air for 12 h. The mixtures were reground and pressed into 13 mm pellets and heated at 1200 °C for two periods of 3 h. The samples were reground between heating cycles, placed in an alumina crucible and directly put in a furnace which was kept at 1200 °C.

6.2.3 $\text{Li}_2\text{SrNb}_2\text{O}_7$

Polycrystalline samples of $\text{Li}_2\text{SrNb}_2\text{O}_7$ were prepared by a ceramic synthesis method from Nb_2O_5 (99.9985%, dried at 900 °C), SrCO_3 (99.8%) and Li_2CO_3 (99.998%). Stoichiometric ratios of Nb_2O_5 and SrCO_3 were ground together in an agate pestle and mortar, and combined with a 5 % excess of Li_2CO_3 (to compensate for the weight loss due to volatilization at high temperature). These mixtures were placed in an alumina crucible and heated at 800 °C in the air for 12 h. The mixtures were reground and pressed into 13 mm pellets and heated at 1150 °C for three periods of 30 min. The samples were reground between heating cycles, placed in an alumina crucible and directly placed in a furnace which was kept at 1150 °C.

6.2.4 $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$

Polycrystalline samples of $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ ($x = 0.25, 1$) were prepared by a ceramic synthesis method from Ta_2O_5 (99.995%, dried at 900 °C), Nb_2O_5 (99.9985%, dried at 900 °C), SrCO_3 (99.8%) and Li_2CO_3 (99.998%). Stoichiometric ratios of Ta_2O_5 , Nb_2O_5 and SrCO_3 were ground together in an agate pestle and mortar and combined with a 5 % excess of Li_2CO_3 (to compensate for the weight loss due to volatilization at high temperature). These mixtures were

placed in an alumina crucible and heated at 800 °C in the air for 12 h. The mixtures were reground and pressed into 13 mm pellets and heated at 1200 °C for two periods of 1 h. The samples were reground between heating cycles, placed in an alumina crucible and directly put in a furnace which was kept at 1200 °C.

6.3 Results and discussion

6.3.1 Results for the $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ phases

6.3.1.1 Optical SHG measurements

$\text{Li}_2\text{SrTa}_2\text{O}_7$ and $\text{Li}_2\text{CaTa}_2\text{O}_7$ both phases are SHG active.^{90,91} SHG responses from $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ (Figure 6.1) samples were collected and compared to a standard sample of $\alpha\text{-SiO}_2$ which show that these samples are also SHG active hence also adopt noncentrosymmetric crystal structures.

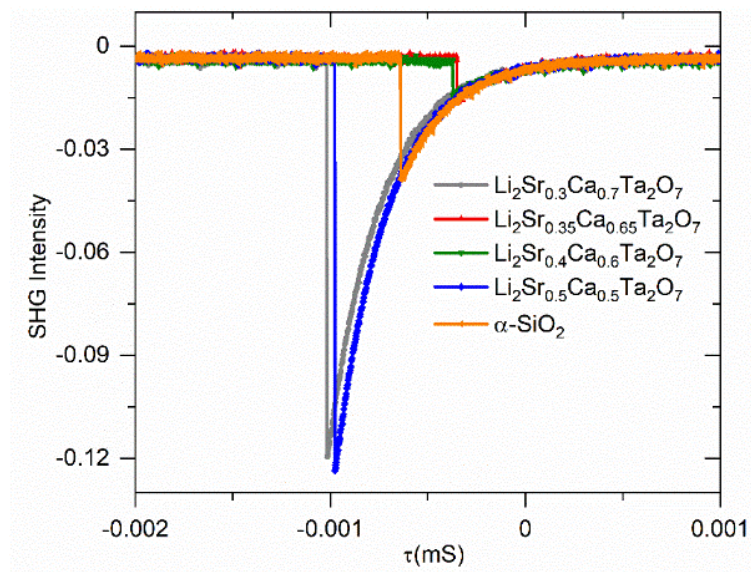


Figure 6.1. SHG activity of several $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ samples.

6.3.1.2 Characterisation of $\text{Li}_2\text{CaTa}_2\text{O}_7$

6.3.1.2.1 Room temperature synchrotron X-ray diffraction data

Room temperature synchrotron X-ray diffraction (SXR) data collected from $\text{Li}_2\text{CaTa}_2\text{O}_7$ could be indexed using the reported lattice parameters of $\text{Li}_2\text{CaTa}_2\text{O}_7$ ^{91,92} ($a = 5.51 \text{ \AA}$, $b = 5.46 \text{ \AA}$, $c = 18.23 \text{ \AA}$). The noncentrosymmetric $Pna2_1$ model^{91,92} of $\text{Li}_2\text{CaTa}_2\text{O}_7$ was refined against

the SXRD data collected at room temperature; which gives a good fit to the data as shown in Figure 6.2.

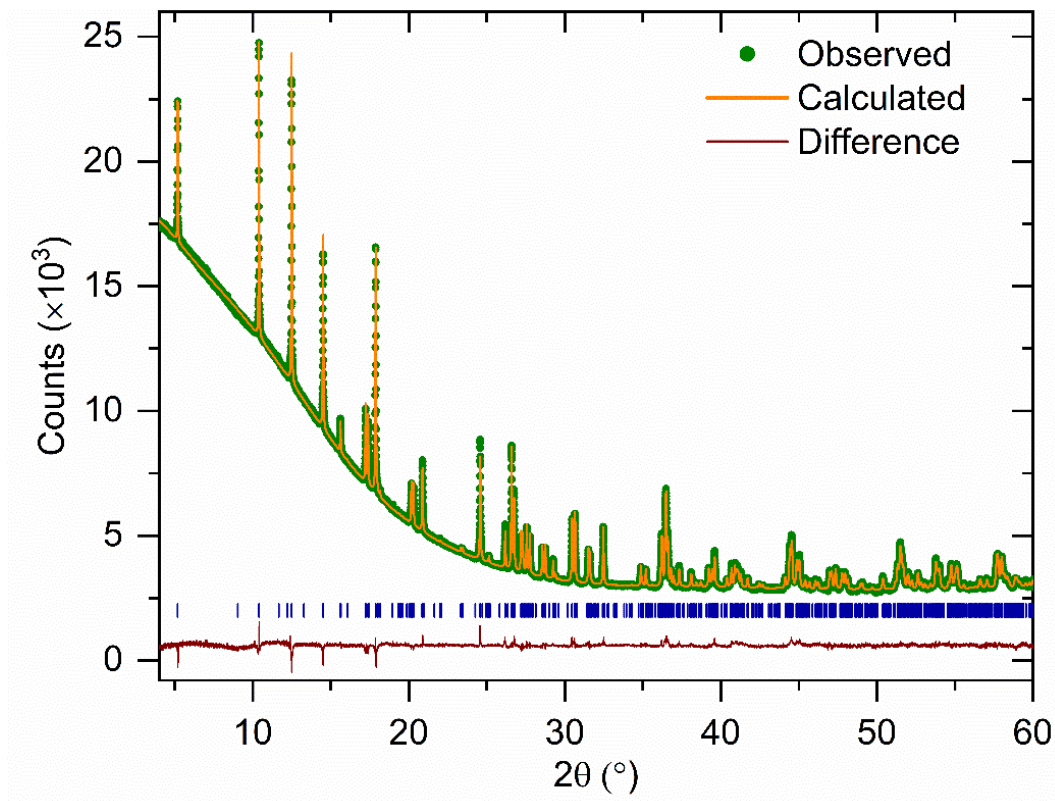


Figure 6.2. Observed, calculated and difference plots from the structure refinements of $\text{Li}_2\text{CaTa}_2\text{O}_7$ against the SXRD data collected at room temperature.

6.3.1.2.2 Room temperature and 10 K neutron diffraction data

Room temperature neutron powder diffraction (NPD) data collected from $\text{Li}_2\text{CaTa}_2\text{O}_7$ could be indexed using the reported orthorhombic unit cell ($a = 5.51 \text{ \AA}$, $b = 5.46 \text{ \AA}$, $c = 18.23 \text{ \AA}$). The $Pna2_1$ model was refined against the NPD data which gives a good fit to the data confirming the reported structure of $\text{Li}_2\text{CaTa}_2\text{O}_7$. The observed, calculated and difference plots from the structure refinement of $\text{Li}_2\text{CaTa}_2\text{O}_7$ against the NPD data collected at room temperature are shown in Figure 6.3. Full details of the refined parameters are shown in Table 6.1.

A similar procedure was followed for the structural characterisation of $\text{Li}_2\text{CaTa}_2\text{O}_7$ at 10 K as described before for the room temperature data. $\text{Li}_2\text{CaTa}_2\text{O}_7$ is isostructural at 298 K and 10 K. Full details of the refined structures are shown in Table 6.2. The observed, calculated and

difference plots from the structure refinement of $\text{Li}_2\text{CaTa}_2\text{O}_7$ against the NPD data collected at 10 K are shown in Figure 6.4.

Atom	Site	x	y	z	Occ.	$B_{\text{eq}} (\text{\AA}^2)$
Li1	4a	0.0040(26)	0.2747(26)	0.2404(8)	1	0.86(10)
Li2	4a	0.4894(24)	0.2843(23)	0.7672(9)	1	0.86(10)
Ca	4a	0.7873(6)	0.0063(5)	0.0128(4)	1	0.90(7)
Ta1	4a	0.7392(10)	0.0033(12)	0.3450(3)	1	0.07(7)
Ta2	4a	0.7480(11)	0.9975(13)	0.6179(3)	1	0.50(9)
O1	4a	0.7689(6)	0.9258(3)	0.5055(6)	1	0.59(5)
O2	4a	0.9598(11)	0.2114(9)	0.1222(3)	1	0.22(7)
O3	4a	0.4762(18)	0.2283(10)	0.5919(4)	1	0.73(12)
O4	4a	0.5261(17)	0.7838(12)	0.9204(4)	1	0.65(12)
O5	4a	0.0428(15)	0.7882(13)	0.3852(4)	1	2.62(16)
O6	4a	0.7443(17)	0.0402(13)	0.2939(3)	1	0.88(11)
O7	4a	0.7463(18)	0.0582(13)	0.7191(3)	1	0.96(13)
$\text{Li}_2\text{CaTa}_2\text{O}_7$ – space group $Pna2_1$ (#33) $a = 5.51185(3) \text{ \AA}$, $b = 5.46121(5) \text{ \AA}$, $c = 18.24012(17) \text{ \AA}$, volume = 549.062 (9) $\text{\AA}^3$ Formula weight = 527.85 g mol $^{-1}$, Z = 4 Radiation source: Neutron Time of Flight Temperature: 298 K $R_p = 4.07 \%$, $wR_p = 4.75 \%$						

Table 6.1. Parameters from the structure refinement of $\text{Li}_2\text{CaTa}_2\text{O}_7$ against the powder neutron diffraction data collected at room temperature.

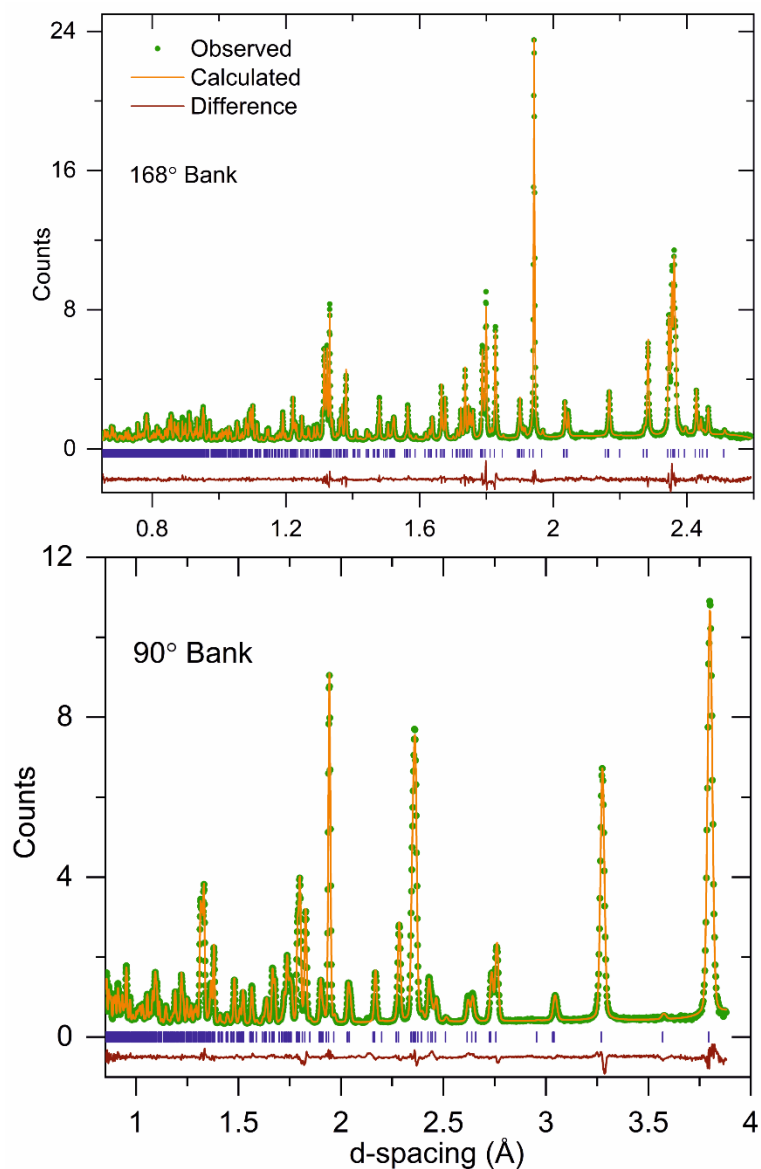


Figure 6.3. Observed, calculated and difference plots from the structure refinement of the $Pna2_1$ model of $\text{Li}_2\text{CaTa}_2\text{O}_7$ against the powder neutron diffraction data collected at room temperature.

Atom	Site	x	y	z	Occ.	$B_{\text{eq}} (\text{\AA}^2)$
Li1	4a	0.0024(27)	0.2854(29)	0.2384(9)	1	0.39(13)
Li2	4a	0.4852(27)	0.2708(27)	0.7659(8)	1	0.39(13)
Ca	4a	0.7899(6)	0.0047(7)	0.0000(7)	1	0.71(9)
Ta1	4a	0.7415(14)	0.9975(14)	0.3926(4)	1	0.17(8)
Ta2	4a	0.7398(13)	0.0041(13)	0.6157(4)	1	0.23(9)
O1	4a	0.7686(7)	0.9244(4)	0.5048(8)	1	0.30(6)
O2	4a	0.9545(17)	0.2034(14)	0.1258(5)	1	1.72(17)
O3	4a	0.4732(17)	0.2119(15)	0.5903(4)	1	0.26(13)

O4	4a	0.5288(18)	0.7698(17)	0.9201(4)	1	0.51(14)
O5	4a	0.0392(13)	0.7883(11)	0.3881(4)	1	0.43(8)
O6	4a	0.7360(16)	0.0578(14)	0.2910(4)	1	0.40(14)
O7	4a	0.7499(17)	0.0410(15)	0.7173(4)	1	0.59(13)
$\text{Li}_2\text{CaTa}_2\text{O}_7$ – space group $Pna2_1$ (#33) $a = 5.50779$ (6) Å, $b = 5.44855$ (7) Å, $c = 18.19424$ (20) Å, volume = 545.999 (11) Å ³ Formula weight = 527.85 g mol ⁻¹ , Z = 4 Radiation source: Neutron Time of Flight Temperature: 10 K $R_p = 3.66$ %, $wR_p = 4.91$ %						

Table 6.2. Parameters from the structure refinement of $\text{Li}_2\text{CaTa}_2\text{O}_7$ against the powder neutron diffraction data collected at 10 K.

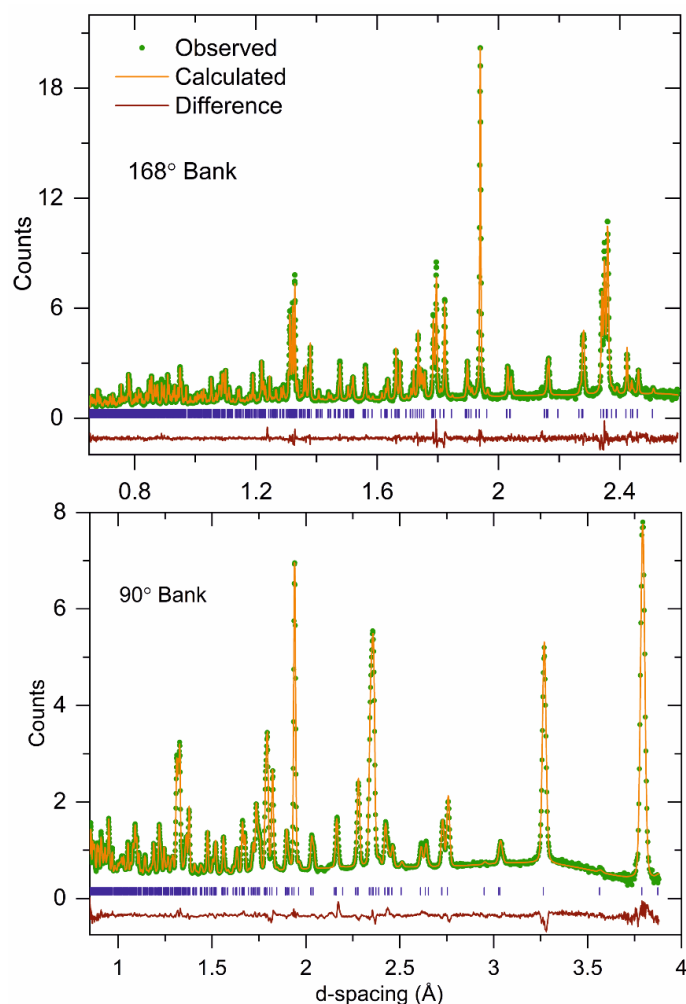


Figure 6.4. Observed, calculated and difference plots from the structure refinement of $Pna2_1$ model against the powder neutron diffraction data collected at 10 K.

6.3.1.3 Structural characterisation of $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ ($x = 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.75$)

6.3.1.3.1 Synchrotron X-ray diffraction data

The room temperature and 5 K structures of $\text{Li}_2\text{SrTa}_2\text{O}_7$ ⁹⁰ are described in polar $A2_1am$ space group with an $a^-a^-c^+/a^-a^-c^+$ tilting pattern of the TaO_6 octahedra. On the other hand, as established before, the room temperature and 10 K structures of $\text{Li}_2\text{CaTa}_2\text{O}_7$ are described using the polar $Pna2_1$ space group with $a^-a^-c^+/a^-a^-c^+$ tilting pattern of the TaO_6 octahedra. Members of the solid solution with $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ composition were synthesized and SXRD data were collected from them. Two end members of this series of compositions have two different structures hence it was of interest to determine the value of x around which this structural change takes place.

Initially an $A2_1am$ model based on the structure of $\text{Li}_2\text{SrTa}_2\text{O}_7$ was refined against the SXRD data collected from the samples. The Sr:Ca ratio was fixed to be the same as in the nominal composition during the structural refinement. The lattice parameters were extracted from the refinement and plotted against x . As shown in Figure 6.5, the orthorhombicity of $\text{Li}_2\text{CaTa}_2\text{O}_7$ is larger than that of $\text{Li}_2\text{SrTa}_2\text{O}_7$. The unit cell volume increases with an increase in Sr-content in the structure as shown in Figure 6.5. This is expected because the ionic radius of Sr^{2+} is larger than Ca^{2+} .⁹⁴ The a - and b -lattice parameters increase with increase in Sr content which is consistent with the volume change but the c -lattice parameter declines on average with increasing Sr-content. In the room temperature $Pna2_1$ structures, the a -lattice parameter is larger than the b -lattice parameter, but in the room temperature $A2_1am$ structure, the b -lattice parameter is larger than the a -lattice parameter. On substitution of Ca by Sr, the difference between the a and b -lattice parameters decreases and after a certain point there is a crossover after which this difference starts to increase again. This crossover indicates the structural

change from the $Pna2_1$ to the $A2_1am$ symmetry structure. As can be seen from Figure 6.5, this cross over takes place in between $x = 0.45$ and $x = 0.5$.

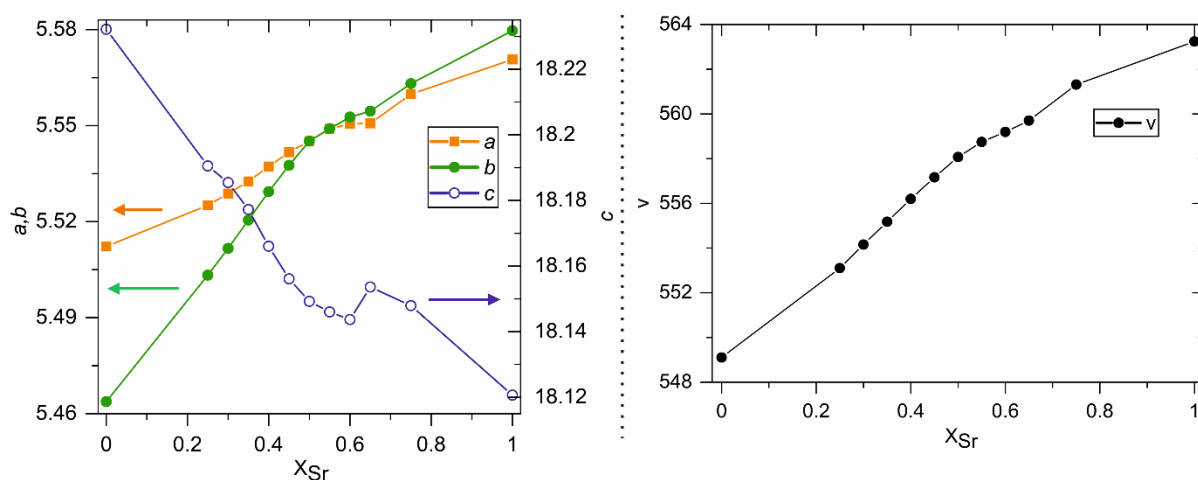


Figure 6.5. Lattice parameters against the Sr-content in $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ as obtained from the structure refinement against the SXRD data collected at room temperature.

6.3.1.3.2 Phase transition behaviour of $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$

There is a structural change from the $Pna2_1$ to $A2_1am$ symmetry with increasing x in the $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ phases at room temperature. A phase transition from room temperature $A2_1am$ to low temperature $Pna2_1$ phases is reported^{88,89,93,95} for the $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ phase, which is also discussed later in the chapter. Therefore, it was expected that a phase transition will be observed for the $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ phases with room temperature $A2_1am$ structure, to the $Pna2_1$ structure at low temperature, for the compositions near $x = 0.5$, where the room temperature structural change takes place. Hence the low-temperature synchrotron X-ray diffraction data (300 K to 100 K) were collected to track down the transition temperature from the high-temperature $A2_1am$ phase to the low-temperature $Pna2_1$ phase, if there is any. If there is any phase transition, the transition temperature is expected to be higher for the samples with more Ca-content and the transition temperature will decrease with lower Ca-content.

The difference between the $A2_1am$ and the $Pna2_1$ structure of the $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ phases is subtle and not easily detected by X-ray diffraction. Therefore, the synchrotron X-ray diffraction data collected from all the $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ phases could also be indexed and refined using the

$A2_1am$ model. Only using neutrons, it can be seen that a P -centering is required to index all the diffraction peaks and the $Pna2_1$ space group is required to describe the structure of the high Ca-containing samples. Due to the similarity between the refinement of the $A2_1am$ and the $Pna2_1$ structures with respect to SXRD data, to determine the transition temperature, subtle indicators e.g., the change of slope in lattice parameters with temperature or the change of slope in the difference between a and b -lattice parameters with temperature or change of slope in $a \times b$ with temperature, were used.

As described above and shown in Figure 6.5, the structural change from the $Pna2_1$ to $A2_1am$ space group at room temperature takes place in between $x = 0.45$ and $x = 0.50$. Hence, as expected, no change in the phase transition indicators was observed for the $\text{Li}_2\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ta}_2\text{O}_7$ phase upon cooling down to 100 K from 300 K as shown in Figure 6.6.

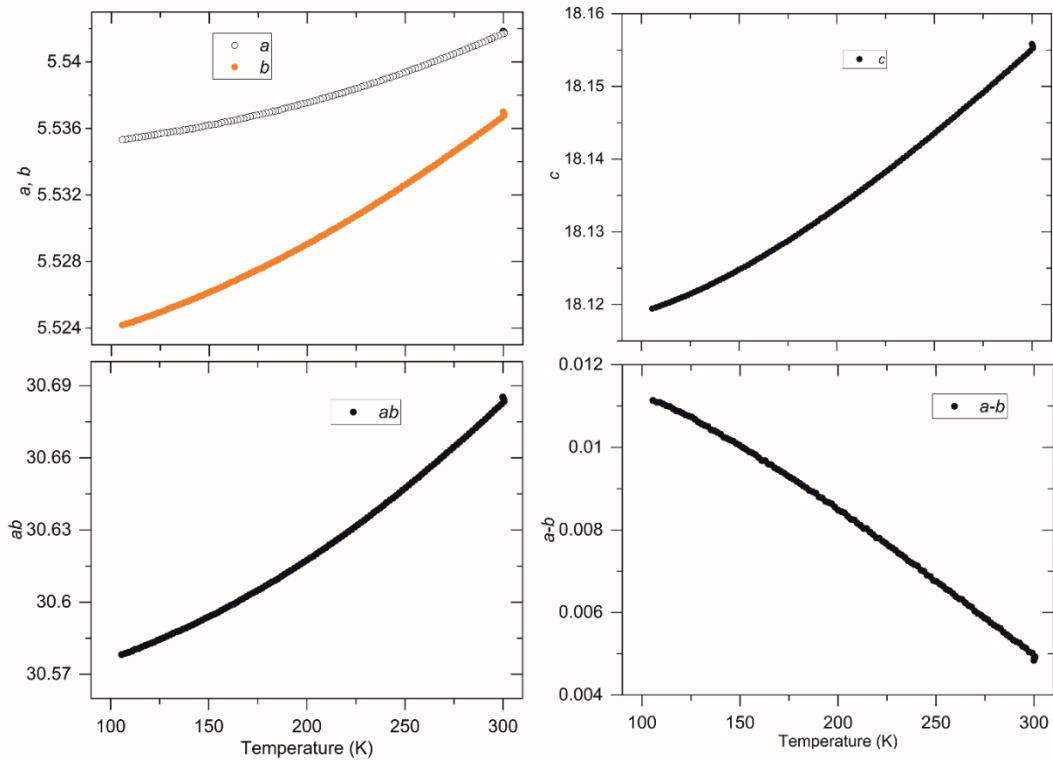


Figure 6.6. Evolution of a , b and c lattice parameter, ab and $a-b$ with temperature as obtained from the structure refinement of $\text{Li}_2\text{Sr}_{0.45}\text{Ca}_{0.55}\text{Ta}_2\text{O}_7$ against the SXRD data

The $\text{Li}_2\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Ta}_2\text{O}_7$ phase shows a change in the slope for the a -lattice parameter and in the magnitude of ab around 278 K as shown in Figure 6.7. This discontinuity in slope indicates the

$A2_1am$ to $Pna2_1$ phase transition. As mentioned before the $Pna2_1$ phase is more orthorhombic than the $A2_1am$, hence some peaks which indicate orthorhombic distortion split into two peaks at low temperature as shown in Figure 6.8.

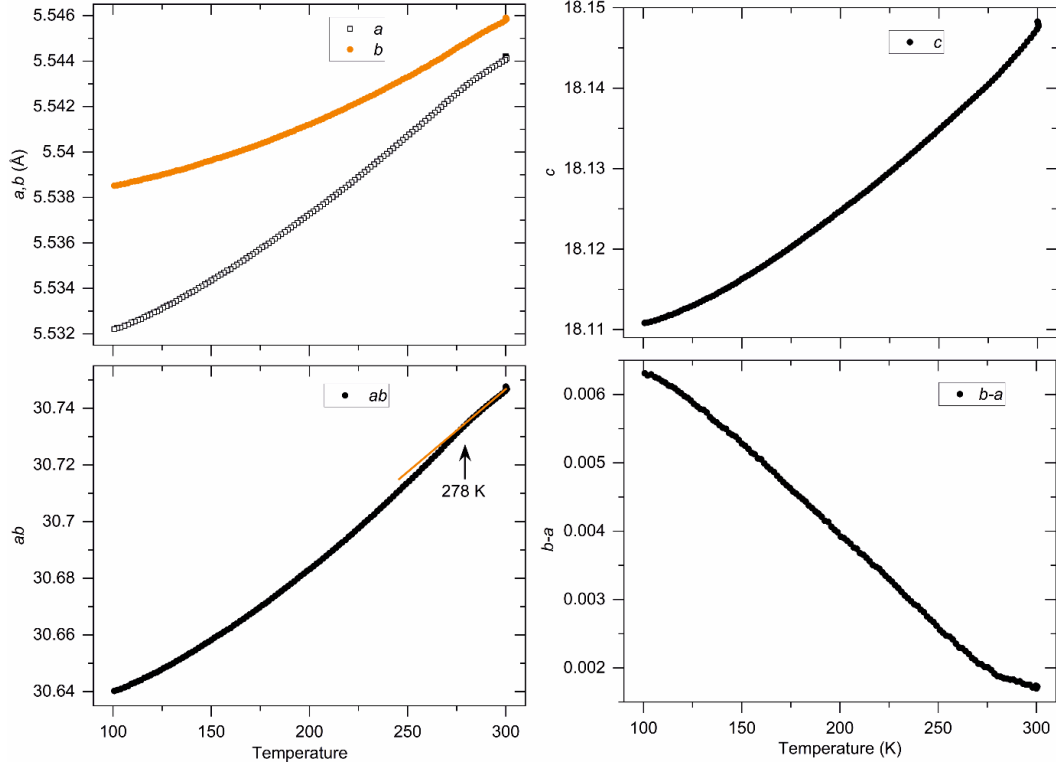


Figure 6.7. Evolution of a , b and c lattice parameters, ab and $b-a$ with temperature as obtained from the structure refinement of $\text{Li}_2\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Ta}_2\text{O}_7$ against the SXRD data. The straight orange line is drawn to guide the eye to indicate the change in slope.

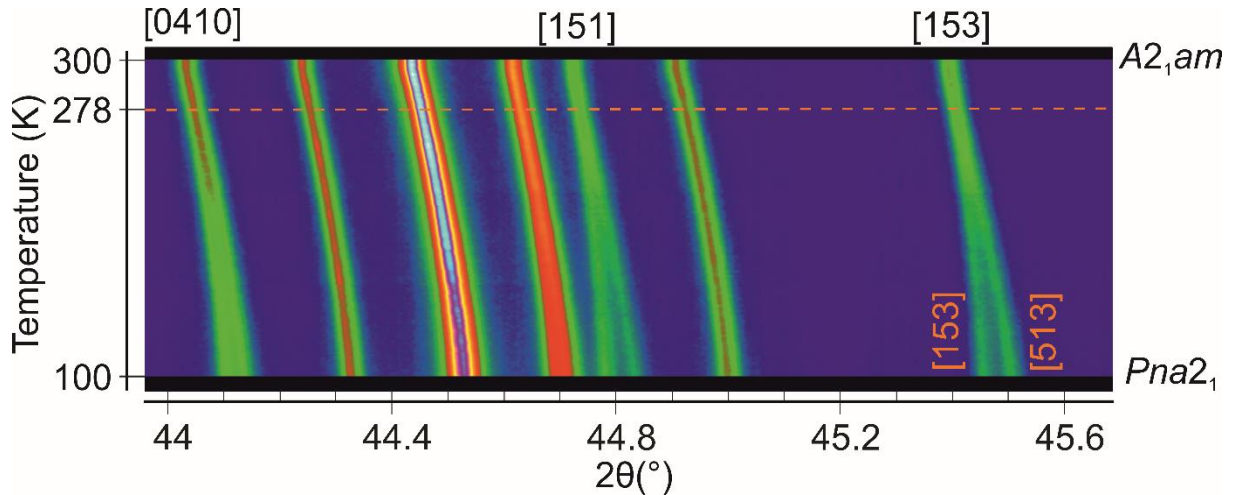


Figure 6.8. Planview of the part of the diffraction patterns from 300 K to 100 K collected from $\text{Li}_2\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Ta}_2\text{O}_7$. Some peaks are split at low temperatures due to the large orthorhombicity of the low-temperature $Pna2_1$ structure of the $\text{Li}_2\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Ta}_2\text{O}_7$ phase.

A similar change in the phase transition indicators was observed for the $\text{Li}_2\text{Sr}_{0.55}\text{Ca}_{0.45}\text{Ta}_2\text{O}_7$ phase at approximately 226 K as shown in Figure 6.9.

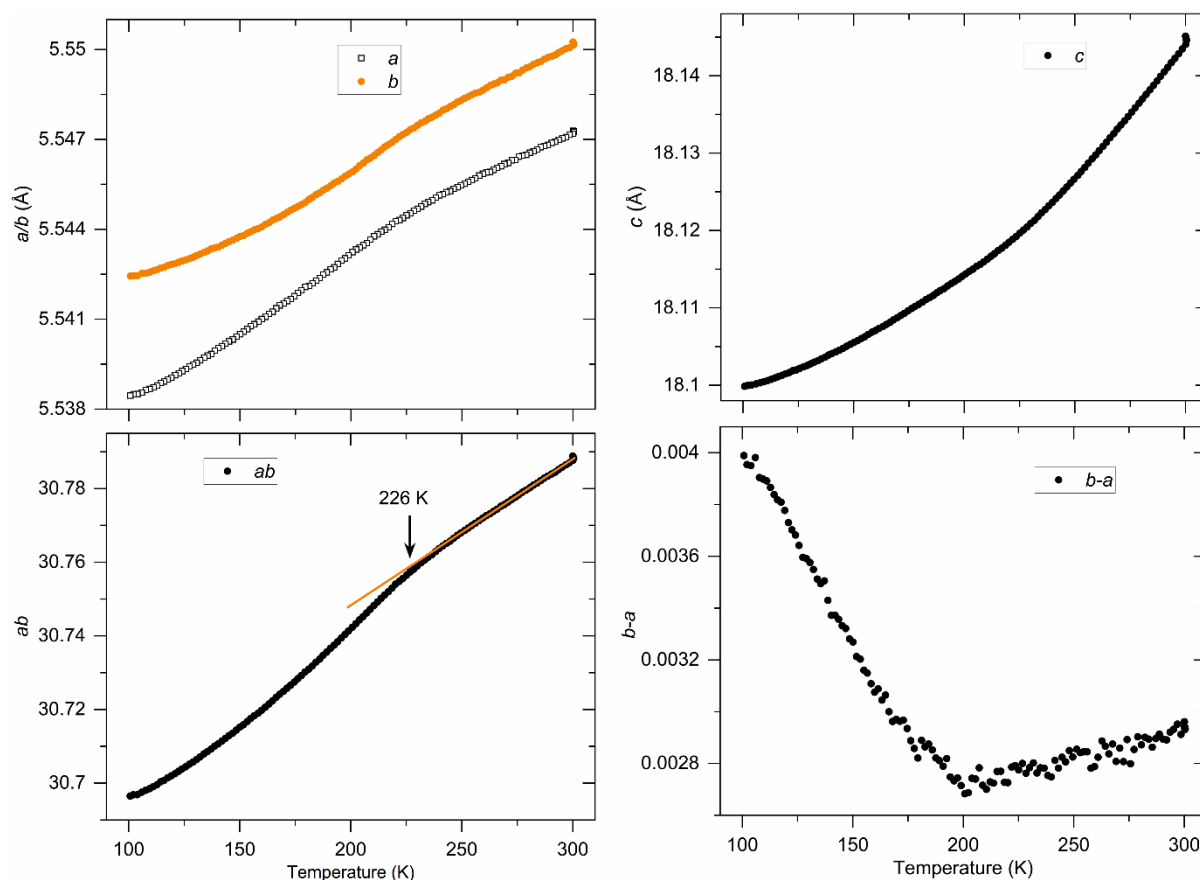


Figure 6.9. Evolution of a , b and c lattice parameters, ab and $b-a$ with temperature as obtained from the structure refinement of $\text{Li}_2\text{Sr}_{0.55}\text{Ca}_{0.45}\text{Ta}_2\text{O}_7$ against the SXRD data. The straight orange line is drawn to guide the eye to indicate the change in slope.

The phase transition for the $\text{Li}_2\text{Sr}_{0.6}\text{Ca}_{0.4}\text{Ta}_2\text{O}_7$ and $\text{Li}_2\text{Sr}_{0.55}\text{Ca}_{0.35}\text{Ta}_2\text{O}_7$ phases takes place at temperatures 182 K and 150 K respectively. The change in lattice parameters and other phase transition indicators are shown in Figure 6.10 and Figure 6.12 for the $\text{Li}_2\text{Sr}_{0.6}\text{Ca}_{0.4}\text{Ta}_2\text{O}_7$ and $\text{Li}_2\text{Sr}_{0.55}\text{Ca}_{0.35}\text{Ta}_2\text{O}_7$ phases respectively. Figure 6.11 and Figure 6.13 show the plan-view of the diffraction patterns from 300 K to 100 K collected from the $\text{Li}_2\text{Sr}_{0.6}\text{Ca}_{0.4}\text{Ta}_2\text{O}_7$ and $\text{Li}_2\text{Sr}_{0.55}\text{Ca}_{0.35}\text{Ta}_2\text{O}_7$ phases respectively. The transition temperatures for the $A2_1am$ to $Pna2_1$ phase transition against the Sr-content of the four samples described above are plotted in Figure 6.14.

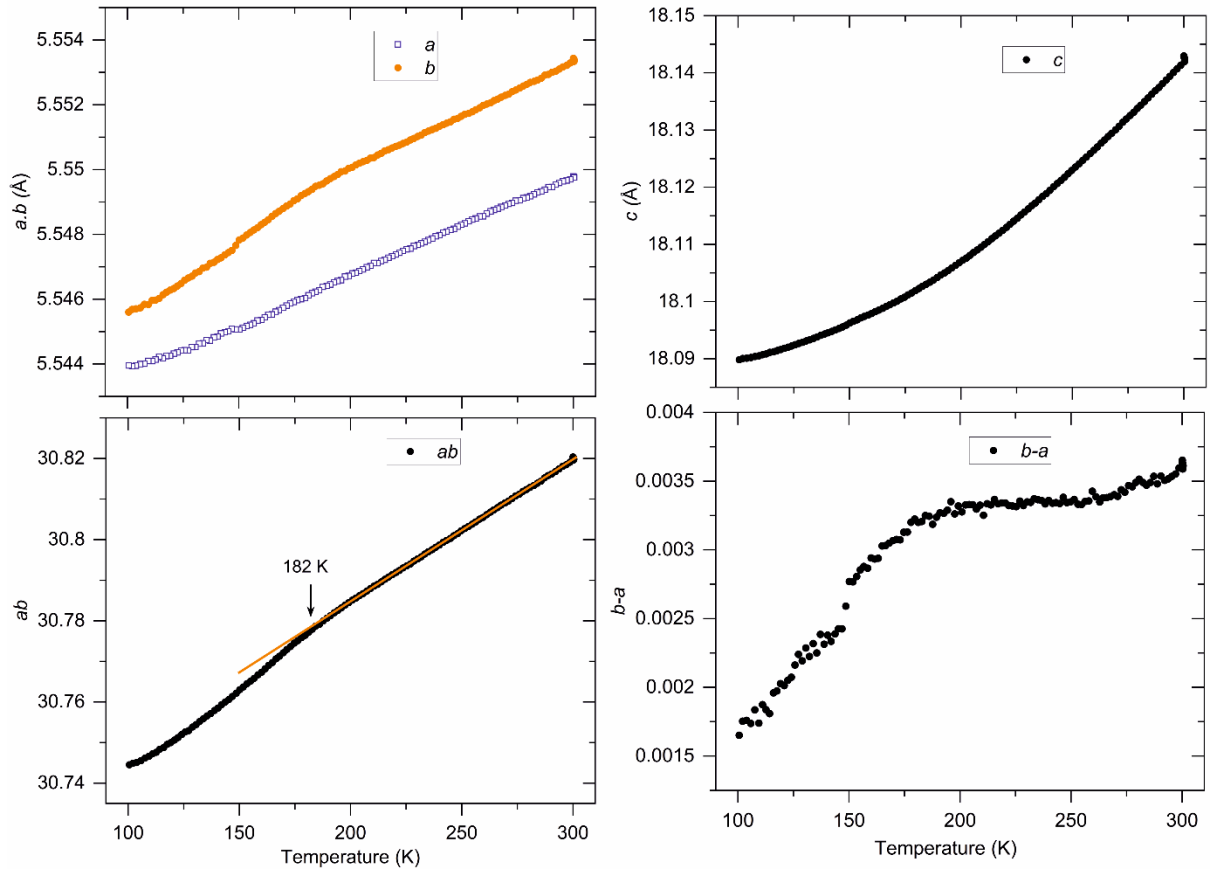


Figure 6.10. Evolution of a , b and c lattice parameters, ab and $b-a$ with temperature as obtained from the structure refinement of $\text{Li}_2\text{Sr}_{0.60}\text{Ca}_{0.40}\text{Ta}_2\text{O}_7$ against the SXRD data. The straight orange line is drawn to guide the eye to indicate the change in slope.

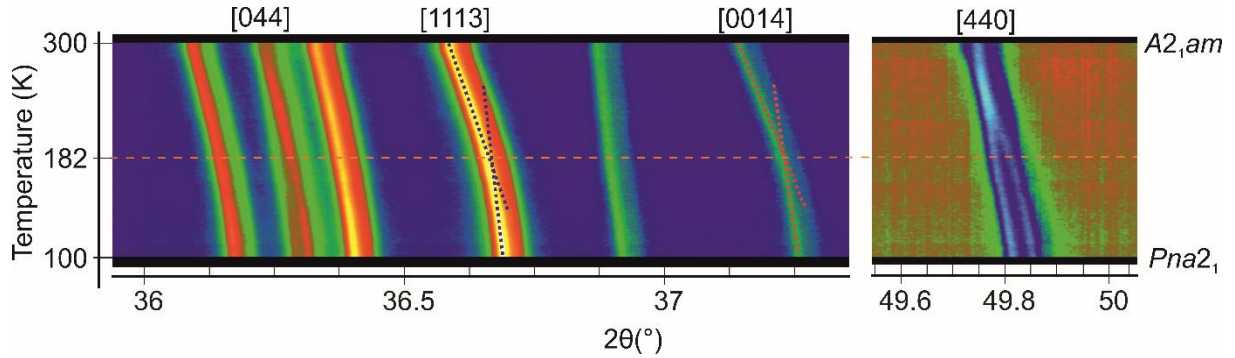


Figure 6.11. Planview of the part of the diffraction patterns from 300 K to 100 K collected from $\text{Li}_2\text{Sr}_{0.60}\text{Ca}_{0.40}\text{Ta}_2\text{O}_7$. The black and orange dotted lines are drawn to indicate the change in slope of the evolution of [1113] and [0014] peaks respectively.

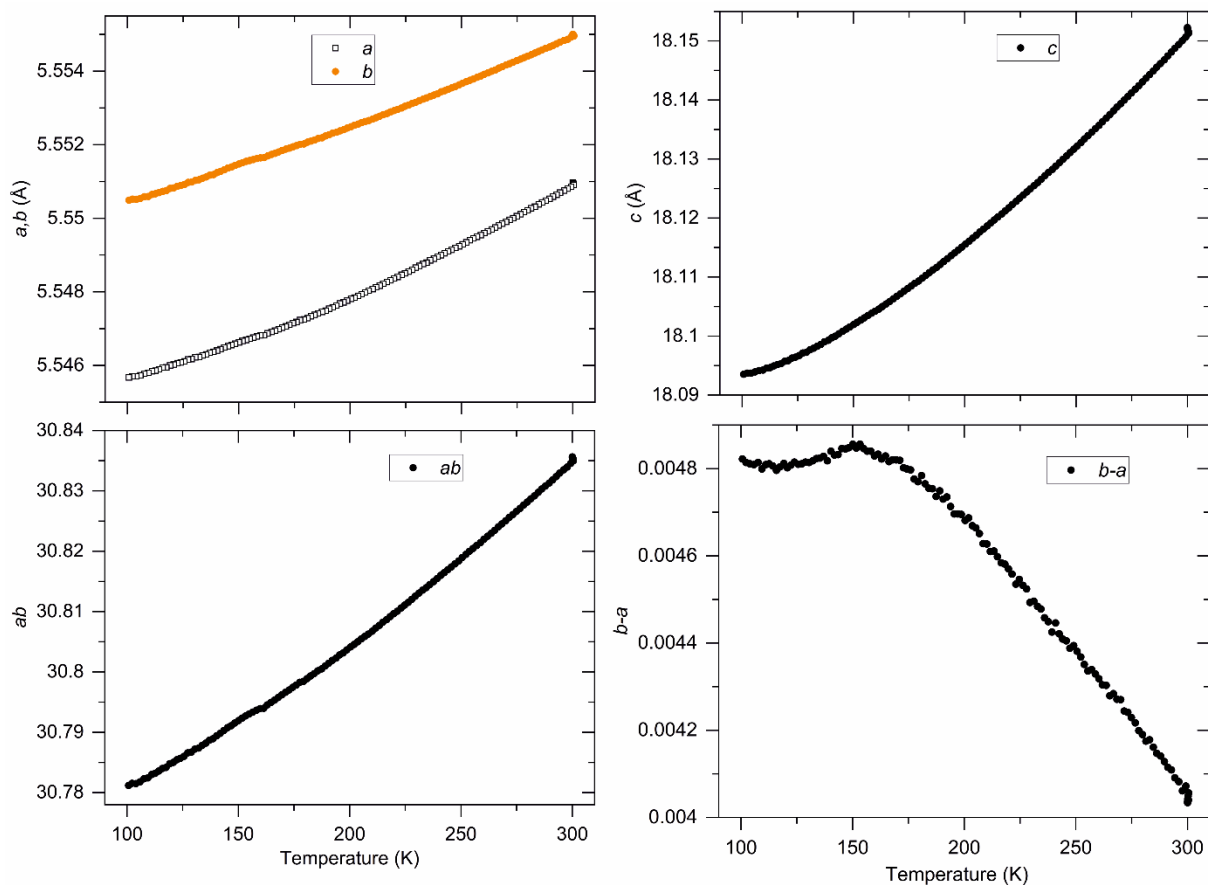


Figure 6.12. Evolution of a , b and c lattice parameters, ab and $b-a$ with temperature as obtained from the structure refinement of $\text{Li}_2\text{Sr}_{0.65}\text{Ca}_{0.35}\text{Ta}_2\text{O}_7$ against the SXRD data. The straight orange line is drawn to guide the eye to indicate the change in slope.

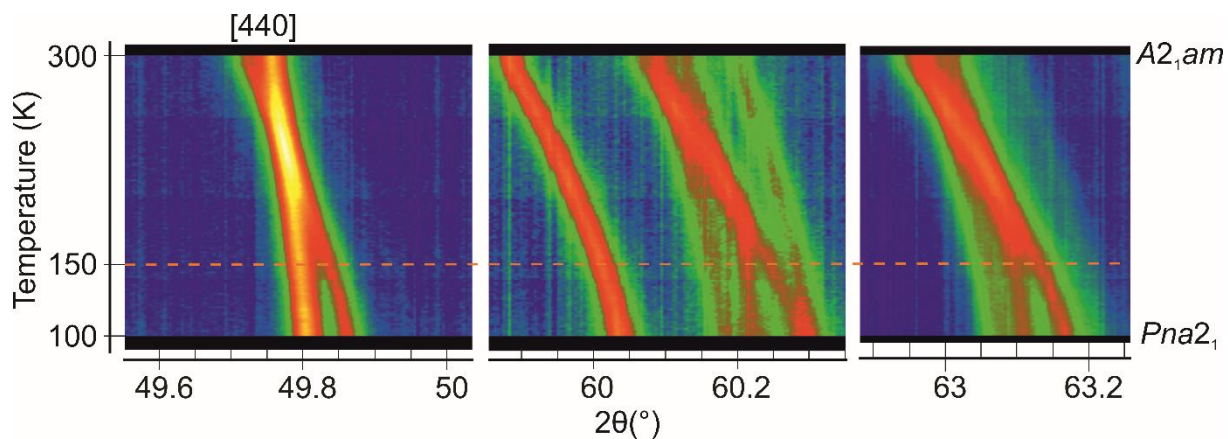


Figure 6.13. Planview of the part of the diffraction patterns from 300 K to 100 K collected from $\text{Li}_2\text{Sr}_{0.65}\text{Ca}_{0.35}\text{Ta}_2\text{O}_7$. Some peaks are split at low temperatures due to the large orthorhombicity of the low-temperature $Pna2_1$ phase of $\text{Li}_2\text{Sr}_{0.65}\text{Ca}_{0.35}\text{Ta}_2\text{O}_7$.

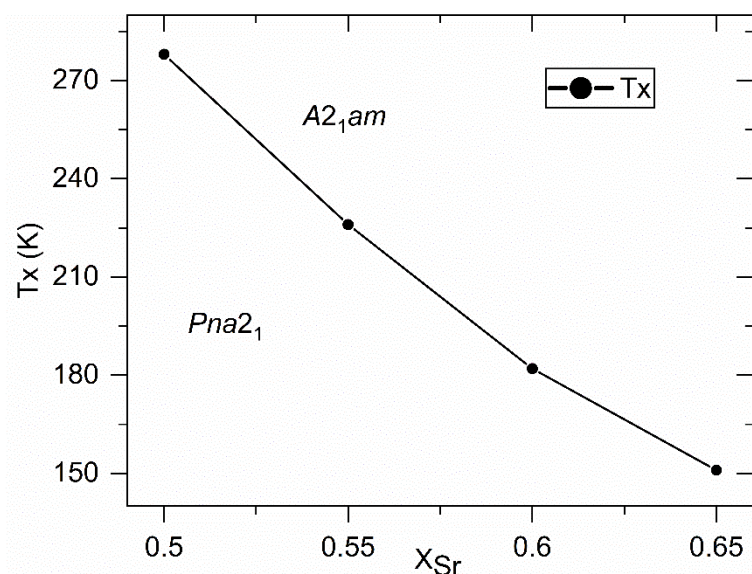


Figure 6.14. Transition temperature from the room temperature $A2_1am$ phase to the low-temperature $Pna2_1$ phase against the Sr-content in $Li_2Sr_xCa_{1-x}Ta_2O_7$ phases.

6.3.2 Discussion for the $Li_2Sr_xCa_{1-x}Ta_2O_7$ phases

The Sr^{2+} cation is substantially larger than Ca^{2+} (ionic radius of Sr^{2+} is 1.44 Å and ionic radius of Ca^{2+} is 1.34 Å in the 12-coordinate site). Hence, the substitution of Ca by Sr in the $Li_2CaTa_2O_7$ structure should increase the volume of the unit cell as well as the lattice parameters. Although the a - and b -lattice parameters and volume of unit cell follow this expected trend, the c -lattice parameter does not, as shown in Figure 6.5. Why is that? The substitution of smaller Ca^{2+} by larger Sr^{2+} in the A-site of layered perovskite structure increases the tolerance factor,³ which lowers the cooperative tilting of TaO_6 octahedra. Now the double perovskite blocks are separated by interlayer Li^+ cations which sit in the 5-coordinate site as shown in Figure 6.15. Because of large tilting in the perovskite blocks of the higher Ca-containing samples and their cooperative nature, the Li^+ cations move up and down alternatively (Figure 6.15) to accommodate themselves in bonding optimized coordination environments. This effect increases the interlayer separation, as well as, the c -parameter of the unit cells of the higher Ca-containing compounds. There is a slight discrepancy of this trend of decreasing c -parameter with Sr-substitution near the compositions where the $Pna2_1$ to $A2_1am$

structural change takes place (Figure 6.5). This is because the structural change also changes the TaO₆ octahedral rotation pattern along the z-axis from $c^+/-c^+$ to c^+/c^+ .

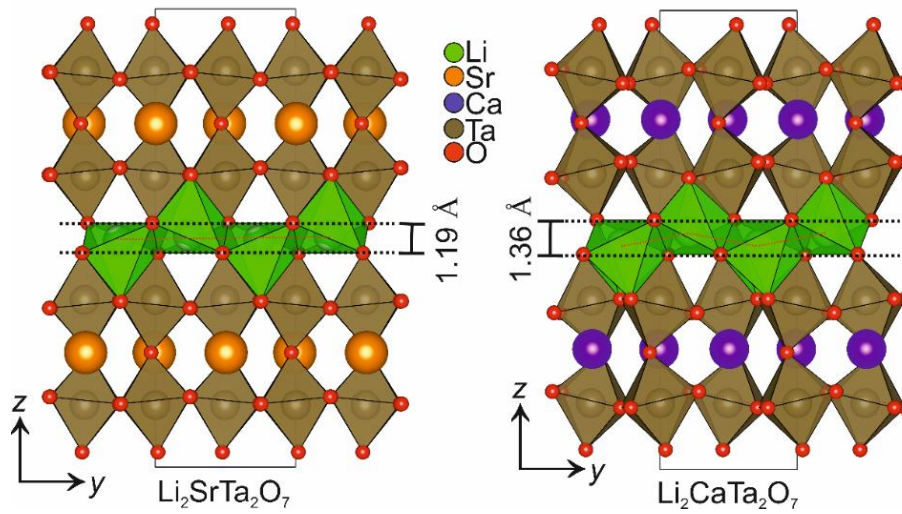


Figure 6.15. Structure and interlayer separation in the Li₂SrTa₂O₇ and Li₂CaTa₂O₇ phases.

Substitution of smaller Ca²⁺ by larger Sr²⁺ in the A-site of the double perovskite blocks increases the tolerance factor which in turn lowers the magnitude of TaO₆ tilting. Li₂SrTa₂O₇ adopts an *A2₁am* symmetry structure described by $a^-a^-c^+/a^-a^-c^+$ tilting of the TaO₆ octahedra. In contrast, the large magnitude of tilting in Li₂CaTa₂O₇ appears to be incompatible with the $a^-a^-c^+/a^-a^-c^+$ tilting pattern. The smaller Ca²⁺ cation changes the crystal packing which favours an inversion of the sense of octahedral rotation along the z-axis ($a^-a^-c^+/a^-a^-(-c^+)$), when there is a large magnitude of tilt. This $a^-a^-c^+/a^-a^-(-c^+)$ tilting pattern should lead to an antipolar structure with *Pnam* symmetry but the presence of d^0 -Ta⁵⁺ cation in a distorted octahedral coordination environment leads to a polarisation along the c-axis via an SOJT driven proper mechanism. With an increase in Sr-content the magnitude of tiling distortion declines and average A-cation size increases, therefore, after a certain point ($X_{Sr} \sim 0.5$) the structure becomes compatible with the $a^-a^-c^+/a^-a^-c^+$ tilting and therefore adopts the *A2₁am* structure at room temperature.

Samples with relatively higher Sr-content, ($X_{Sr} = 0.5, 0.55, 0.6, 0.65$) adopt *A2₁am* structure at room temperature, at low temperature, there is a phase transition to the SOJT driven proper

$Pna2_1$ structure as discussed in the results section. With an increase in Sr-content, $a^-a^-c^+/a^-a^-c^+$ tilting pattern becomes easily compatible and this transition temperature goes down.

6.3.3 Results for the $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ phases

The reported room temperature and the low-temperature structure of the $\text{Li}_2\text{SrNb}_2\text{O}_7$ phase are conflicting. A study from Uppuluri *et al.* reported a structural transition from a polar $A2_1am$ phase at room temperature to an antipolar $Pnam$ phase at low temperature.⁸⁸ In contrast, Nagai *et al.* reported the phase transition from nonpolar $Amam$ structure at room temperature to polar $Pna2_1$ structure at low temperature.⁸⁹ The SHG activity from the $\text{Li}_2\text{SrNb}_2\text{O}_7$ as shown in Figure 6.16 confirms that the room temperature structure is indeed noncentrosymmetric $A2_1am$. At low temperatures, Nagai *et al.* have observed weak ferroelectricity from $\text{Li}_2\text{SrNb}_2\text{O}_7$ which is consistent with the polar $Pna2_1$ symmetry. Moreover, the temperature-dependent SHG activity as shown in the supporting information of ref [88] indicates that with lowering in temperature the SHG intensity goes up which is not consistent with their assignment of the low-temperature phase as antipolar $Pnam$. The increase in SHG activity at low temperatures further confirms the noncentrosymmetric $Pna2_1$ structure of $\text{Li}_2\text{SrNb}_2\text{O}_7$.

Along with the above-mentioned events, the observation that the $\text{Li}_2\text{Sr}_x\text{Ca}_{1-x}\text{Ta}_2\text{O}_7$ phases undergo a related phase transition from the room temperature $A2_1am$ structure to the low temperature $Pna2_1$ structure as discussed earlier, it is likely that the phase transition for the $\text{Li}_2\text{SrNb}_2\text{O}_7$ phase is also from room temperature $A2_1am$ symmetry structure to low-temperature $Pna2_1$ symmetry structure. The structure and phase transition behaviour of $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ ($x = 0, 0.25, 0.5$) phases are therefore revisited.

6.3.3.1 Optical SHG measurement

Particle-size dependent SHG measurements show that $\text{Li}_2\text{SrNb}_2\text{O}_7$ is SHG active and the activity increases with an increase in particle size (Figure 6.16). This indicates that $\text{Li}_2\text{SrNb}_2\text{O}_7$

adopts a noncentrosymmetric crystal structure. SHG data collected from $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ sample also show SHG activity, indicating a noncentrosymmetric crystal structure.

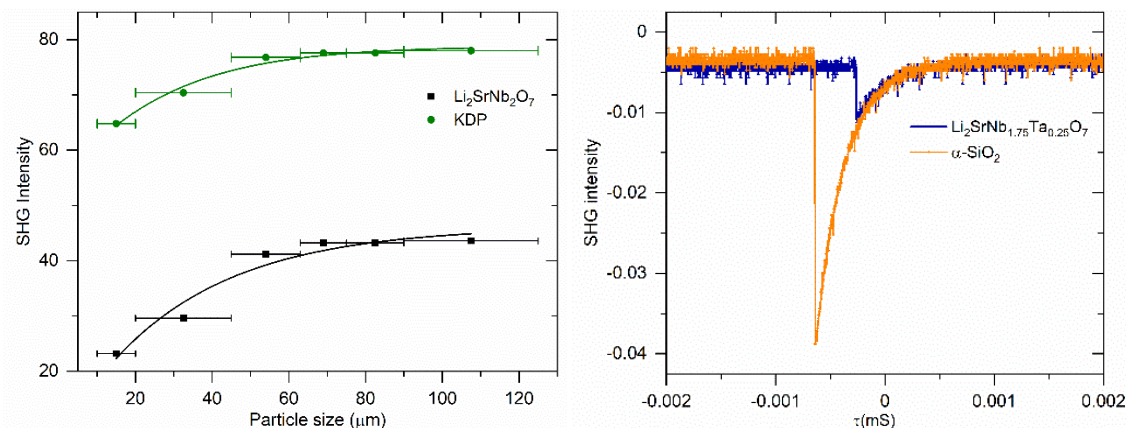


Figure 6.16. (Left) Particle size dependent SHG activity of $\text{Li}_2\text{SrNb}_2\text{O}_7$. (Right) SHG activity of $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$.

6.3.3.2 Characterisation of $\text{Li}_2\text{SrNb}_2\text{O}_7$

6.3.3.2.1 Room temperature synchrotron X-ray diffraction data

Synchrotron X-ray diffraction (SXR) data collected from $\text{Li}_2\text{SrNb}_2\text{O}_7$ could be indexed using an A-centred orthorhombic unit cell ($a = 5.592 \text{ \AA}$, $b = 5.600 \text{ \AA}$, $c = 18.01 \text{ \AA}$), which is $\sqrt{2} \times \sqrt{2} \times 2$ geometric expansion of the aristotype unit cell of $n = 2$ Ruddlesden-Popper structure. The structure of the $\text{Li}_2\text{SrNb}_2\text{O}_7$ phase is reported in both the centrosymmetric Amm ⁸⁹ and the noncentrosymmetric $A2_1am$ ⁸⁸ space group. Since it is SHG active (the activity is 0.56 times that of standard KDP as shown in Figure 6.16), the $A2_1am$ model was used for structure refinement against the synchrotron X-ray diffraction data, which resulted in a good fitting to the data. The observed, calculated and difference plots from the structure refinement of the $A2_1am$ model of $\text{Li}_2\text{SrNb}_2\text{O}_7$ against the SXR data collected at room temperature are shown in Figure 6.17.

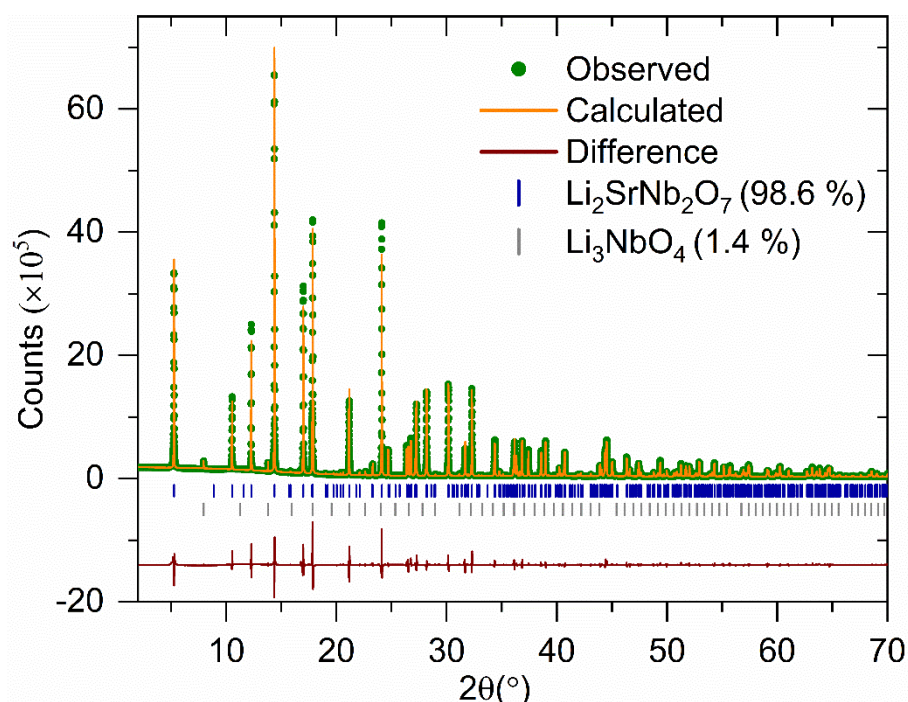


Figure 6.17. Observed, calculated and difference plots from the structure refinement of $\text{Li}_2\text{SrNb}_2\text{O}_7$ against the SXRD data collected at room temperature. Li_3NbO_4 was added as a secondary phase.

6.3.3.2.2 Variable temperature synchrotron X-ray diffraction data

$\text{Li}_2\text{SrNb}_2\text{O}_7$ was warmed from 100 K to 300 K followed by cooling down to 100 K and almost 105 diffraction patterns were collected at each sweep. The room temperature phase is reported to undergo a phase transition to the $Pna2_1$ phase⁸⁹ at low temperature. The $A2_1am$ model was refined against the diffraction data and the lattice parameters were extracted; which were plotted against the temperature (Figure 6.18).

The lattice parameters show a clear anomaly around 219 K during warming and 211 K during cooling as shown in Figure 6.18; which indicates the high-temperature $A2_1am$ to the low temperature $Pna2_1$ phase transition.

Figure 6.19 shows a plan-view of the selected region of the diffraction patterns collected from $\text{Li}_2\text{SrNb}_2\text{O}_7$ between the temperatures 300 K and 100 K. The appearance of [114], [314] and [209] peaks at low temperature violates the A -centering ($k + l = 2n$) condition and the indexing of all the peaks in the diffraction patterns requires a primitive unit cell.

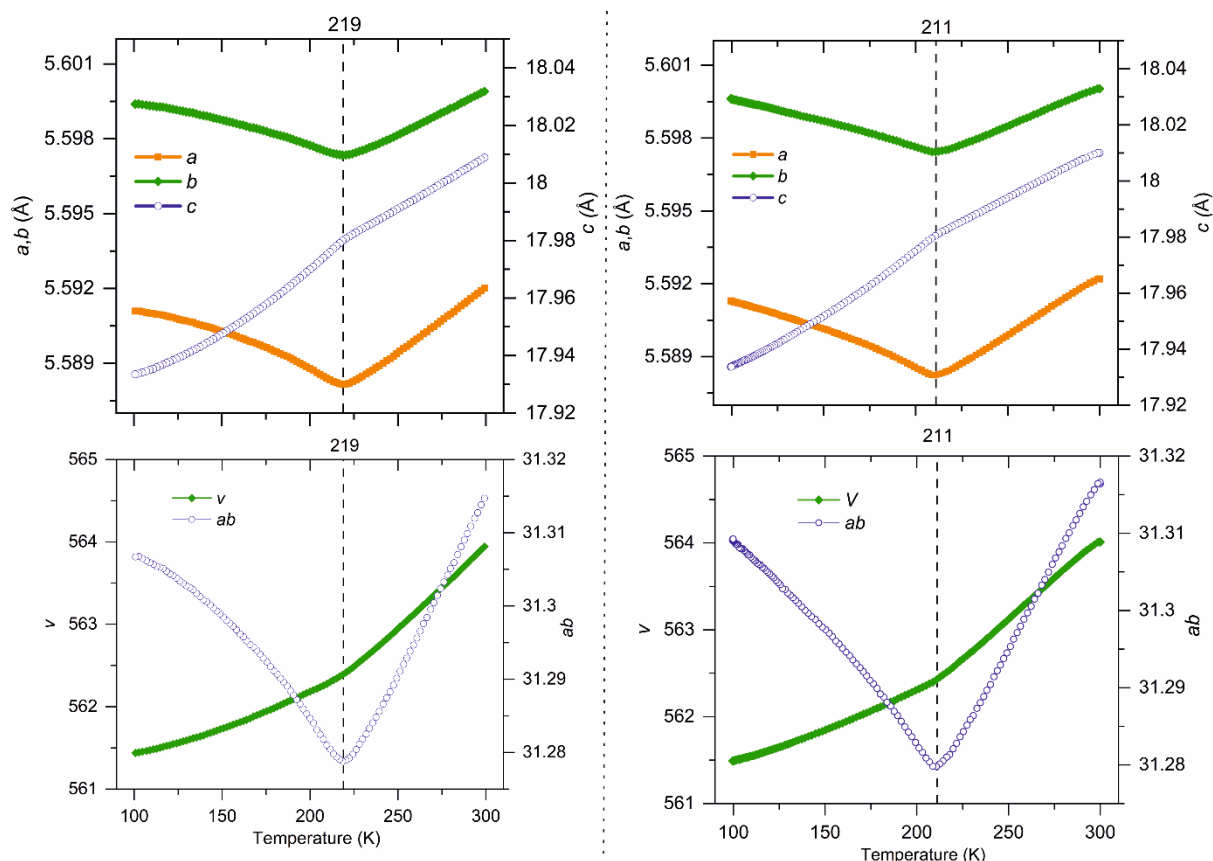


Figure 6.18. Evolution of lattice parameters, ab and volume (v) of $\text{Li}_2\text{SrNb}_2\text{O}_7$ with temperature. The left panel shows the lattice parameters for the warming regime and the right panel shows the lattice parameters for the cooling regime as obtained from the structure refinement of $\text{Li}_2\text{SrNb}_2\text{O}_7$ against the synchrotron X-ray diffraction data.

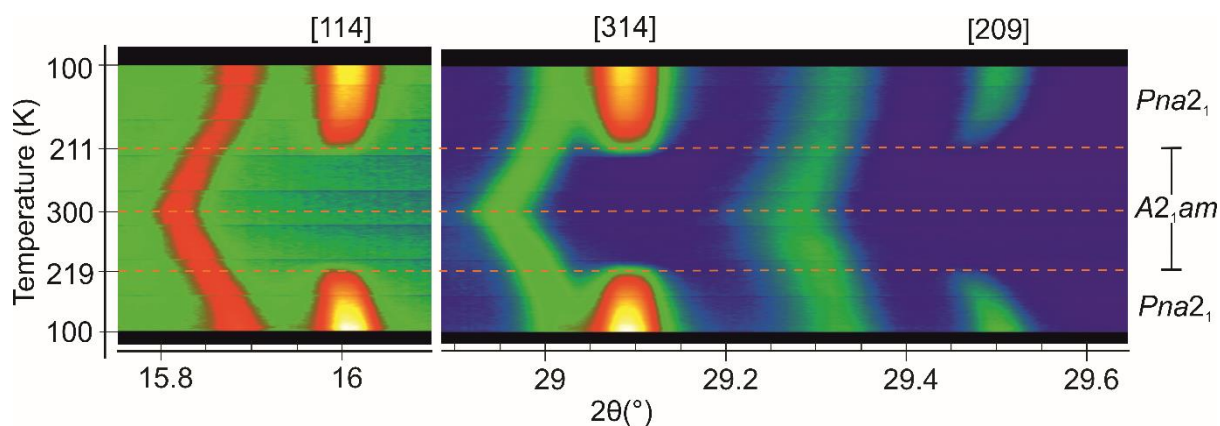


Figure 6.19. Evolution of specific diffraction peaks from SXRD of $\text{Li}_2\text{SrNb}_2\text{O}_7$ with temperature.

6.3.3.3 Characterisation of $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$

Synchrotron X-ray diffraction data collected from $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ could be indexed using an A -centred orthorhombic unit cell ($a = 5.587 \text{ \AA}$, $b = 5.594 \text{ \AA}$, $c = 18.014 \text{ \AA}$), which is $\sqrt{2} \times$

$\sqrt{2} \times 2$ geometric expansion of the aristotype unit cell of $n = 2$ Ruddlesden-Popper structure.

As the sample is SHG active as shown in Figure 6.2, The $A2_1am$ model was constructed and refined against the SXRD data, which resulted in a good fit to the data as shown in Figure 6.20.

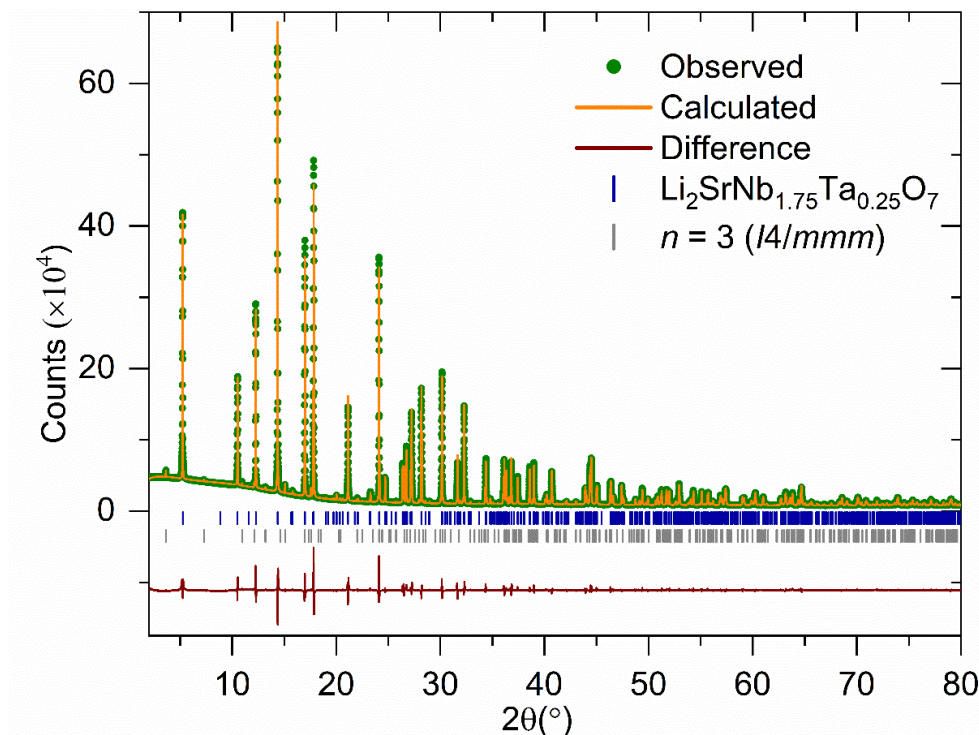


Figure 6.20. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ against the SXRD data collected at room temperature. An $n = 3$ phase with $I4/mmm$ symmetry was added as a secondary phase.

$\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ was warmed from 100 K to 300 K and diffraction patterns were collected. The $A2_1am$ model was refined against the diffraction data and the lattice parameters were extracted; which were plotted against the temperature (Figure 6.21). The lattice parameters show a clear twitch around 135 K as shown in Figure 6.21, which indicates the high-temperature $A2_1am$ to low temperature $Pna2_1$ phase transition. Figure 6.22 shows a plan-view of the selected region of the diffraction patterns collected from $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ between 300 K and 100 K. The appearance of $[314]$ and $[209]$ peaks at low temperatures confirms the phase transition to the $Pna2_1$ structure.

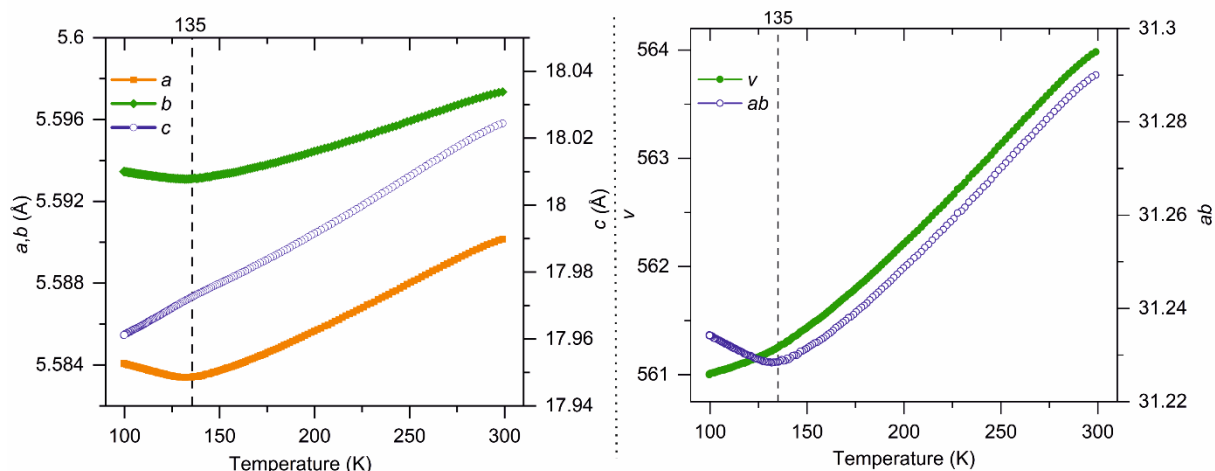


Figure 6.21. Evolution of lattice parameters, ab and volume (v) with temperature as obtained from structural refinement of $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$

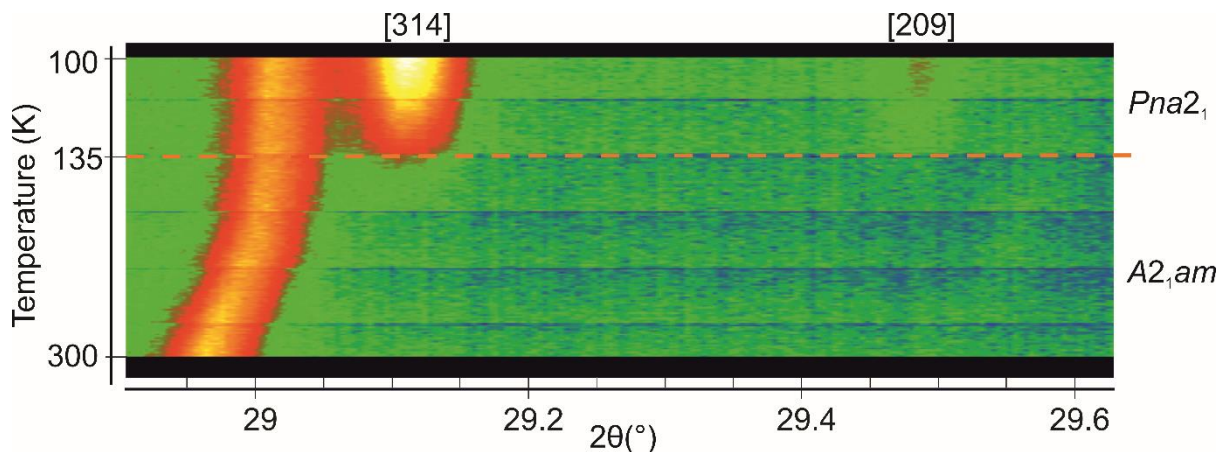


Figure 6.22. Evolution of specific diffraction peaks from SXRD of $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ with temperature

6.3.3.4 Structural characterisation of $\text{Li}_2\text{SrNbTaO}_7$

6.3.3.4.1 Synchrotron X-ray diffraction data

SXRD data collected from $\text{Li}_2\text{SrNbTaO}_7$ could be indexed using an A-centred orthorhombic unit cell ($a = 5.579$ Å, $b = 5.585$ Å, $c = 18.087$ Å), which is $\sqrt{2} \times \sqrt{2} \times 2$ geometric expansion of the aristotype unit cell of $n = 2$ Ruddlesden-Popper structure. The $A2_1am$ model analogous to the room temperature structure of $\text{Li}_2\text{SrTa}_2\text{O}_7$ ⁹⁰ but with Ta replaced by a 1:1 disordered mixture of Nb and Ta were constructed and refined against the SXRD data to achieve a good fit to the data as shown in Figure 6.23. The room temperature $A2_1am$ model was further refined against the SXRD data collected down to 100 K and the extracted lattice parameters were

plotted against the temperature; which do not show any indication of phase transition as shown in Figure 6.24.

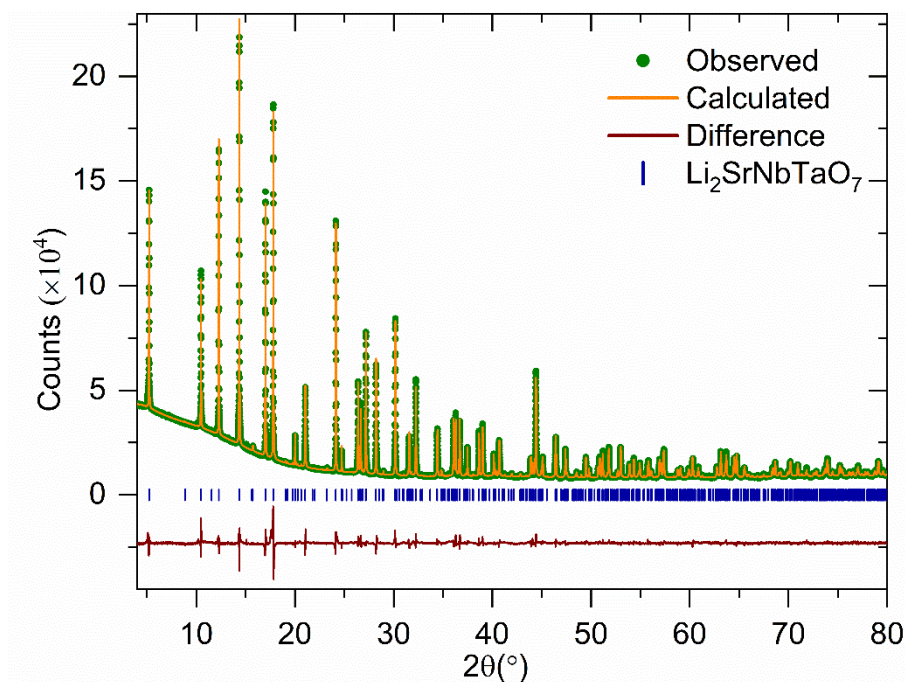


Figure 6.23. Observed, calculated and difference plots from the structure refinement of $\text{Li}_2\text{SrNbTaO}_7$ against the SXRD data collected at room temperature.

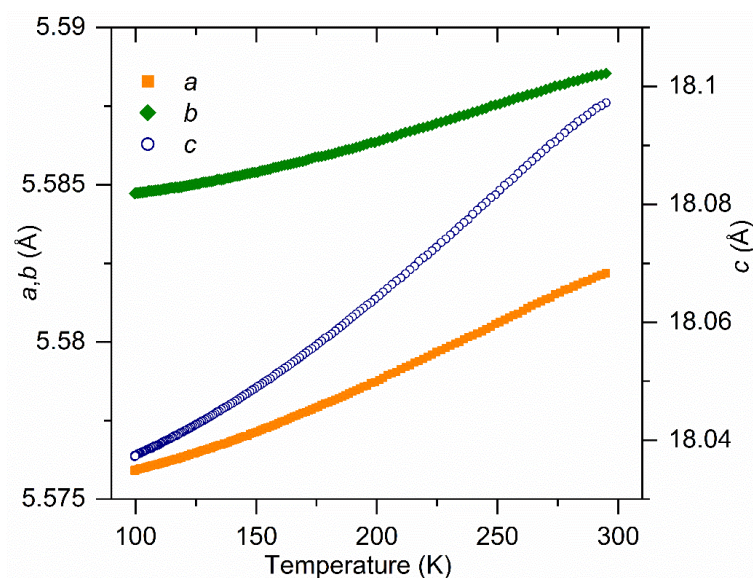


Figure 6.24. Evolution of lattice parameters with temperature as obtained from the structural refinement of $\text{Li}_2\text{SrNbTaO}_7$.

6.3.3.4.2 Room temperature neutron diffraction data

Room temperature neutron powder diffraction (NPD) data collected from $\text{Li}_2\text{SrNbTaO}_7$ can be indexed using an orthorhombic unit cell ($a = 5.58 \text{ Å}$, $b = 5.586 \text{ Å}$, $c = 18.09 \text{ Å}$) which is

consistent with a $\sqrt{2} \times \sqrt{2} \times 1$ geometric expansion of an undistorted aristotype $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Extinction conditions observed in the powder diffraction data are consistent with an A -centered unit cell. The $A2_1am$ structure model along with some other related structure models with different octahedral tilting distortions as listed in Table 6.3 were constructed and refined against the NPD data collected at room temperature. An $a^-a^-c^+/a^-a^-(-c^+)$ distorted structure described in space group $Pna2_1$ (#33) was also considered, as structures of this type have been observed for other $Li_2AB_2O_7$ Ruddlesden-Popper phases.^{89,91–93,95}

The best numerical fits to the data were achieved for the models described in space groups $A2_1am$ and $Pna2_1$ as shown in 6.3. The fitting statistics from the refinement of the $Pna2_1$ model ($wR_p = 5.51\%$, $R_p = 5.68\%$) are comparable to those from the $A2_1am$ structural model ($wR_p = 5.48\%$, $R_p = 5.45\%$). To assign the correct structure we examined the displacement of the cations in the refined models. In the $Pna2_1$ structure, x co-ordinate of Li (1), Sr and Nb/Ta (1) are within the error of the corresponding special positions. In contrast, the displacements of cations from the special position along a -direction are real (considering the error) in the refined $A2_1am$ structure as shown in Table 6.4. There are two sites for Nb/Ta in the $Pna2_1$ structure in contrast to only one site in $A2_1am$. The bond valence sums of the two B -sites are slightly different. Also, careful inspection of the refinement plot indicates some intensities in the calculated pattern using the $Pna2_1$ space group where there is no peak in the observed plot (Figure 6.25). Hence the $A2_1am$ model was selected as the correct structure description for $Li_2SrNbTaO_7$ at room temperature. Full details of the refined structure of $Li_2SrNbTaO_7$ are given in Table 6.5, with a plot of the fitted diffraction pattern shown in Figure 6.26.

Li ₂ SrNbTaO ₇ , Room temperature			
	Glazer tilt	wR_p	R_p
$Amam$	$a^-a^-c^0/a^-a^-c^0$	5.568	5.508
$A2_1am$	$a^-a^-c^+/a^-a^-c^+$	5.482	5.446

<i>Pnam</i>	$a^-a^-c^+/a^-a^-(-c^+)$	6.342	6.736
<i>Pna2₁</i>	$a^-a^-c^+/a^-a^-(-c^+)$	5.513	5.682

Table 6.3. Fitting statistics from the structural refinement of different models of $\text{Li}_2\text{SrNbTaO}_7$ against the neutron diffraction data collected at room temperature.

$\text{Li}_2\text{SrNbTaO}_7$, Room temperature					
Space Group		x	y	z	BVS
<i>A2₁am</i>	Li	0.7417(44)	0.9956(60)	0.2408(4)	0.909
	Sr	0.5065(22)	0.2474(7)	0	2.220
	Nb/Ta	0.0126(7)	0.2541(6)	0.1153(1)	5.048
<i>Pna2₁</i>	Li (1)	0.0053(74)	0.2606(93)	0.2726(7)	0.897
	Li (2)	0.4629(33)	0.7343(48)	0.7499(9)	0.949
	Sr	0.7490(32)	0.9992(8)	0.0106(4)	2.234
	Nb/Ta (1)	0.7527(30)	0.9959(14)	0.3919(3)	5.016
	Nb/Ta (2)	0.7543(33)	0.9997(12)	0.6221(3)	5.134

Table 6.4. Fractional coordinates and bond valence sums from the structural refinement of the *A2₁am* and the *Pna2₁* model of $\text{Li}_2\text{SrNbTaO}_7$ against the NPD data collected at room temperature.

Atom	Site	x	y	z	Occ.	B _{eq} (Å ²)
Li	8b	0.7417(44)	0.9956(60)	0.2408(4)	1	0.73(12)
Sr	4a	0.5065(22)	0.2474(7)	0	1	0.81(4)
Nb/Ta	8b	0.0126(7)	0.2541(6)	0.1153(1)	0.5/0.5	0.18(2)
O1	4a	0.9936(16)	0.2165(8)	0	1	0.72(8)
O2	8b	0.7494(21)	0.9965(21)	0.4028(1)	1	0.34(4)
O3	8b	0.2506(24)	0.9959(21)	0.8868(1)	1	0.52(5)
O4	8b	0.0118(12)	0.2745(6)	0.2181(1)	1	0.61(3)
$\text{Li}_2\text{SrNbTaO}_7$ – space group <i>A2₁am</i> (#36) $a = 5.58008(4)$ Å, $b = 5.58654(4)$ Å, $c = 18.09049(10)$ Å, volume = 563.941(6) Å ³ Formula weight = 487.350 g mol ⁻¹ , Z = 4 Radiation source: Neutron Time of Flight Temperature: 298 K R _p = 5.446 %, wR _p = 5.482 %						

Table 6.5. Parameters from the structural refinement of $\text{Li}_2\text{SrNbTaO}_7$ against the powder neutron diffraction data collected at room temperature.

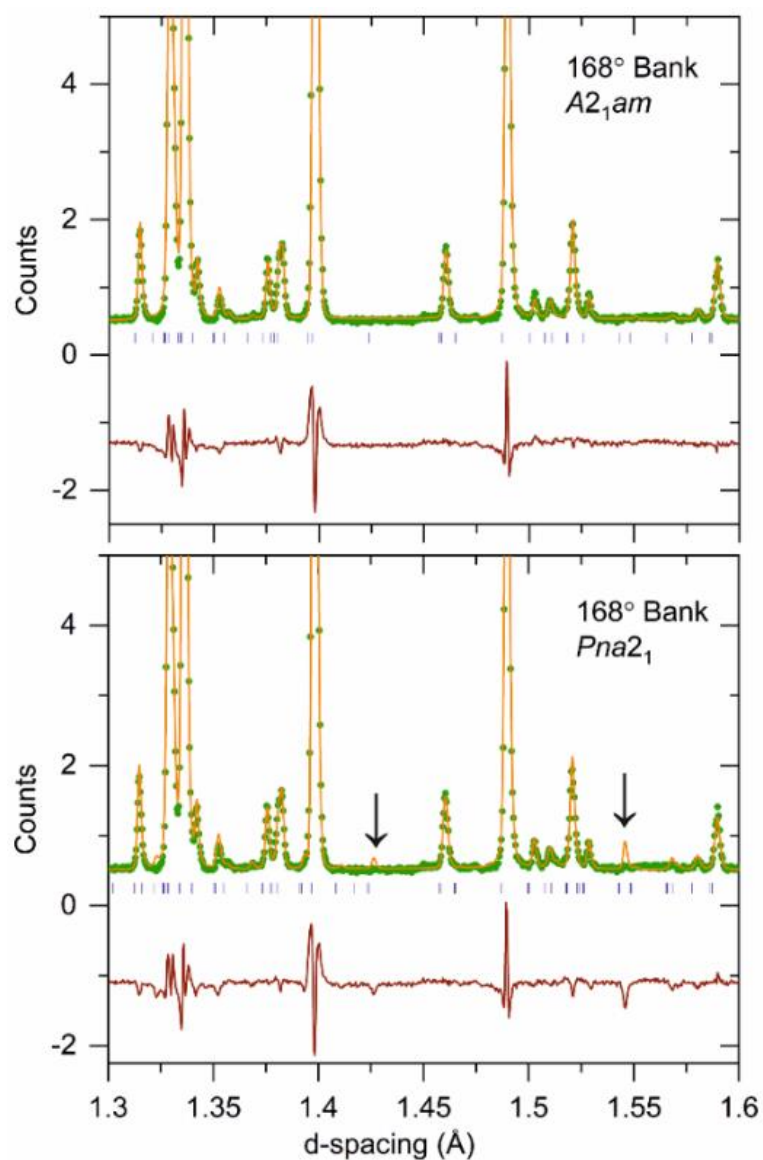


Figure 6.25. Observed, calculated and difference plots from the structural refinement of $A2_1am$ and $Pna2_1$ models in the d -spacing range 1.3 Å to 1.6 Å with respect to the powder neutron diffraction data collected from $\text{Li}_2\text{SrNbTaO}_7$ at room temperature. The black arrows indicate the positions where the $Pna2_1$ structure results in extra intensity.

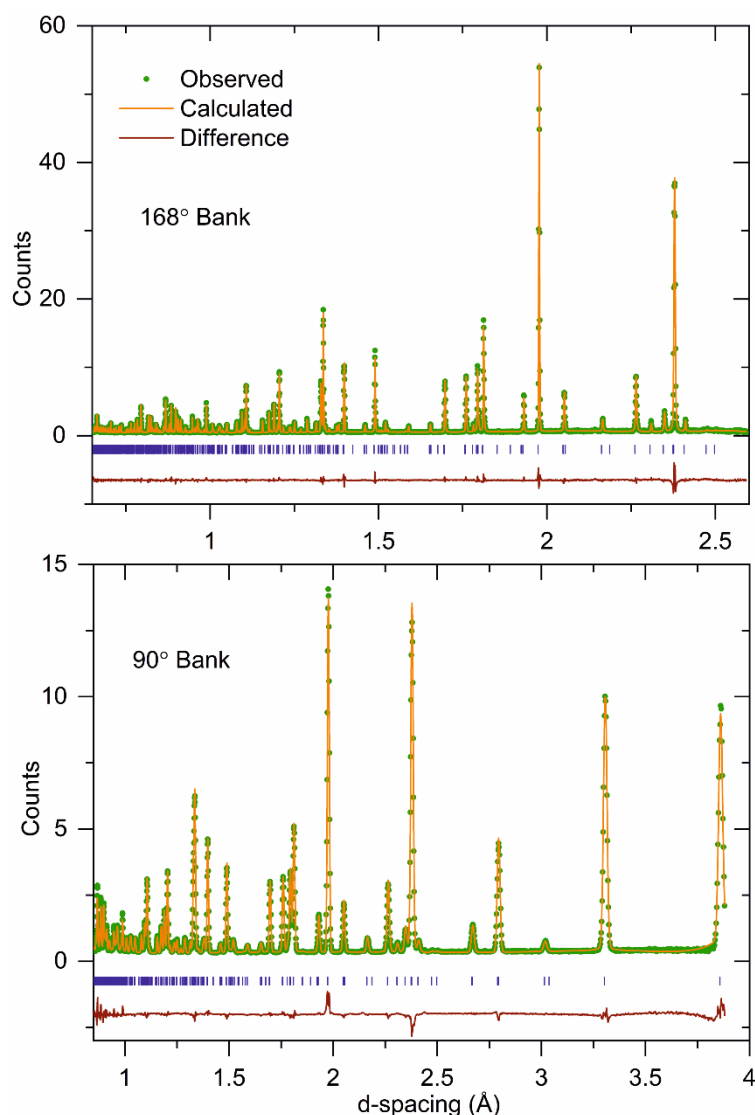


Figure 6.26. Observed, calculated and difference plots from the structural refinement of the $A2_1am$ model of $\text{Li}_2\text{SrNbTaO}_7$ against the powder neutron diffraction data collected at room temperature.

6.3.3.4.3 10 K neutron diffraction data

A similar procedure was followed for the structural characterization of $\text{Li}_2\text{SrNbTaO}_7$ at 10 K as described above for the 298 K data. $\text{Li}_2\text{SrNbTaO}_7$ is isostructural at 298 K and 10 K. Comparison of fitting statistics for the refinement of different structure models against the neutron diffraction data collected at 10 K is shown in Table 6.6. The fractional coordinates and bond valence sums of the cations as obtained from the refinement of $A2_1am$ and $Pna2_1$ symmetry model are listed in Table 6.7; which shows the displacements of cations are real in the $A2_1am$ structure whereas the displacements of several cations in the $Pna2_1$ structure are

within the errors of the corresponding special positions. Also, careful inspection of the refinement plot indicates some intensities in the calculated pattern using the $Pna2_1$ space group where there is no peak in the observed plot (Figure 6.27). Full details of the refined parameters at 10 K are shown in Table 6.8. Observed, calculated and difference plots from the refinement of the $A2_1am$ model of $\text{Li}_2\text{SrNbTaO}_7$ at 10 K are shown in Figure 6.28.

$\text{Li}_2\text{SrNbTaO}_7$; 10 K			
	Glazer tilt	wR_p	R_p
$Amam$	$a^-a^-c^0/a^-a^-c^0$	5.803	4.902
$A2_1am$	$a^-a^-c^+/a^-a^-c^+$	5.594	4.769
$Pnam$	$a^-a^-c^+/a^-a^-(-c^+)$	5.856	4.994
$Pna2_1$	$a^-a^-c^+/a^-a^-(-c^+)$	6.067	5.300

Table 6.6. Fitting statistics from the structural refinement of different models of $\text{Li}_2\text{SrNbTaO}_7$ against the neutron diffraction data collected at 10 K.

$\text{Li}_2\text{SrNbTaO}_7$; 10 K					
Space Group		x	y	z	BVS
$A2_1am$	Li	0.7887(50)	0.0010(67)	0.2390(3)	0.933
	Sr	0.5254(12)	0.2464(5)	0	2.283
	Nb/Ta	0.0388(7)	0.2535(5)	0.1155(1)	5.045
$Pna2_1$	Li (1)	0.0039(125)	0.2570(150)	0.2749(8)	0.943
	Li (2)	0.4893(141)	0.7459(183)	0.7558(10)	0.918
	Sr	0.7529(37)	0.9982(6)	0.0114(4)	2.292
	Nb/Ta (1)	0.7450(36)	0.9916(12)	0.3917(4)	4.982
	Nb/Ta (2)	0.7493(44)	0.0018(12)	0.6224(3)	5.172

Table 6.7. Fractional coordinates and bond valence sums from the structural refinement of the $A2_1am$ and the $Pna2_1$ model of $\text{Li}_2\text{SrNbTaO}_7$ against the NPD data collected at 10 K.

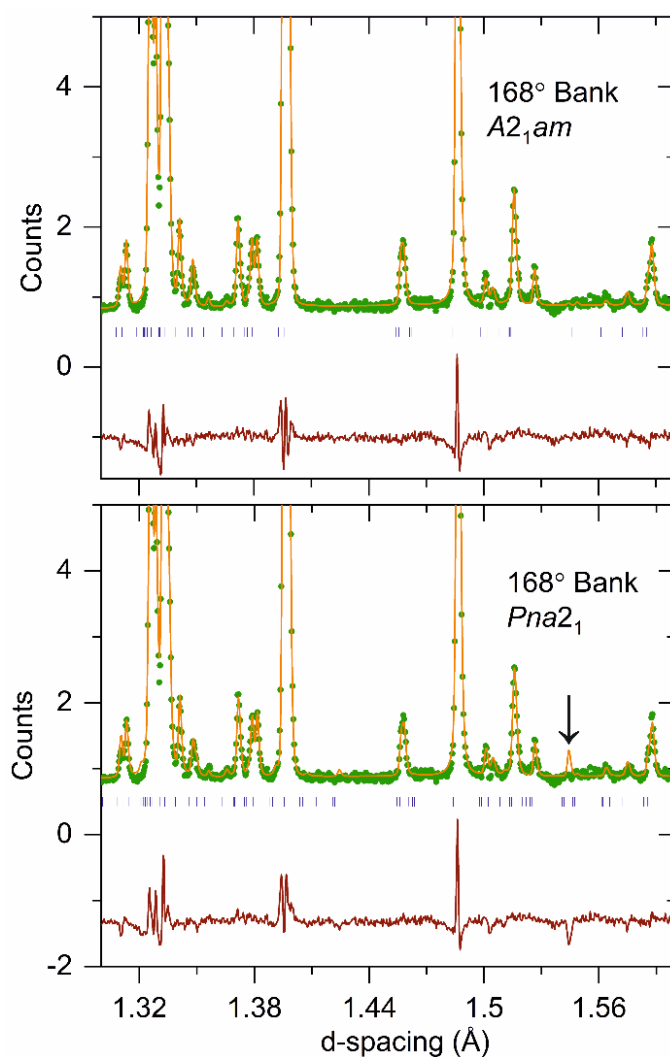


Figure 6.27. Observed, calculated and difference plots from the structural refinement of the $A2_1am$ and $Pna2_1$ model against the NPD data collected from $Li_2SrNbTaO_7$ at 10 K. The black arrow indicates the positions where the $Pna2_1$ structure results in extra intensity.

Atom	Site	x	y	z	Occ.	$B_{eq} (\text{\AA}^2)$
Li	8b	0.7887(50)	0.0010(67)	0.2390(3)	1	0.31(9)
Sr	4a	0.5254(12)	0.2464(5)	0	1	0.32(4)
Nb/Ta	8b	0.0388(7)	0.2535(5)	0.1155(1)	0.5/0.5	0.05(2)
O1	4a	0.0331(24)	0.2094(5)	0	1	0.51(6)
O2	8b	0.7821(20)	0.0038(20)	0.4042(1)	1	0.14(4)
O3	8b	0.2868(16)	0.0038(21)	0.8852(1)	1	0.23(4)
O4	8b	0.0214(8)	0.2795(4)	0.2187(1)	1	0.27(4)
$Li_2SrNbTaO_7$ – space group $A2_1am$ (#36) $a = 5.57167(3) \text{ \AA}$, $b = 5.58247(3) \text{ \AA}$, $c = 18.02559(10) \text{ \AA}$, volume = $560.662(6) \text{ \AA}^3$ Formula weight = $487.350 \text{ g mol}^{-1}$, $Z = 4$						

Radiation source: Neutron Time of Flight

Temperature: 10 K

$R_p = 4.769 \%$, $wR_p = 5.594 \%$

Table 6.8. Parameters from the structural refinement of $\text{Li}_2\text{SrNbTaO}_7$ against the powder neutron diffraction data collected at 10 K.

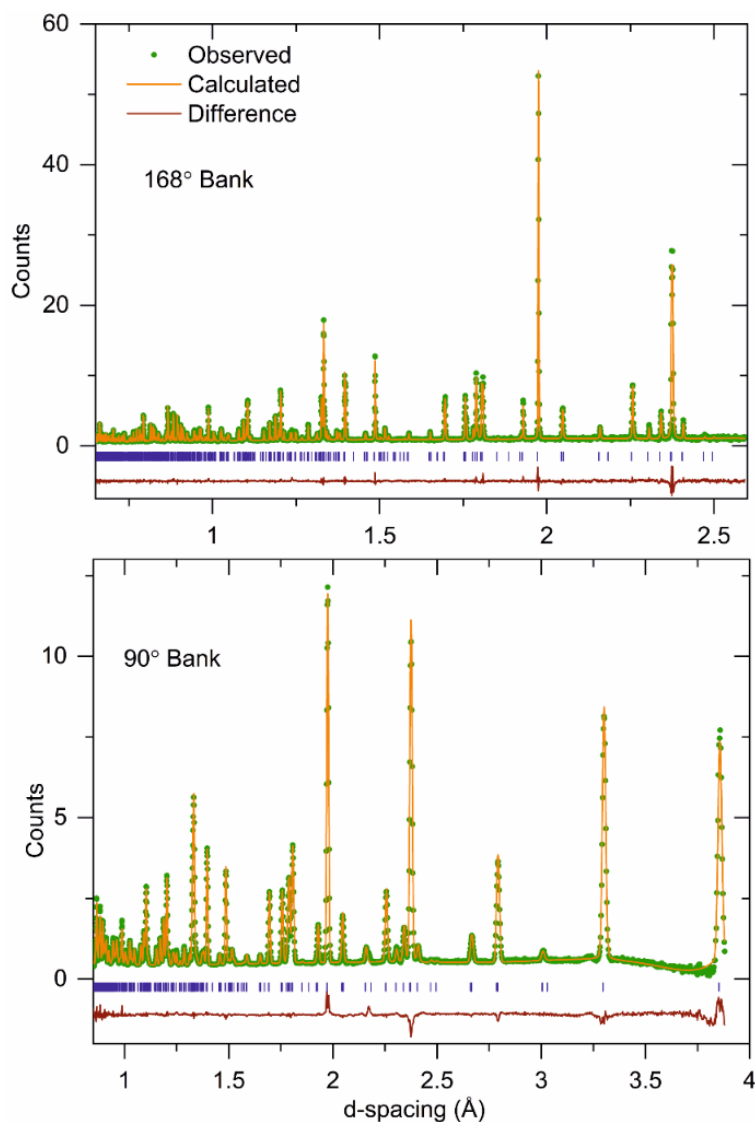


Figure 6.28. Observed, calculated and difference plots from the structure refinement of $\text{Li}_2\text{SrNbTaO}_7$ against the powder neutron diffraction data collected at 10K.

6.3.3.5 Structural characterisation of $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$

6.3.3.5.1 Synchrotron X-ray diffraction data

SXRD data collected from $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$ could be indexed using an *A*-centred orthorhombic unit cell ($a = 5.584 \text{ \AA}$, $b = 5.591 \text{ \AA}$, $c = 17.993 \text{ \AA}$), which is $\sqrt{2} \times \sqrt{2} \times 2$

geometric expansion of the aristotype unit cell of $n = 2$ Ruddlesden-Popper structure. The $A2_1am$ model analogous to the room temperature structure of $\text{Li}_2\text{SrNb}_2\text{O}_7$ ⁸⁸ was constructed and refined against the SXRD data to achieve a good fit as shown in Figure 6.29.

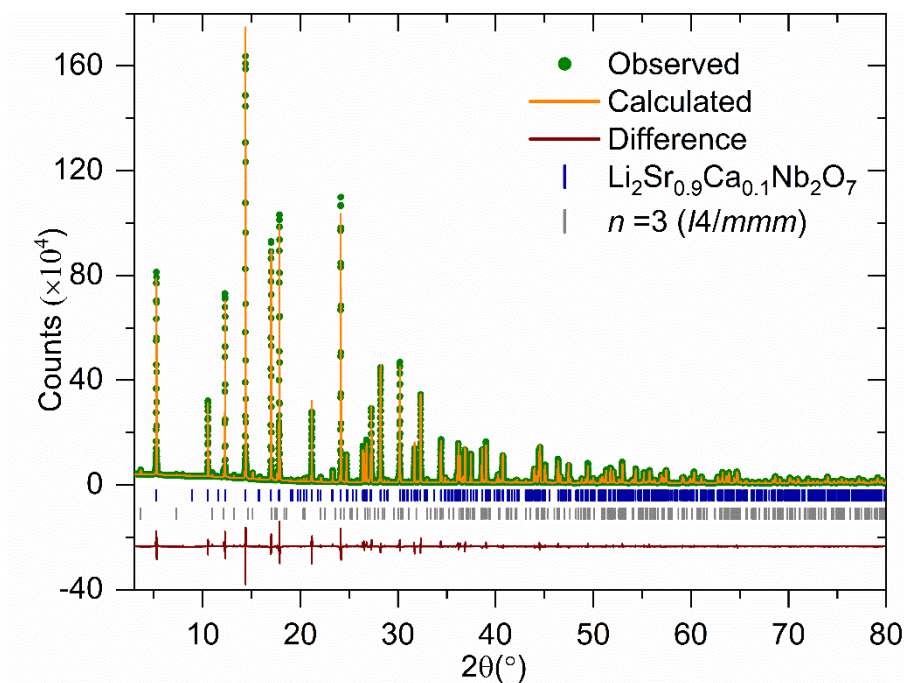


Figure 6.29. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$ against the SXRD data collected at 300 K. An $n = 3$ phase with $I4/mmm$ symmetry was added as a secondary phase.

$\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$ was warmed from 100 K to 300 K and diffraction patterns were collected. The $A2_1am$ model was refined against the diffraction data and the lattice parameters were extracted; which were plotted against the temperature (Figure 6.30). The lattice parameters show a clear anomaly around 278 K as shown in Figure 6.30, which indicates the high-temperature $A2_1am$ to low temperature $Pna2_1$ phase transition. Figure 6.31 shows a plan-view of the selected region of the diffraction patterns collected from $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$ between 300 K and 100 K. The appearance of $[114]$, $[314]$ and $[209]$ peaks at 278 K confirms the phase transition to the $Pna2_1$ structure.

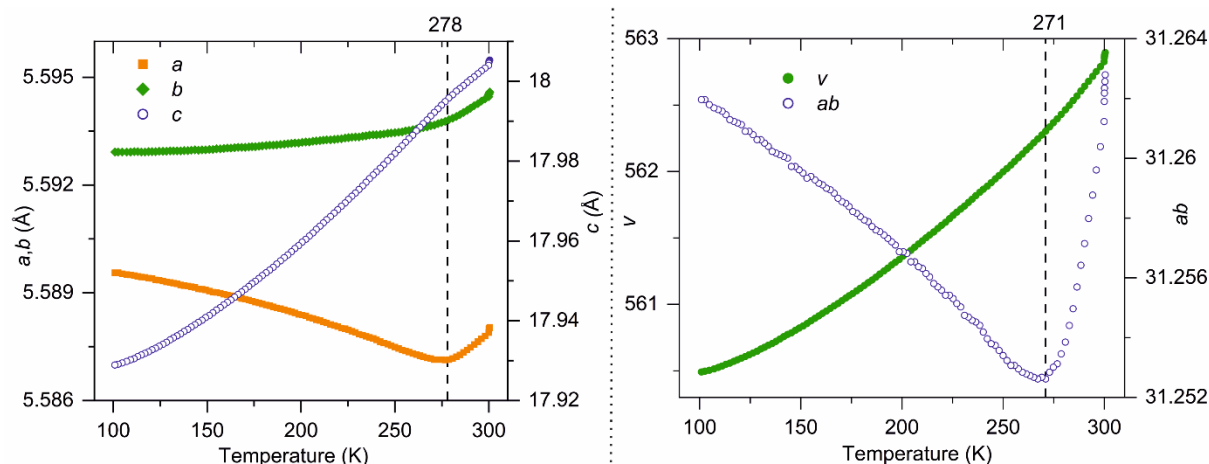


Figure 6.30. Evolution of lattice parameters, ab and volume (v) with temperature as obtained from structural refinement of $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$.

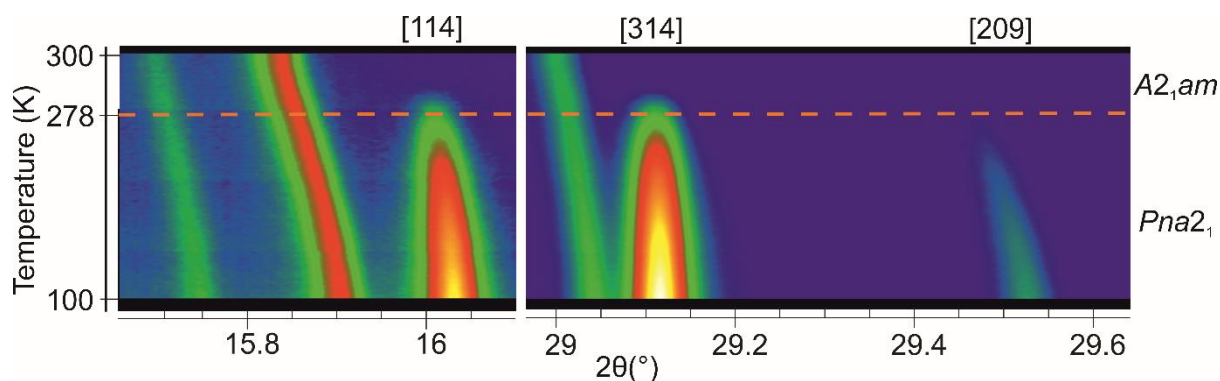


Figure 6.31. Evolution of specific diffraction peaks from SXRD of $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$ with temperature.

6.3.4 Discussion for the $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ phases

We can analyse the $A2_1am$ and $Pna2_1$ structure of $\text{Li}_2\text{SrNb}_2\text{O}_7$ in terms of the distortion modes which need to be applied to get the distorted structures from the aristotype $I4/mmm$ symmetry structure. Let's consider the $A2_1am$ structure first. The NbO_6 octahedra adopt an $a^-a^-c^0/a^-a^-c^0$ tilting distortion in the xy -plane, described by the X_3^- irreducible representation of the aristotype $I4/mmm$ structure, and an in-phase $a^0a^0c^+/a^0a^0c^+$ rotation around the z -axis, described by the X_2^+ irreducible representation. This combination of X_3^- and X_2^+ tilting distortion results in a structure that cannot be described in a centrosymmetric space group, but which retains the inversion symmetry in the arrangement of atoms. However, the presence of these two nonpolar

distortion modes in combination couple to a third polar Γ_5^- distortion mode via a trilinear coupling mechanism to yield the hybrid improper polar $A2_1am$ structure of $\text{Li}_2\text{SrNb}_2\text{O}_7$.

Now for the $Pna2_1$ structure, the $a^-a^-c^0/a^-a^-c^0$ tilting of NbO_6 octahedra in the xy -plane described by the X_3^- distortion mode is accompanied by the $a^0a^0c^+/a^0a^0-c^+$ rotation of NbO_6 octahedra along the z -axis, described by the X_2^+ irreducible representation. The combination of these two distortion modes yields a centrosymmetric structure, described by the $Pnam$ space group. But interestingly, these two modes do not couple to or stabilize a third polar mode via the trilinear coupling mechanism. The bulk polarity of the $Pna2_1$ structure comes from the Γ_3^- distortion mode. The stabilisation of the Γ_3^- distortion mode, which breaks the inversion symmetry of the low-temperature structure of $\text{Li}_2\text{SrNb}_2\text{O}_7$, arises from a conventional or proper mechanism. The out of centre displacement of the SOJT active Nb^{5+} cation allows the mixing of the empty $4d$ and filled oxygen $2p$ orbitals, which lowers the energy of the system as well as lowers the crystal symmetry, which drives the Γ_3^- distortion in the $Pna2_1$ structure of $\text{Li}_2\text{SrNb}_2\text{O}_7$.

Substitution of Nb by Ta moves the phase transition to a lower temperature or in other words, the stability region of the $Pna2_1$ phase moves to a lower temperature. Niobium involves its $4d$ orbitals to hybridise with the oxygen $2p$ orbitals, whereas, tantalum involves its $5d$ orbitals. As $2p$ orbitals are energetically closer to the Nb- $4d$ orbitals than the Ta- $5d$ orbitals, the hybridisation between the Nb- $4d$ and O- $2p$ orbitals is stronger than the hybridisation between the Ta- $5d$ and O- $2p$ orbitals. Therefore, with Ta-substitution, the SOJT distortion becomes weaker and the transition temperature moves to a lower temperature. This drop in the transition temperature with Ta-substitution is very sharp as evidenced by the neutron diffraction study of $\text{Li}_2\text{SrNbTaO}_7$, which confirms that the $\text{Li}_2\text{SrNbTaO}_7$ phase adopts an $A2_1am$ structure at room temperature as well as temperatures down to 10 K. The $A2_1am$ phase is also the most stable structure of the $\text{Li}_2\text{SrTa}_2\text{O}_7$ phase⁹⁰ at 5 K as well as at 300 K.

Substitution of only 10% Sr by Ca in the $\text{Li}_2\text{SrNb}_2\text{O}_7$ structure significantly increases the transition temperature to 278 K from 211 K. The ionic radius of Ca^{2+} is smaller than Sr^{2+} , hence by introducing Ca in the A-site of layered perovskite structure, the tolerance factor is lowered. As a result, the tilting and rotation of the NbO_6 octahedra are enhanced. An increase in the $A2_1am$ to $Pna2_1$ phase transition temperature indicates that although the SOJT mechanism is the origin of polarity in the $Pna2_1$ phase, the introduction of a smaller A-cation enhances this effect.

The ionic radii of Ta^{5+} and Nb^{5+} are essentially the same. So, we would not expect much change in the lattice parameters or volume with Ta substitution in the $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ phase. But as shown in Figure 6.32, the c -lattice parameter and the volume of the unit cell increase significantly with Ta substitution. In contrast, the a - and b -lattice parameters decrease with more Ta-content in the unit cell, but the change in a - and b -lattice parameters is insignificant compared to the change in the c -lattice parameter. This large increase in c and hence in volume can be explained by considering the tilting distortions of the $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ phase. Figure 6.32 (Right) shows the Nb-O-Nb bond angle which can be used as a measure of the a^-a^- tilt angle. The larger is the tilt, the smaller is the angle and without any tilting distortion, the angle would be 180° . If we consider the NbO_6 octahedra as rigid units then straightening the Nb-O-Nb bond will increase the c -lattice parameter. Hence c -lattice parameter will be shortened as a result of stronger a^-a^- tilting. Table 6.9 lists the distortion mode magnitudes as extracted from the room temperature $A2_1am$ structure of $\text{Li}_2\text{SrTa}_2\text{O}_7$ and $\text{Li}_2\text{SrNb}_2\text{O}_7$ with respect to their aristotype $I4/mmm$ structure. The magnitude of X_3^- distortion mode is significantly larger in the $\text{Li}_2\text{SrNb}_2\text{O}_7$ than in the $\text{Li}_2\text{SrTa}_2\text{O}_7$ phase, which is also the measure of the a^-a^- tilting distortion. Hence the larger out of phase tilting in the xy -plane of $\text{Li}_2\text{SrNb}_2\text{O}_7$ leads to a smaller c -lattice parameter than $\text{Li}_2\text{SrTa}_2\text{O}_7$ which has a smaller a^-a^- tilting.

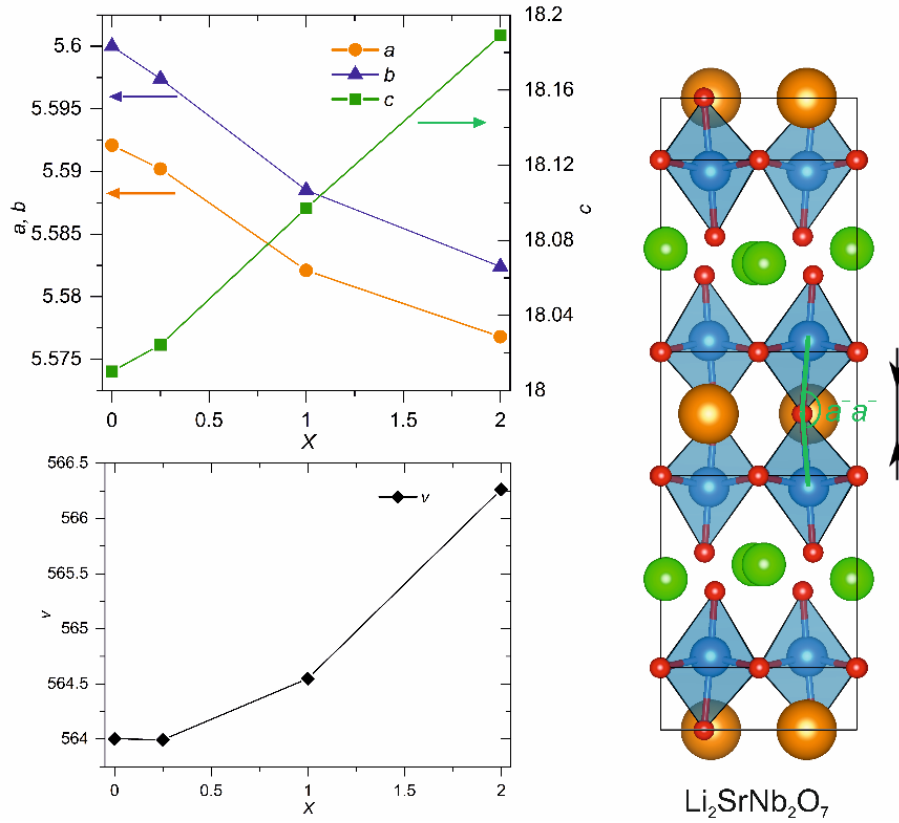


Figure 6.32. (Left) Lattice parameters and volume of the $\text{Li}_2\text{SrNb}_{2-x}\text{Ta}_x\text{O}_7$ phases at room temperature as obtained from the structural refinement against the SXRD data. (Right) The a^-a^- tilt angle of $\text{Li}_2\text{SrNb}_2\text{O}_7$.

	$\text{Li}_2\text{SrTa}_2\text{O}_7$		$\text{Li}_2\text{SrNb}_2\text{O}_7$	
	A_s	A_p	A_s	A_p
Γ_1^+	0.2059	0.1456	0.0693	0.0490
Γ_5^-	0.5456	0.3858	0.9090	0.6427
X_2^+	0.2782	0.1967	0.3207	0.2268
X_3^-	0.5536	0.3914	0.7244	0.5122

Table 6.9. Distortion mode magnitudes extracted from the room temperature $A2_1am$ structures of $\text{Li}_2\text{SrTa}_2\text{O}_7$ ⁹⁰ and $\text{Li}_2\text{SrNb}_2\text{O}_7$.⁸⁸

The phase transition of $\text{Li}_2\text{SrNb}_2\text{O}_7$ is from a high-temperature $A2_1am$ structure with $a^-a^-c^+/a^-a^-c^+$ tilting to a low-temperature $Pna2_1$ structure with $a^-a^-c^+/a^-a^-(-c^+)$ tilting of NbO_6 octahedra. This phase transition is of the first order in nature as there is a discontinuity in the tilting pattern i.e. from c^+/c^+ tilt to $c^+/-c^+$ tilt, between these two phases. Further, the phase transition shows a hysteresis of about 10 K between the heating and cooling process as can be

seen from the transition temperatures in Figure 6.17, which is very common in a first-order phase transition.

An interesting feature of the low-temperature $Pna2_1$ structure of the $\text{Li}_2\text{SrNb}_2\text{O}_7$ phase is the negative thermal expansion (NTE) of a - and b -lattice parameters. Table 6.10 lists the coefficients of thermal expansion (CTE) and coefficient of volume expansion along the principal axes for $\text{Li}_2\text{SrNb}_2\text{O}_7$, $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ and $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$ in their respective low-temperature $Pna2_1$ phase region as calculated using PASCAL⁹⁶ software. Figure 6.33 shows the expansivity indicatrix along the principal axes X_1 , X_2 and X_3 for the $Pna2_1$ phase of $\text{Li}_2\text{SrNb}_2\text{O}_7$, $\text{Li}_2\text{SrNb}_{1.75}\text{Ta}_{0.25}\text{O}_7$ and $\text{Li}_2\text{Sr}_{0.9}\text{Ca}_{0.1}\text{Nb}_2\text{O}_7$. As noticed from Figure 6.33 and Table 6.10, the a -lattice parameters of all three phases have the negative thermal expansion. Similar axial negative thermal expansion in layered perovskites has been observed before.^{97–}

¹⁰⁰ For example, $\text{Ca}_3\text{Mn}_2\text{O}_7$ has a negative thermal expansion along the c -axis in the high-temperature $Acaa$ phase,¹⁰¹ whereas the low-temperature $A2_1am$ phase shows a positive thermal expansion. In that case, the NTE has been observed as a result of symmetry trapping of the X_3^- distortion mode by the high-temperature $Acaa$ phase. X_3^- distortion mode is frozen in the $A2_1am$ phase but not in the $Acaa$ phase. In the present $\text{Li}_2\text{SrNb}_2\text{O}_7$ case, the negative expansion is observed in the low-temperature $Pna2_1$ phase. The atomic displacement which takes place as a result of symmetry lowering from the aristotype $I4/mmm$ structure to the distorted $Pna2_1$ structure can be deconvoluted into contributions from the distortion modes which need to be applied to get the distorted structure with the help of ISODISTORT⁶⁶ software. Table 6.11 shows that in addition to X_2^+ and X_3^- distortion modes which are causing the $c^+/-c^+$ and $a^-a^-c^0/a^-a^-c^0$ tilting distortions respectively, there is another M_5^- distortion mode that has significant magnitude. The M_5^- distortion mode is absent in the high-temperature $A2_1am$ phase. The M_5^- distortion mode is an antipolar mode which although causes local polarity, the polarity of one layer cancels the polarity of the next layer as shown in Figure 6.34.

The M_5^- distortion mode displaces the Nb^{5+} and Sr^{2+} cations along the x -axis. Now at low temperature, the magnitude of M_5^- distortion mode will be large and with an increase in temperature the magnitude of M_5^- , as well as the displacement of the cations along the x -direction as a result of the M_5^- mode, will decrease. This will release some strain along the x -axis which will cause the a -lattice parameter to decrease. The effect of strain release as a result of a decrease in the M_5^- distortion mode in the $Pna2_1$ structure with an increasing temperature towards the lattice parameters overcomes the effect of thermal motions towards the lattice parameters with increasing temperature.

Phase	CTE (MK^{-1}) along the principal axes			Volume (MK^{-1})
	X_1	X_2	X_3	
$Li_2SrNb_2O_7$	-4.72(6)	-3.45(2)	22.63(22)	14.52(14)
$Li_2SrNb_{1.75}Ta_{0.25}O_7$	-4.20(5)	-2.23(4)	17.69(7)	11.33(15)
$Li_2Sr_{0.9}Ca_{0.1}Nb_2O_7$	-2.60(4)	0.75(2)	21.18(30)	19.56(28)

Table 6.10. Linear coefficients of thermal expansion along the principal axis for the low-temperature $Pna2_1$ phase of $Li_2SrNb_2O_7$, $Li_2SrNb_{1.75}Ta_{0.25}O_7$ and $Li_2Sr_{0.9}Ca_{0.1}Nb_2O_7$.

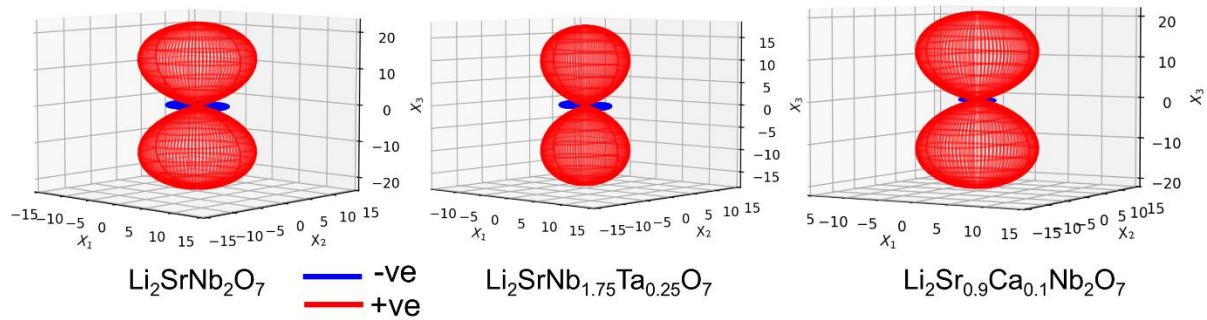


Figure 6.33. Expansivity indicatrix plots along the principal axes X_1 , X_2 and X_3 for the $Pna2_1$ phase of $Li_2SrNb_2O_7$, $Li_2SrNb_{1.75}Ta_{0.25}O_7$ and $Li_2Sr_{0.9}Ca_{0.1}Nb_2O_7$.

Distortion mode	A_s	A_p
Γ_1^+	0.19396	0.09698
Γ_3^-	0.08129	0.04065
X_2^+	0.16816	0.08408
X_4^+	0.03277	0.01639
X_1^-	0.05883	0.02941

X_3^-	1.13248	0.56624
M_5^+	0.16525	0.08263
M_5^-	0.35231	0.17616

Table 6.11. Distortion mode magnitudes extracted from the reported low-temperature $Pna2_1$ phase of $Li_2SrNb_2O_7$ with respect to the aristotype $I4/mmm$ structure.

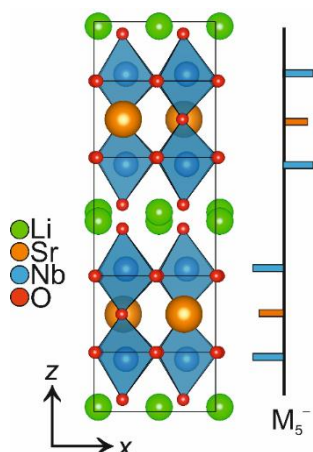


Figure 6.34. Representation of $Pna2_1$ structure of $Li_2SrNb_2O_7$. The solid bars represent the direction and magnitude of the displacement of corresponding cations as a result of the M_5^- distortion mode.

The phase diagram of the synthesized $Li_2SrNb_2O_7$, $Li_2SrTa_2O_7$ and $Li_2CaTa_2O_7$ and the solid solutions from room temperature to low temperature is shown in Figure 6.35.

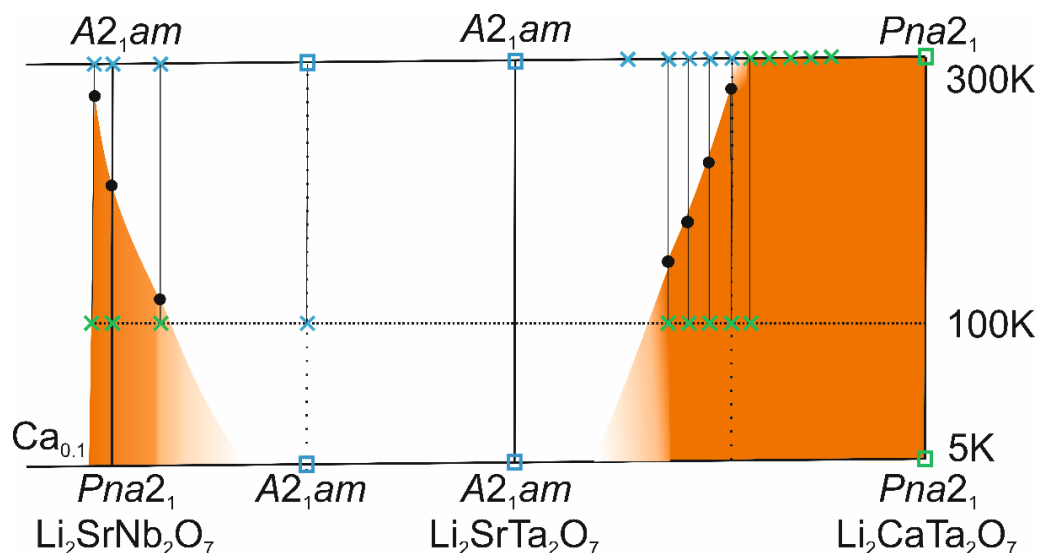


Figure 6.35. Phase diagram of $Li_2SrNb_2O_7$, $Li_2SrTa_2O_7$, $Li_2CaTa_2O_7$ and their solid solutions. Blue colour symbols indicate the $A2_1am$ structure where as the green colour symbols indicate the $Pna2_1$ structure. A cross symbol is used for the structures obtained from SXRD data and an open square is used for the structures obtained from neutron diffraction data. A filled black circle indicates the phase transition temperature.

6.4 Conclusion

$\text{Li}_2\text{SrTa}_2\text{O}_7$ and $\text{Li}_2\text{CaTa}_2\text{O}_7$ adopt $A2_1am$ and $Pna2_1$ structures respectively at room temperature as well as at low temperatures. The introduction of smaller Ca^{2+} cation in the A -site of double perovskite layers changes the crystal packing which leads to an inversion of the sense of octahedral rotation along the z -axis. $\text{Li}_2\text{SrNb}_2\text{O}_7$ adopts a hybrid improper polar structure at room temperature which can be described by the $A2_1am$ space group with $a^-a^-c^+/a^-a^-c^+$ tilting of NbO_6 octahedra. It undergoes a phase transition to a polar structure described by the $Pna2_1$ space group with $a^-a^-c^+/a^-a^-(-c^+)$ tilt. The polarity in the $Pna2_1$ phase is driven by the SOJT effect of the $4d^0\text{-Nb}^{5+}$ cation. Substitution of $4d\text{-Nb}$ by $5d\text{-Ta}$ in the $\text{Li}_2\text{SrNb}_2\text{O}_7$ structure lowers the SOJT effect which lowers the stability region of the $Pna2_1$ phase.

New $n = 2$ Ruddlesden-Popper phases with analogous structure could be prepared by trading charges between the A -site and B -site cations. For example, instead of having a $2+$ cation in the A -site, there could be a lanthanide $3+$ cation which will require the B -site to have one $4+$ and one $5+$ cations instead of two $5+$ cations. In the next chapter, the synthesis and characterisation of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ will be discussed.

Chapter 7 – Synthesis and characterisation of $\text{Li}_2\text{La}(\text{BTi})\text{O}_7$ ($B = \text{Ta, Nb}$) and $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$

7.1 Introduction

The trilinear-coupled hybrid-improper mechanism does not appear to impose any strong chemical constraints on ferroelectric materials. However, in practice, it is generally only possible to stabilize the required large-magnitude tilting distortions by including large B -site cations in the layered perovskite frameworks. As the ionic radius of metal cations declines across the transition series, the largest ions suitable for inclusion on the B -sites of layered perovskite oxides are early transition-metal cations in their group oxidation states. As a consequence many of the hybrid-improper ferroelectric phases reported to date contain Ti^{4+} ,³⁶ Zr^{4+} ,³⁷ Nb^{5+} or Ta^{5+} ^{11,42,90} on their B -sites. The presence of these d^0 transition-metal ions raises the prospect of competition between trilinear-coupled hybrid-improper stabilization and SOJT stabilization of polar distorted phases. Here two polar $n = 2$ Ruddlesden-Popper phases, $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$, the former stabilized by the trilinear-coupled hybrid-improper mechanism, the latter by an SOJT distortion, are described, and the role of the Li^+ and Na^+ cations in mediating the competition between these two classes of polar distortion are discussed.

Results from this chapter are published as: **Mallick, S.**; Fortes, A. W.; Zhang, W.; Halasyamani, Hayward, M. A. Switching between Proper and Hybrid-Improper Polar Structures via Cation Substitution in $\text{A}_2\text{La}(\text{TaTi})\text{O}_7$ ($A = \text{Li, Na}$). *Chem. Mater.* **2021**, 33 (7), 2666–2672.

7.2 synthesis

Polycrystalline samples of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ were synthesized by high-temperature solid-state synthesis from La_2O_3 (99.999%, dried at 900 °C), TiO_2 (99.995%),

Ta₂O₅ (99.993%, dried at 900 °C) or Nb₂O₅ (99.9985%, dried at 900 °C) and Li₂CO₃ (99.999%). Suitable stoichiometric ratios of the oxides were ground together in an agate mortar and pestle and mixed with a 10% excess of Li₂CO₃ to compensate for the weight loss due to volatilization at high temperatures. These mixtures were then placed in alumina crucibles and heated at 850 °C for 12 h in air, reground, and pressed into 13 mm diameter pellets. Samples of Li₂La(TaTi)O₇ and Li₂La(NbTi)O₇ were then heated in flowing oxygen for three periods of 6 h at 1200 °C or three periods of 6 h at 1250 °C respectively. An oxygen atmosphere is required to avoid the formation of LaTiO₃ as a secondary phase.

Polycrystalline samples of Na₂La(TaTi)O₇ were synthesized by high-temperature solid-state synthesis from La₂O₃ (99.999%, dried at 900 °C), TiO₂ (99.995%), Ta₂O₅ (99.993%, dried at 900 °C) or Nb₂O₅ (99.9985%, dried at 900 °C) and Na₂CO₃ (>99 %). Suitable stoichiometric ratios of the oxides were ground together in an agate mortar and pestle and mixed with a 5% excess of Na₂CO₃ to compensate for the weight loss due to volatilization at high temperatures. These mixtures were then placed in alumina crucibles and heated at 850 °C for 12 h in air, reground, and pressed into 13 mm diameter pellets. Samples of Na₂La(TaTi)O₇ were heated in air for three periods of 30 min at 1100 °C. This specific heating regimen was required to avoid the formation of Na₂La₂Ti₃O₁₀ as a secondary phase

7.3 Results

7.3.1 Optical SHG measurements

Powder SHG data collected from Li₂La(TaTi)O₇, Li₂La(NbTi)O₇ and Na₂La(TaTi)O₇ indicate that all three compounds are SHG active and the activity is 0.78, 0.75 and 0.53 times of α-SiO₂ respectively. This observation indicates that all three phases adopt non-centrosymmetric crystal structures.

7.3.2 Structural characterization of Li₂La(TaTi)O₇

7.3.2.1 Room temperature synchrotron X-ray diffraction data

Synchrotron X-ray diffraction (SXR) data collected from $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ can be indexed using an orthorhombic unit cell ($a = 5.496 \text{ \AA}$, $b = 5.511 \text{ \AA}$, $c = 18.229 \text{ \AA}$). This unit cell is consistent with an $a' = \sqrt{2}a$, $b' = \sqrt{2}b$, $c' = c$ expansion of an undistorted aristotype, $I4/mmm$ symmetry unit cell of an $n = 2$ pseudo-Ruddlesden-Popper phase. Extinction conditions observed in the powder diffraction data are consistent with an A-centered unit cell. Symmetry analysis of the $n = 2$ Ruddlesden-Popper framework,^{42,66} in combination with the observation that $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ is SHG active (activity 0.78 times $\alpha\text{-SiO}_2$), suggests an $a^-a^-c^+/a^-a^-c^+$ distorted structure described in space group $A2_1am$ (#36), analogous to the reported room-temperature structure of $\text{Li}_2\text{SrNb}_2\text{O}_7$,⁸⁸ in which the Li^+ cations reside in tetrahedral sites within the rock salt layers. There is no evidence for any Ta/Ti ordering, so a model based on the room-temperature structure $\text{Li}_2\text{SrNb}_2\text{O}_7$,⁸⁸ but with Sr replaced by La and Nb replaced by a 1:1 disordered mixture of Ta:Ti was constructed and refined against the SXR data to achieve a good fit as shown in Figure 7.1.

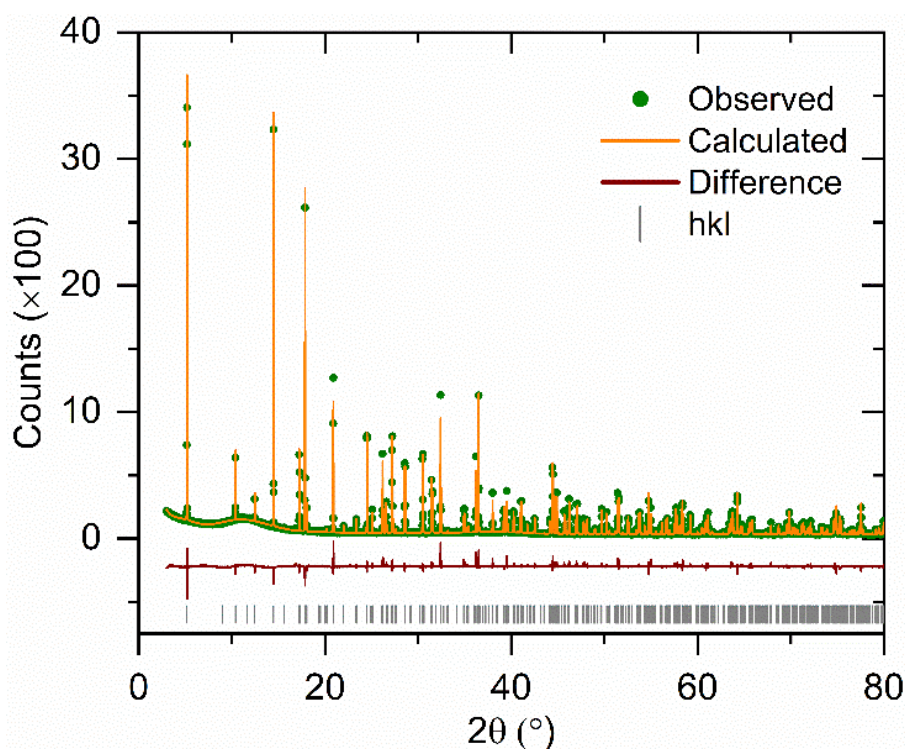


Figure 7.1. Observed, calculated and difference plots from the refinement of a structural model in space group $A2_1am$ against high-resolution X-ray synchrotron data collected from $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ at room temperature.

7.3.2.2. Room temperature neutron diffraction data

Neutron powder diffraction (NPD) data collected from $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ can be indexed using an orthorhombic unit cell ($a = 5.496 \text{ \AA}$, $b = 5.511 \text{ \AA}$, $c = 18.229 \text{ \AA}$) which is consistent with a $\sqrt{2} \times \sqrt{2} \times 1$ geometric expansion of an undistorted aristotype $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Extinction conditions observed in the powder diffraction data are consistent with an A -centered unit cell. The $A2_1am$ structure model along with some other related structure models with different octahedral tilting distortions as listed in Table 7.1 were constructed and refined against the NPD data collected at room temperature. An $a^-a^-c^+/a^-a^-(-c^+)$ distorted structure described in space group $Pna2_1$ (#33) was also considered, as structures of this type have been observed for other $\text{Li}_2\text{AB}_2\text{O}_7$ Ruddlesden-Popper phases.^{89,91}

The best numerical fits to the data are achieved by the models described in space groups $A2_1am$ and $Pna2_1$ as shown in Table 7.1. The fitting statistics from the refinement of the $Pna2_1$ model ($wR_p = 5.88\%$, $R_p = 5.87\%$) are comparable to those from the $A2_1am$ structural model ($wR_p = 5.98\%$, $R_p = 5.78\%$). To assign the correct structure, the displacement of the cations in the refined models were examined. The $8b$ Li and Ti/Ta sites present in the $A2_1am$ model are split into two $4a$ sites each in the $Pna2_1$ model, as shown in Table 7.2. It can be seen that although c is the polar direction for the $Pna2_1$ model, there is mirror symmetry present between two Li sites along c direction (Li(1) $z = 0.24 = 0.5 - 0.26$; Li(2) $z = 0.76 = 0.5 + 0.26$). In addition, the z -coordinate of La remains at $z = 0$, within error, again consistent with the presence of a mirror plane perpendicular to the z -axis. Therefore, the atomic configuration obtained using the $Pna2_1$ model is centrosymmetric, within error which is not physically reasonable given the SHG activity of the phase. In contrast, the polar displacements of cations in the $A2_1am$ structure (parallel to the x -axis) are significant considering the errors. Further, close inspection of the diffraction pattern reveals peak intensities in the calculated pattern for the $Pna2_1$ structure

which are not observed in the diffraction data, as shown in Figure 7.2. Hence the $A2_1am$ structural model is preferred over the $Pna2_1$ model. Full details of the refined structure of $Li_2La(TaTi)O_7$ are given in Table 7.3, with a plot of the fitted diffraction data shown in Figure 7.3. Selected bond lengths are given in Table 7.4.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
$Acam$ (#64)	$a^0a^0c^+/a^0a^0c^+$	54	10.33	11.09
$Amam$ (#63)	$a^-a^-c^0/a^-a^-c^0$	58	6.109	5.888
$A2_1am$ (#36)	$a^-a^-c^+/a^-a^-c^+$	68	5.985	5.778
$Pnam$ (#62)	$a^-a^-c^+/a^-a^-(-c^+)$	68	6.070	5.920
$Pna2_1$ (#33)	$a^-a^-c^+/a^-a^-(-c^+)$	90	5.889	5.876

Table 7.1. Fitting statistics from the structural refinement of $Li_2La(TaTi)O_7$ against the neutron powder diffraction data collected at 298 K.

	atom	site	x	y	z	BVS
$A2_1am$	Li	8b	0.6847(21)	0.0038(47)	0.2412(4)	0.916
	La	4a	0.4345(19)	0.2406(5)	0	3.051
	Ta/Ti	8b	0.9343(78)	0.2478(22)	0.1179(3)	4.656
$Pna2_1$	Li (1)	4a	0.0208(63)	0.2551(69)	0.2447(13)	1.099
	Li (2)	4a	0.5104(65)	0.2611(66)	0.7610(11)	0.831
	La	4a	0.7491(27)	0.0095(5)	0.9995(5)	3.050
	Ta/Ti (1)	4a	0.7689(83)	0.9788(50)	0.3760(14)	4.834
	Ta/Ti (2)	4a	0.7690(74)	0.0142(41)	0.6110(11)	4.637

Table 7.2. Fractional coordinates and bond valence sums from the structural refinement of $Li_2La(TaTi)O_7$ against NPD data collected at 298 K using models in space groups $A2_1am$ and $Pna2_1$.

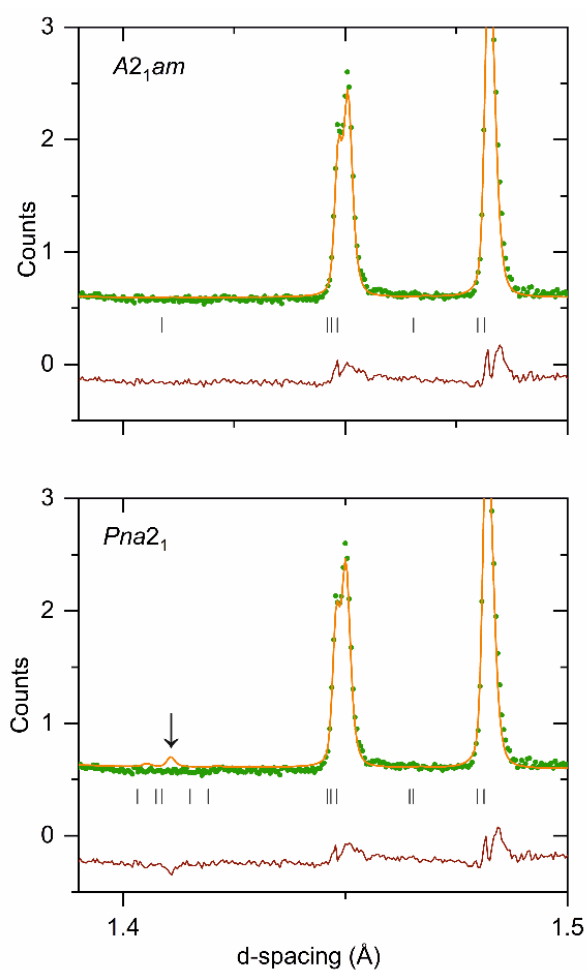


Figure 7.2. Observed, calculated and difference plots from the refinement of structural models in space groups $A2_1am$ and $Pna2_1$ against the NPD data collected from $Li_2La(TaTi)O_7$ at 298 K. Black arrows indicate positions of excess intensity in the calculated pattern of the $Pna2_1$ model.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	Uiso (Å ²)
Li	0.6847(21)	0.0038(47)	0.2412(4)	1	0.007(2)
La	0.4345(19)	0.2406(5)	0	1	0.005(1)
Ta/Ti	0.9343(78)	0.2478(22)	0.1179(3)	0.5/0.5	0.008(2)
O(1)	0.9185(16)	0.2027(7)	0	1	0.010(1)
O(2)	0.6807(51)	0.9979(19)	0.4090(1)	1	0.007(4)
O(3)	0.1836(31)	0.0102(14)	0.8883(2)	1	0.007(4)
O(4)	0.9297(27)	0.2820(5)	0.2158(1)	1	0.009(1)
$Li_2La(TaTi)O_7$ - space group $A2_1am$ (#36) $a = 5.49668(4)$ Å, $b = 5.51162(4)$ Å, $c = 18.22989(16)$ Å Formula weight = 493.60 g mol ⁻¹ , Z = 4 Radiation source: Neutron Time of Flight					

Temperature: 298 K
wRp = 5.985 %, Rp = 5.778 %

Table 7.3. Parameters from the structural refinement of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ against NPD data collected at 298 K.

Cation	Anion	Bond length (Å)	BVS
Li	O3×1	2.362(9)	+0.916
	O4×1	1.99(3)	
	O4×1	1.98(3)	
	O4×1	2.09(3)	
	O4×1	2.16(3)	
La	O1×1	2.445(5)	+3.051
	O1×1	2.669(14)	
	O1×1	2.844(14)	
	O1×1	3.070(5)	
	O2×2	2.603(18)	
	O2×2	2.568(17)	
	O3×2	2.768(11)	
	O3×2	2.816(11)	
Ta/Ti	O1×1	2.165(6)	+4.656
	O2×1	2.01(4)	
	O2×1	2.02(4)	
	O3×1	1.90(4)	
	O3×1	1.98(4)	
	O4×1	1.795(6)	

Table 7.4. Selected bond lengths from the refined structure of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ at 298 K.

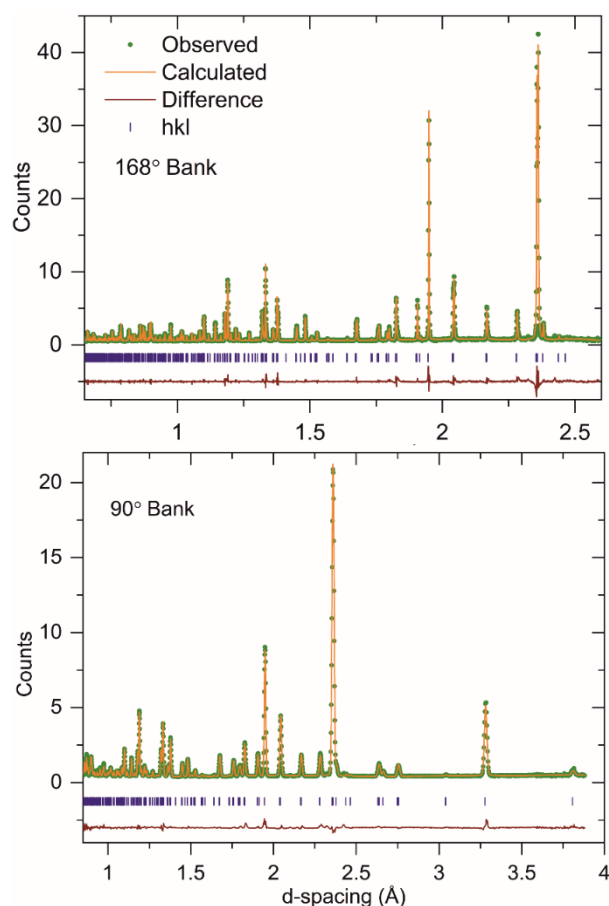


Figure 7.3. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ against NPD data collected at 298 K.

7.3.2.3 10 K neutron diffraction data

A similar procedure was followed for the structural characterization of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ at 10 K as described above for the 298 K data. $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ is isostructural at 298 K and 10 K. Comparison of fitting statistics for the refinement of different structure models against the neutron diffraction data collected at 10 K is shown in Table 7.5. Full details of the refined parameters at 10 K is shown in Table 7.6 with selected bond lengths from the refined structure of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ at 10 K in Table 7.7. Observed, calculated and difference plots from the refinement of $A2_1am$ model of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ at 10 K are shown in Figure 7.4.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
$Amam$ (#63)	$a^-a^-c^0/a^-a^-c^0$	58	6.833	5.669
$A2_1am$ (#36)	$a^-a^-c^+/a^-a^-c^+$	68	6.762	5.593

<i>Pnam</i> (#62)	$a^-a^-c^+/a^-a^-(-c^+)$	68	6.835	5.669
<i>Pna2₁</i> (#33)	$a^-a^-c^+/a^-a^-(-c^+)$	90	6.655	5.593

Table 7.5. Fitting statistics from the structural refinement of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ against the neutron powder diffraction data collected at 10 K.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> _{iso} (Å ²)
Li	8 <i>b</i>	0.7012(69)	0.9975(58)	0.2417(4)	1	0.0026(15)
La	4 <i>a</i>	0.4631(11)	0.2396(5)	0	1	0.0013(7)
Ta/Ti	8 <i>b</i>	0.9458(57)	0.2581(22)	0.1179(4)	0.5/0.5	0.0044(18)
O(1)	4 <i>a</i>	0.9540(39)	0.2002(7)	0	1	0.0067(11)
O(2)	8 <i>b</i>	0.7029(30)	0.9968(22)	0.4090(1)	1	0.0016(6)
O(3)	8 <i>b</i>	0.2086(32)	0.0078(20)	0.8877(2)	1	0.0044(7)
O(4)	8 <i>b</i>	0.9493(18)	0.2841(5)	0.2169(1)	1	0.0049(8)
$\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ - space group <i>A2₁am</i> (#36) <i>a</i> = 5.49032(4) Å, <i>b</i> = 5.50935(5) Å, <i>c</i> = 18.15479(20) Å Formula weight = 493.60 g mol⁻¹, <i>Z</i> = 4 Radiation source: Neutron Time of Flight Temperature: 10 K <i>w</i>R_p = 6.818 %, R_p = 5.660 %						

Table 7.6. Parameters from the structural refinement of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ against NPD data collected 10 K.

Cation	Anion	Bond length (Å)	BVS
Li	O3×1	2.352(9)	+0.945
	O4×1	1.99(5)	
	O4×1	2.14(5)	
	O4×1	2.12(5)	
	O4×1	1.94(5)	
La	O1×1	2.821(19)	+3.099
	O1×1	3.088(15)	
	O1×1	2.423(5)	
	O1×1	2.686(19)	
	O2×2	2.618(12)	
	O2×2	2.545(12)	

Ta/Ti	O3×2	2.772(11)	+4.596
	O3×2	2.805(11)	
	O1×1	2.156(8)	
	O2×1	1.95(4)	
	O2×1	2.00(4)	
	O3×1	1.97(4)	
	O3×1	1.98(4)	
	O4×1	1.814(8)	

Table 7.7. Selected bond lengths from the refined structure of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ at 10 K.

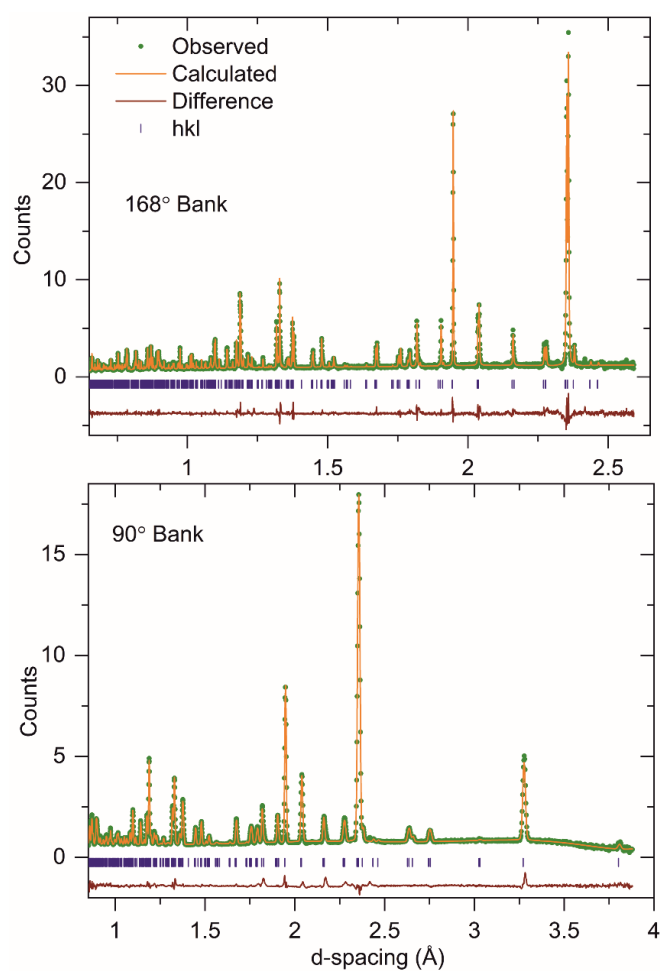


Figure 7.4. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ against NPD data collected at 10 K.

7.3.3 Structural characterisation of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$

7.3.3.1 Room temperature synchrotron X-ray diffraction data

Synchrotron X-ray diffraction data collected from $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ can be indexed using an orthorhombic unit cell ($a = 5.497 \text{ \AA}$, $b = 5.514 \text{ \AA}$, $c = 18.158 \text{ \AA}$). This unit cell is consistent with an $a' = \sqrt{2}a$, $b' = \sqrt{2}b$, $c' = c$ expansion of an undistorted aristotype, $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Extinction conditions observed in the powder diffraction data are consistent with an A-centered unit cell. Symmetry analysis of the $n = 2$ Ruddlesden-Popper framework,^{42,66} in combination with the observation that $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ is SHG active (activity 0.75 times $\alpha\text{-SiO}_2$) suggests an $a^-a^-c^+/a^-a^-c^+$ distorted structure^{8,9} described in space group $A2_1am$ (#36), analogous to the structure of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ phase. There is no evidence for any Nb/Ti ordering, so a model based on the room temperature structure of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ ¹⁰² but with Ta replaced by Nb was constructed and refined against the SXRD data to achieve a good fit as shown in Figure 7.5.

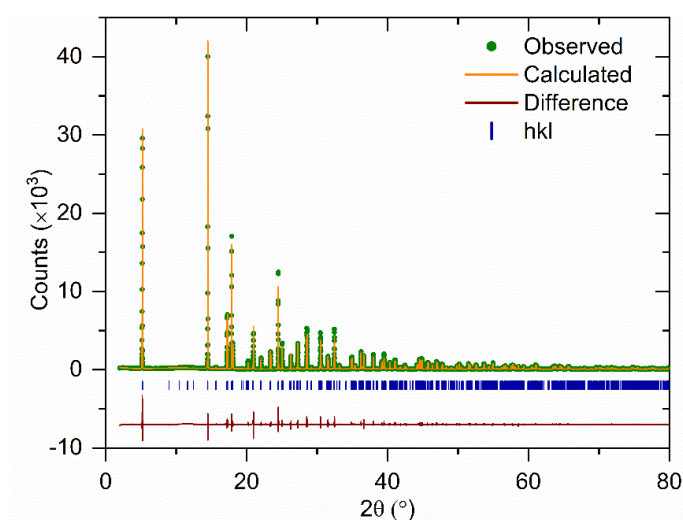


Figure 7.5. Observed, calculated and difference plots from the refinement of the structural model in space group $A2_1am$ against synchrotron X-ray diffraction data collected from $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ at room temperature.

7.3.3.2 Room temperature neutron diffraction data

Neutron powder diffraction (NPD) data collected from $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ can be indexed using an orthorhombic unit cell ($a = 5.497 \text{ \AA}$, $b = 5.514 \text{ \AA}$, $c = 18.158 \text{ \AA}$) which is consistent with a $\sqrt{2} \times \sqrt{2} \times 1$ geometric expansion of an undistorted aristotype $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Extinction conditions observed in the powder diffraction

data are consistent with an *A*-centered unit cell. The *A2₁am* structure model along with some other related structure models with different octahedral tilting distortions as listed in Table 7.8 were constructed and refined against the NPD data collected at room temperature.

The best numerical fits to the data are achieved by the models described in space groups *A2₁am* and *Pna2₁* as shown in Table 7.8. The fitting statistics from the refinement of the *Pna2₁* model ($wR_p = 8.26\%$, $R_p = 6.88\%$) are comparable to those from the *A2₁am* structural model ($wR_p = 8.42\%$, $R_p = 7.03\%$). To assign the correct structure we examined the displacement of the cations in the refined models. The *8b* Li and Ti/Ta sites present in the *A2₁am* model are split into two *4a* sites each in the *Pna2₁* model, as shown in Table 7.9. It can be seen that some of the atomic sites in the *Pna2₁* model, although are general positions, are actually present in the special positions within errors. For example *x*-coordinates of Li(1), Li(2) and La are in the special positions within errors as shown in Table 7.9. In addition, the *z*-coordinate of La remains at $z = 0$, within error, consistent with the presence of a mirror plane perpendicular to the *z*-axis. In contrast, the polar displacements of cations in the *A2₁am* structure (parallel to the *x*-axis) are significant considering the errors. Further, close inspection of the diffraction pattern reveals peak intensities in the calculated pattern for the *Pna2₁* structure which are not observed in the diffraction data, as shown in Figure 7.6. Hence the *A2₁am* structural model of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ is preferred over the *Pna2₁* model. Full details of the refined structure of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ are given in Table 7.10, with a plot of the fitted diffraction data shown in Figure 7.7. Selected bond lengths are given in Table 7.11.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
<i>Amam</i> (#63)	$a^-a^-c^0/a^-a^-c^0$	58	8.482	7.047
<i>A2₁am</i> (#36)	$a^-a^-c^+/a^-a^-c^+$	68	8.419	7.034
<i>Pnam</i> (#62)	$a^-a^-c^+/a^-a^-(-c^+)$	68	8.465	7.062
<i>Pna2₁</i> (#33)	$a^-a^-c^+/a^-a^-(-c^+)$	90	8.258	6.887

Table 7.8. Fitting statistics from the structural refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against the neutron powder diffraction data collected at 298 K.

	atom	site	x	y	z	BVS
$A2_1am$	Li	8b	0.7186(65)	0.0013(73)	0.2461(7)	+0.954
	La	4a	0.4668(17)	0.2410(7)	0	+3.040
	Nb/Ti	8b	0.9359(26)	0.2570(27)	0.1201(4)	+4.689
$Pna2_1$	Li (1)	4a	0.9980(90)	0.2662(70)	0.2583(16)	+0.873
	Li (2)	4a	0.5049(90)	0.2421(70)	0.7483(11)	+1.081
	La	4a	0.7468(34)	0.0101(7)	0.9921(6)	+3.030
	Nb/Ti (1)	4a	0.7355(83)	0.0153(53)	0.3680(15)	+4.766
	Nb/Ti (2)	4a	0.7219(83)	0.9703(39)	0.6048(14)	+4.674

Table 7.9. Fractional coordinates and bond valence sums from the structural refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against NPD data collected at 298 K using models in space groups $A2_1am$ and $Pna2_1$.

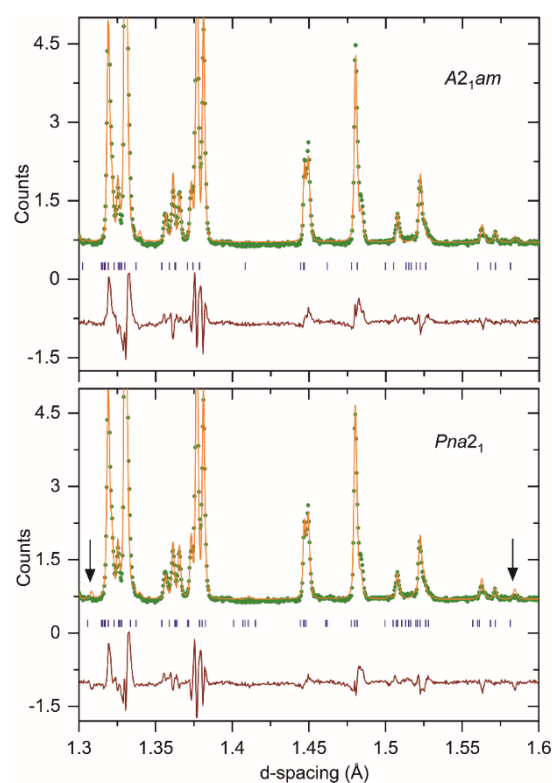


Figure 7.6. Observed, calculated and difference plots from the refinement of structural models in space groups $A2_1am$ and $Pna2_1$ against NPD data collected from $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ at 298 K. Black arrows indicate positions of excess intensity in the calculated pattern of $Pna2_1$ model.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
Li	8b	0.7186(65)	0.0013(73)	0.2461(7)	1	1.10(15)

La	4a	0.4668(17)	0.2410(7)	0	1	0.37(7)
Nb/Ti	8b	0.9359(26)	0.2570(27)	0.1201(4)	0.5/0.5	0.06(18)
O(1)	4a	0.9709(25)	0.2016(10)	0	1	0.77(14)
O(2)	8b	0.7101(13)	0.0012(31)	0.4083(2)	1	0.32(7)
O(3)	8b	0.2286(10)	0.0068(20)	0.8881(2)	1	0.44(8)
O(4)	8b	0.9485(10)	0.2839(6)	0.2166(2)	1	0.33(7)
$\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ - space group $A2_1am$ (#36) $a = 5.49712(5) \text{ \AA}$, $b = 5.51420(5) \text{ \AA}$, $c = 18.1577(2) \text{ \AA}$ Formula weight = 405.56 g mol⁻¹, Z = 4 Radiation source: Neutron Time of Flight Temperature: 298 K wRp = 8.419 %, Rp = 7.034 %						

Table 7.10. Parameters from the structural refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against NPD data collected at 298 K.

Cation	Anion	Bond length (Å)	BVS
Li	O3×1	2.44(1)	+0.954
	O4×1	2.02(4)	
	O4×1	2.23(4)	
	O4×1	2.08(4)	
	O4×1	1.87(4)	
La	O1×1	2.74(2)	+3.040
	O1×1	3.074(7)	
	O1×1	2.441(7)	
	O1×1	2.78(2)	
	O2×2	2.605(12)	
	O2×2	2.573(12)	
	O3×2	2.741(9)	
	O3×2	2.840(9)	
Nb/Ti	O1×1	2.210(8)	+4.689
	O2×1	2.077(19)	
	O2×1	1.90(2)	
	O3×1	1.854(18)	

	O3×1	2.125(17)	
	O4×1	1.760(9)	

Table 7.11. Selected bond lengths from the refined structure of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ at 298 K.

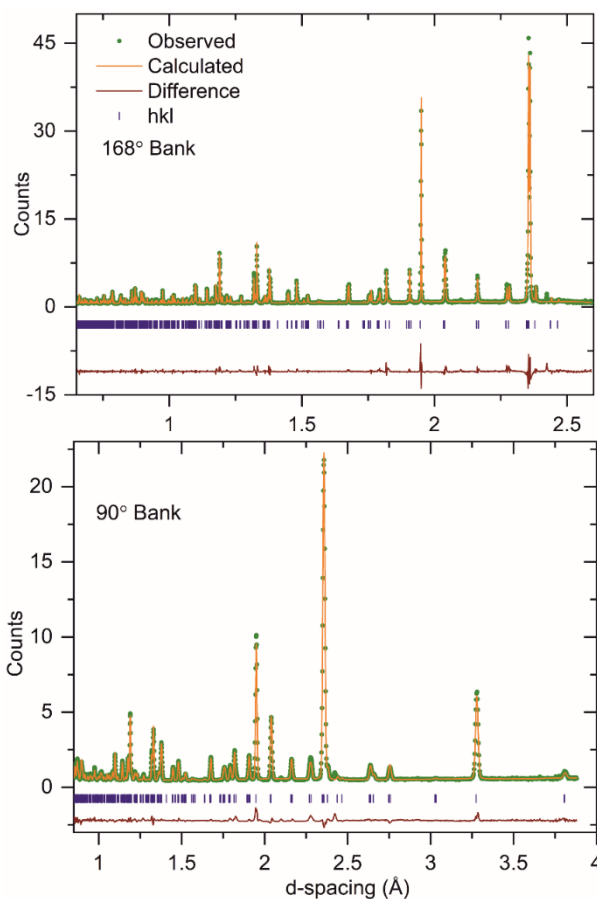


Figure 7.7. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against NPD data collected at 298 K.

7.3.3.3 10 K neutron diffraction data

A similar procedure was followed for the structural characterization of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ at 10 K as described above for the 298 K data. $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ is isostructural at 298 K and 10 K. Comparison of fitting statistics for the refinement of different structure models against the neutron diffraction data collected at 10 K is shown in Table 7.12. Full details of the refined parameters at 10 K are shown in Table 7.13 with selected bond lengths from the refined structure of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ at 10 K in Table 7.14. Observed, calculated and difference plots from the refinement of the $A2_1am$ model of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ at 10 K are shown in Figure 7.8.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
<i>Amam</i> (#63)	$a^-a^-c^0/a^-a^-c^0$	58	8.345	6.212
<i>A2₁am</i> (#36)	$a^-a^-c^+/a^-a^-c^+$	68	8.219	6.061
<i>Pnam</i> (#62)	$a^-a^-c^+/a^-a^-(-c^+)$	68	8.361	6.267
<i>Pna2₁</i> (#33)	$a^-a^-c^+/a^-a^-(-c^+)$	90	8.165	6.033

Table 7.12. Fitting statistics from the structural refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against the neutron powder diffraction data collected at 10 K.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	B_{iso} ($\text{\AA}^2$)
Li	8 <i>b</i>	0.7290(67)	0.0019(59)	0.2410(5)	1	0.35(14)
La	4 <i>a</i>	0.4834(20)	0.2401(6)	0	1	0.08(6)
Nb/Ti	8 <i>b</i>	0.9595(24)	0.2500(25)	0.1194(4)	0.5/0.5	0.05*
O(1)	4 <i>a</i>	0.9873(30)	0.1981(9)	0	1	0.39(12)
O(2)	8 <i>b</i>	0.7257(16)	0.0016(45)	0.4091(1)	1	0.24(7)
O(3)	8 <i>b</i>	0.2397(15)	0.0035(30)	0.8866(2)	1	0.32(7)
O(4)	8 <i>b</i>	0.9697(16)	0.2853(6)	0.2172(2)	1	0.42(7)
$\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ - space group <i>A2₁am</i> (#36) $a = 5.48998(5) \text{ \AA}$, $b = 5.51150(5) \text{ \AA}$, $c = 18.0846(2) \text{ \AA}$ Formula weight = 405.56 g mol ⁻¹ , Z = 4 Radiation source: Neutron Time of Flight Temperature: 10 K $wR_p = 8.219 \%$, $R_p = 6.061 \%$						

Table 7.13. Parameters from the structural refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against NPD data collected at 10 K.

Cation	Anion	Bond length ($\text{\AA}$)	BVS
Li	O3×1	2.309(10)	+0.958
	O4×1	2.17(4)	
	O4×1	1.99(4)	
	O4×1	1.93(4)	
	O4×1	2.09(4)	
La	O1×1	2.73(2)	+3.090
	O1×1	2.415(6)	

	O1×1	3.096(6)	
	O1×1	2.78(2)	
	O2×2	2.594(17)	
	O2×2	2.559(17)	
	O3×2	2.774(13)	
	O3×2	2.826(13)	
Nb/Ti	O1×1	2.184(11)	+4.651
	O2×1	1.96(3)	
	O2×1	2.07(3)	
	O3×1	1.85(2)	
	O3×1	2.055(19)	
	O4×1	1.780(9)	

Table 7.14. Selected bond lengths from the refined structure of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ at 10 K.

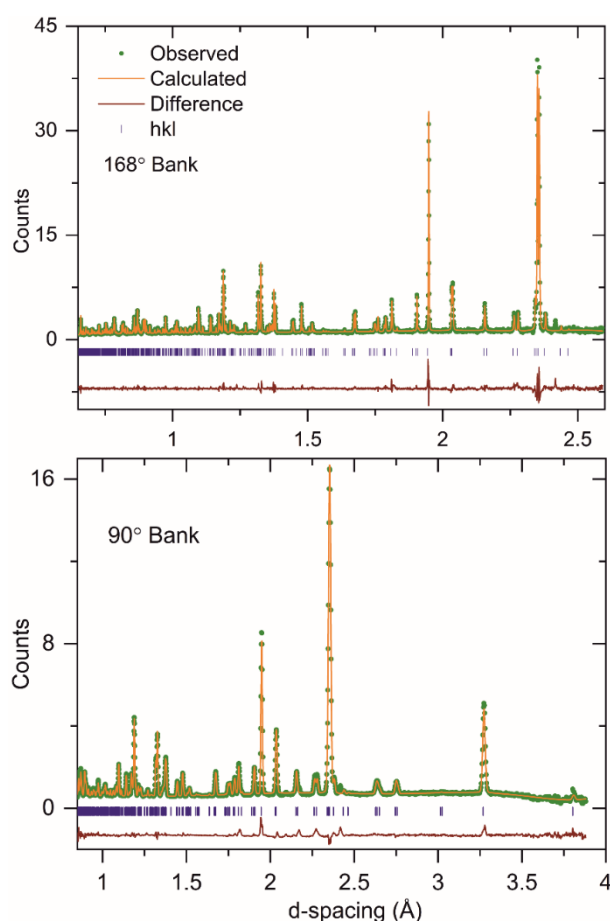


Figure 7.8. Observed, calculated and difference plots from the structural refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against NPD data collected at 10 K.

7.3.3.4 Variable temperature synchrotron X-ray diffraction data

Variable temperature synchrotron X-ray diffraction data were collected from $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ sample within the temperature range of 25 °C to 1000 °C. As established before, the room temperature structure of this phase is polar $A2_1am$ symmetry with $a^-a^-c^+/a^-a^-c^+$ octahedral tilting. The $A2_1am$ model was refined against the SXRD data, and the refined lattice parameters were extracted and plotted against the temperature. The slopes of the lattice parameters against temperature plots are not uniform. There are two sudden changes in the slope which are shown in Figure 7.9. The first one is around 250 °C and the other one is around 800 °C. These two discontinuities in slope correspond to two phase transitions.

Considering the 250 °C anomaly first, all the peaks in the diffraction patterns collected between 250 °C and 800 °C, could be indexed using an orthorhombic unit cell which is a $\sqrt{2} \times \sqrt{2} \times 1$ geometric expansion of an undistorted aristotype $I4/mmm$ symmetry unit cell. The SXRD patterns in this region could still be indexed using an A -centred unit cell. Close observation of the diffraction patterns reveals that the orthorhombic distortion of the a - and b -lattice parameters is smaller in this temperature region compared to the $A2_1am$ phase region. Symmetry analysis of $n=2$ Ruddlesden-Popper framework and systematic absences present in the diffraction pattern indicate that the phase is consistent with $A2_1am$ or $Amam$ symmetry. Given that the low-temperature structure is $A2_1am$ with $a^-a^-c^+/a^-a^-c^+$ tilting distortion, it is possible that it would undergo a phase transition to $Amam$ symmetry with $a^-a^-c^0$ tilting distortion. Thus, the structure of the $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ phase between 250 °C and 800 °C was described to adopt the $Amam$ symmetry structure. The only difference between the $A2_1am$ and $Amam$ structures is that the $Amam$ structure will have zero rotation of BO_6 octahedra around the z -axis. This small change in oxide ion position is not detectable using X-ray diffraction, hence for complete characterisation neutron diffraction data will be required.

Now considering the 800 °C anomaly, the a - and b -lattice parameters are identical above this temperature as shown in Figure 7.10, indicating an orthorhombic to a tetragonal phase transition. The peaks in the diffraction patterns above 800 °C could be indexed using a body centred unit cell and the systematic absences are consistent with the $I4/mmm$ symmetry. This high-temperature phase was assigned as the aristotype structure described in $I4/mmm$ space group.

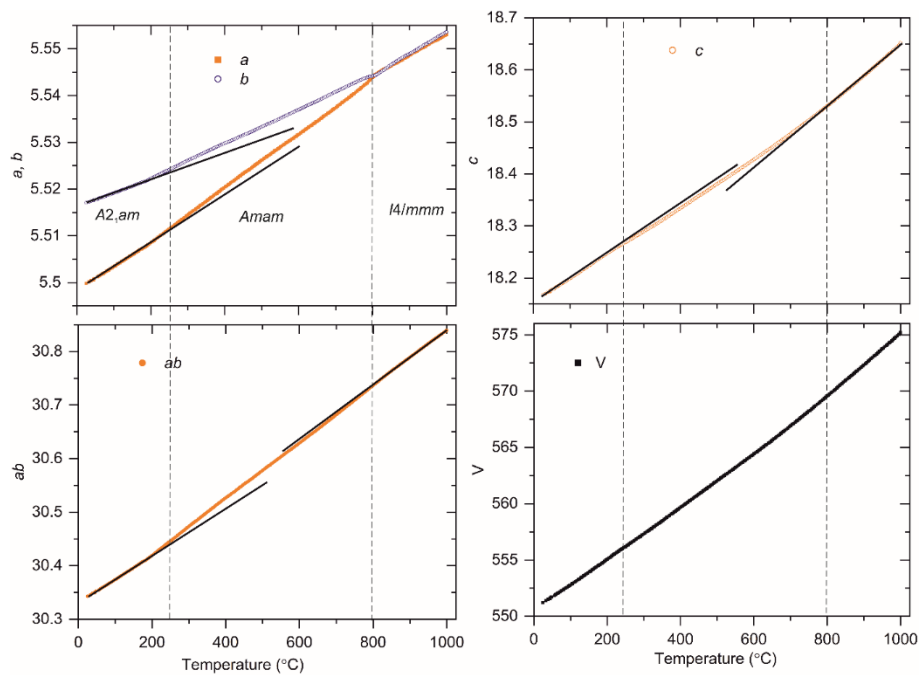
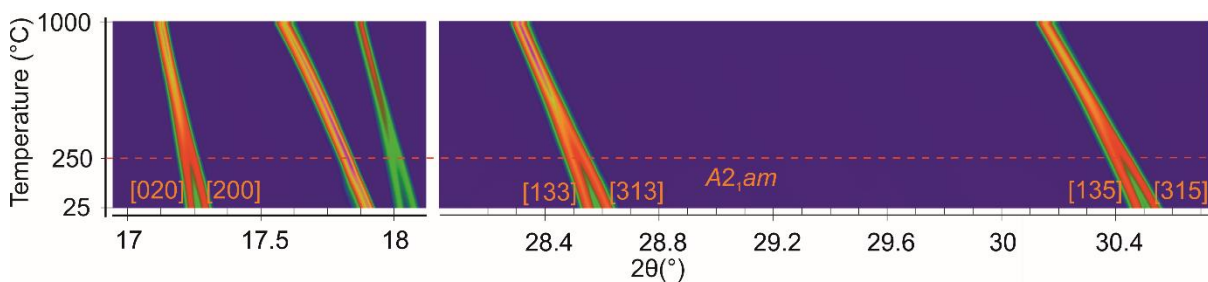


Figure 7.9. Evolution of the lattice parameters, ab and volume (v) with temperature as obtained from the structure refinement of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ against the synchrotron X-ray diffraction data. The solid black lines on the plots are to guide the eye, indicating the change in slope.



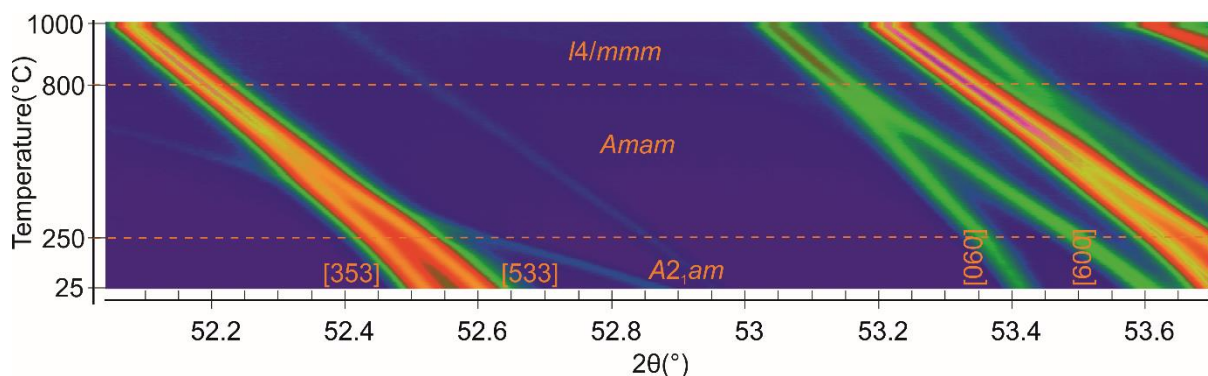


Figure 7.10 Plan view of the diffraction patterns collected from $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ from 25 °C to 1000 °C.

7.3.4 Structural characterisation of $\text{Na}_2\text{La}(\text{TiTa})\text{O}_7$

7.3.4.1 Room temperature synchrotron X-ray diffraction data

SXRD data collected from $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ were indexed with an orthorhombic unit cell ($a = 5.47 \text{ \AA}$, $b = 5.48 \text{ \AA}$, $c = 20.52 \text{ \AA}$), consistent with an $a' = \sqrt{2}a$, $b' = \sqrt{2}b$, $c' = c$ expansion of an undistorted aristotype $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Although the $A2_1am$ symmetry model can account for all the peaks in the diffraction pattern, further analysis of NPD data reveals that a primitive unit cell is required to index all the peaks. Hence the further structural analysis was based on neutron diffraction data.

7.3.4.2 Room temperature neutron diffraction data

NPD data collected from $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ were indexed with an orthorhombic unit cell ($a = 5.47 \text{ \AA}$, $b = 5.48 \text{ \AA}$, $c = 20.52 \text{ \AA}$), consistent with an $a' = \sqrt{2}a$, $b' = \sqrt{2}b$, $c' = c$ expansion of an undistorted aristotype, $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Refinement of an $A2_1am$ symmetry model, analogous to the refined structure of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$, revealed a series of weak diffraction reflections which violate the A-centering extinction conditions. In addition, the refinement indicated that the Na^+ cations are located in the ‘conventional’ 9-coordinate rock-salt-layer cation sites (in contrast to the Li cations in $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$). Furthermore, the refined atomic configuration indicated that the $a^-a^-c^0/a^-a^-c^0$ octahedral tilting distortion, described by the X_3^- irreducible representation of the $I4/mmm$ space group, is present in the structure of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$, but the $a^0a^0c^+/a^0a^0c^+$ distortion,

described by the X_2^+ irreducible representation, is not. Using this information two further models were constructed: an $a^-a^-c^+/a^-a^-(-c^+)$ distortion (X_3^- and X_2^+) in space group $Pnam$ (#62) and an $a^-a^-c^-/a^-a^-(-c^-)$ distortion (X_3^- and X_1^-) in space group $Pnab$ (#60). Refinement of these models against the NPD data revealed that the $Pnab$ model achieved a superior fit to the data and a physically reasonable structure, in contrast to the $Pnam$ model, as described in the fitting statistics listed in Table 7.15.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
$Amam$ (#63)	$a^-a^-c^0/a^-a^-c^0$	57	7.98	6.80
$A2_1am$ (#36)	$a^-a^-c^+/a^-a^-c^+$	65	7.72	6.73
$Pnam$ (#62)	$a^-a^-c^+/a^-a^-(-c^+)$	63	7.75	6.68
$A2/a$ (#16)	$a^-a^-c^-/a^-a^-c^-$	64	7.36	6.65
$Pnab$(#60)	$a^-a^-c^-/a^-a^-(-c^-)$	63	7.34	6.45

Table 7.15. Fitting statistics from the structural refinement of $Na_2La(TaTi)O_7$ against the neutron powder diffraction data collected at 298 K.

However, measurements revealed that $Na_2La(TaTi)O_7$ is SHG active (activity 0.53 times α - SiO_2) and thus has a non-centrosymmetric crystal structure. This indicated that the structure of $Na_2La(TaTi)O_7$ is subject to further symmetry-lowering distortion. Thus, we considered further distortions of the $Pnab$ model by incorporating polar Γ -point distortion modes generated using the ISODISTORT software.⁶⁶ Four noncentrosymmetric structure models were constructed and refined against the NPD data; which results in comparable fitting statistics as shown in Table 7.16.

Space group	Additional polar mode	No. of independent parameters	wR_p (%)	R_p (%)
$P2_122_1$ (#18)	Γ_1^-	86	7.21	6.49
$P2_1ab$ (#29)	Γ_2^-	86	7.22	6.43
$Pna2_1$ (#33)	Γ_3^-	86	7.20	6.35
$Pn2b$ (#30)	Γ_4^-	86	7.49	7.12

Table 7.16. Fitting statistics from the refinement of a series of polar structural models against NPD data collected from $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ at 298K.

To establish which is the correct structure, the refined models as shown in Table 7.17 (atomic coordinates, bonding environment, etc) were compared taking the refined centrosymmetric *Pnab* model as reference.

***Pn2b* model:** There are 2 independent sites for Na, La and Ti/Ta. Although the *x* and *z* coordinates of both the La sites are still defined by symmetry, the bond valence sums of the two La sites are very different. Also, the Ti/Ta(1) site has a very large bond valence sum parameter (4.973 compared to the expected 4.5). Therefore this structure was discarded based on an unreasonable bonding environment.

***P2₁ab* model:** There are 2 independent sites for Na and Ti/Ta ions. Ti/Ta(2) is highly over bonded (BVS = 5.011). In addition, the *y* and *z* coordinates of the La site are at general positions, but the displacement of the La site along the *y* and *z* directions away from the corresponding special position is zero within error. In the *P2₁ab* space group the polar direction is parallel to the *x*-axis, but there is a mirror relation (within error) between the *x* positions of the two Na sites ($0.24 = 0.5 - 0.26$; $0.76 = 0.5 + 0.26$). For these reasons, the *P2₁ab* model is discounted.

***P2₁22₁* model:** There are two independent sites for Na, La and Ti/Ta. Bond valence sums for the two La and the two Na sites are significantly different. In addition, the *y* co-ordinates of the Ti/Ta(2), La(1) and Na(1) sites stay on their special positions after refinement, within error, hence, this model is also discarded.

***Pna2₁* model:** There are two sites for Na and Ti/Ta. Similar bond valence sums for corresponding sites imply that the structure is chemically plausible. In addition, the displacement of cations from special positions is significant with respect to the error bounds. The *Pna2₁* model is truly polar and gives the best fit to the data so it is assigned as the correct structure for $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ at room temperature.

<i>Pnab</i>				
	<i>x</i>	<i>y</i>	<i>z</i>	BVS
Ta/Ti	0.2518(50)	0.7571(31)	0.3927(4)	4.653
La	0.75	0.2503(11)	0	2.896
Na	0.2748(20)	0.7549(19)	0.1941(3)	0.872
<i>Pn2b</i>				
Ta/Ti(1)	0.4683(37)	0.2689(38)	0.3847(9)	4.973
Ta/Ti(2)	0.9875(56)	0.2822(43)	0.8983(9)	4.679
La(1)	0	0.8049(28)	0	3.087
La(2)	0.5	0.3019(29)	0	2.692
Na(1)	0.5435(80)	0.2943(75)	0.1947(13)	0.910
Na(2)	0.0125(33)	0.2990(35)	0.6876(6)	0.837
<i>P2₁ab</i>				
Ta/Ti(1)	0.2274(60)	0.4858(56)	0.1514(9)	4.500
Ta/Ti(2)	0.7109(44)	0.4780(35)	0.6366(7)	5.011
La	0.7330(25)	0.0004(12)	0.7504(5)	0.927
Na(1)	0.2406(49)	0.5056(37)	0.9478(7)	0.917
Na(2)	0.7633(48)	0.4978(46)	0.4403(8)	0.889
<i>P2₁22₁</i>				
Ta/Ti(1)	0.4776(45)	0.4836(40)	0.3872(6)	4.750
Ta/Ti(2)	0.0195(56)	0.9903(60)	0.5991(10)	4.623
La(1)	0	0.0011(18)	0	2.883
La(2)	0	0.4969(15)	0.5	3.012
Na(1)	0.4872(47)	0.4984(33)	0.1981(8)	0.970
Na(2)	0.9712(27)	0.0117(31)	0.8072(8)	0.780
<i>Pna2₁</i>				
Ta/Ti(1)	0.7410(48)	0.4783(46)	0.6103(8)	4.726
Ta/Ti(2)	0.7314(54)	0.5304(42)	0.3961(8)	4.750
La	0.2484(19)	0.9980(15)	0.0082(6)	2.923
Na1	0.7354(29)	0.5054(22)	0.8186(4)	0.906
Na2	0.7029(22)	0.5065(25)	0.1961(4)	0.905

Table 7.17. Fractional coordinates and bond valence sums of cations from the structural refinement of Na₂La(TaTi)O₇ against the neutron powder diffraction data collected at 298 K.

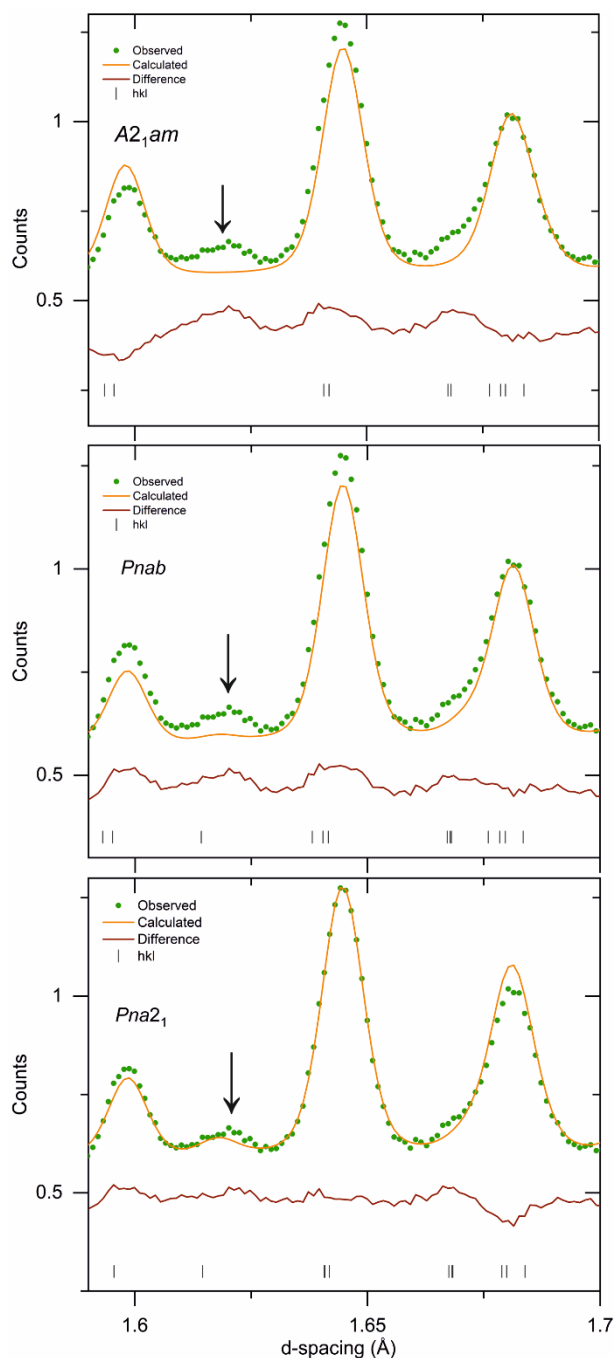


Figure 7.11. Observed, calculated and difference plots from the refinement of models in space groups $A2_1am$, $Pnab$ and $Pna2_1$ against NPD data collected from $Na_2La(TaTi)O_7$ at 298 K. The black arrow indicates the peak which violates the A-centering.

Full details of the refined structure of $Na_2La(TaTi)O_7$ are given in Table 7.18, with a plot of the fitted diffraction data shown in Figure 7.12. Selected bond lengths are given in Table 7.19.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	U_{iso}
Na(1)	0.735(3)	0.505(2)	0.8086(4)	1	0.002(1)

Na(2)	0.703(2)	0.507(2)	0.1961(4)	1	0.002(1)
La	0.248(1)	0.998(1)	0.0083(9)	1	0.003(1)
Ta/Ti(1)	0.741(4)	0.478(4)	0.6103(8)	0.5/0.5	0.002*
Ta/Ti(2)	0.731(5)	0.530(4)	0.3961(8)	0.5/0.5	0.002*
O(1)	0.044(2)	0.286(2)	0.4101(10)	1	0.025(1)
O(2)	0.483(3)	0.265(3)	0.6087(10)	1	0.025(1)
O(3)	0.477(2)	0.736(2)	0.4234(9)	1	0.015(1)
O(4)	0.019(2)	0.721(3)	0.5986(6)	1	0.015(1)
O(5)	0.753(2)	0.541(2)	0.3141(9)	1	0.014(2)
O(6)	0.755(2)	0.523(2)	0.7027(9)	1	0.014(2)
O(7)	0.254(3)	0.548(1)	0.0086(10)	1	0.015(2)
Na₂La(TaTi)O₇ – space group <i>Pna</i>2₁ (#33) $a = 5.4695(2)$ Å, $b = 5.4813(2)$ Å, $c = 20.5206(8)$ Å Formula weight = 525.70 g mol⁻¹, Z = 4 Radiation source: Neutron Time of Flight Temperature: 298 K wRp = 7.20%, Rp = 6.35%					

Table 7.18. Parameters from the structural refinement of Na₂La(TaTi)O₇ against NPD data collected at 298 K.

Cation	Anion	Bond length (Å)	BVS
Na(1)	O(1)×1	3.01(2)	+0.906
	O(1)×1	2.67(3)	
	O(3)×1	2.94(2)	
	O(3)×1	3.19(2)	
	O(5)×1	2.68(2)	
	O(5)×1	2.55(1)	
	O(5)×1	2.94(1)	
	O(5)×1	2.81(2)	
	O(6)×1	2.18(3)	
Na(2)	O(2)×1	2.86(3)	+0.905
	O(2)×1	2.44(3)	
	O(4)×1	2.81(2)	

	O(4)×1	2.82(2)	
	O(5)×1	2.44(3)	
	O(6)×1	2.97(2)	
	O(6)×1	2.84(2)	
	O(6)×1	2.67(2)	
	O(6)×1	2.51(2)	
La	O(1)×1	2.59(3)	+2.923
	O(1)×1	3.01(3)	
	O(2)×1	2.91(3)	
	O(2)×1	2.73(3)	
	O(3)×1	2.72(2)	
	O(3)×1	2.50(3)	
	O(4)×1	2.56(2)	
	O(4)×1	2.82(2)	
	O(7)×1	2.78(2)	
	O(7)×1	3.01(1)	
	O(7)×1	2.47(1)	
	O(7)×1	2.71(2)	
Ta/Ti(1)	O(2)×1	1.83(3)	+4.726
	O(2)×1	1.88(3)	
	O(4)×1	2.06(3)	
	O(4)×1	2.04(3)	
	O(6)×1	1.91(3)	
	O(7)×1	2.09(3)	
Ta/Ti(2)	O(1)×1	2.03(3)	+4.750
	O(1)×1	2.19(3)	
	O(3)×1	1.88(3)	
	O(3)×1	1.94(3)	
	O(5)×1	1.69(3)	
	O(7)×1	2.35(3)	

Table 7.19. Selected bond lengths from the refined structure of Na₂La(TaTi)O₇ at 298 K.

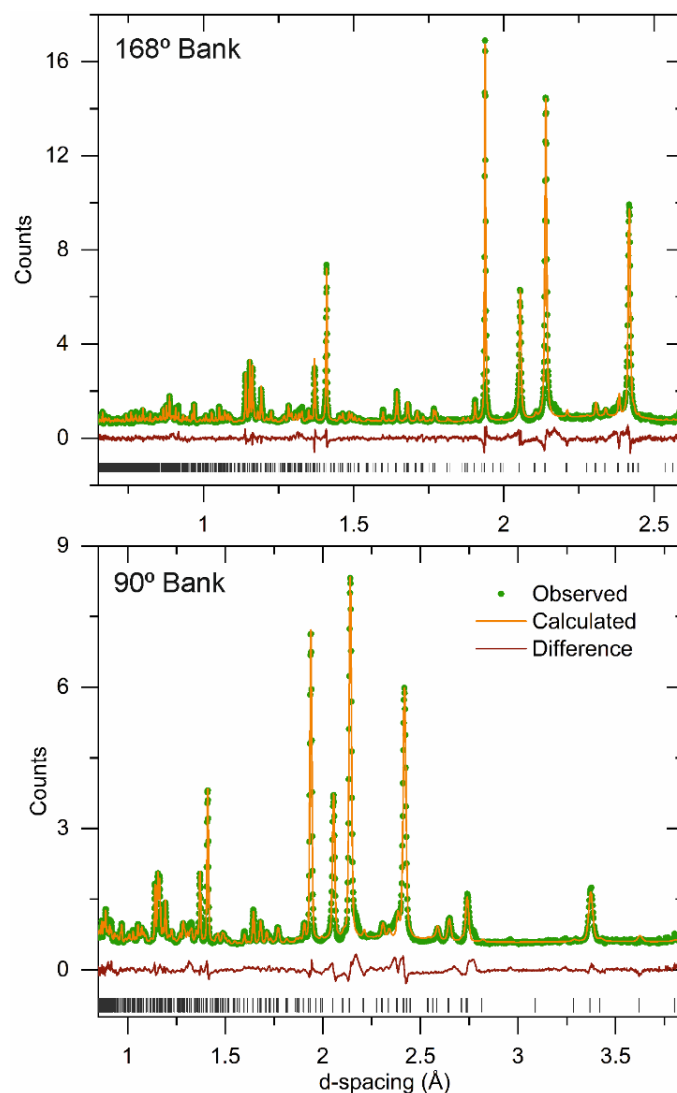


Figure 7.12. Observed, calculated and difference plots from the structural refinement of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ against NPD data collected at 298 K.

7.3.4.3 10 K neutron diffraction data

A similar procedure was followed for the structural characterization of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ at 10 K as described above for the 298 K data. $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ is isostructural at 298 K and 10 K. Full details of the refined parameters at 10 K are shown in Table 7.12 with selected bond lengths from the refined structure of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ at 10 K in Table 7.21. Observed, calculated and difference plots from the refinement of the $Pna2_1$ model of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ at 10 K are shown in Figure 7.13.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occ	$U_{\text{iso}} (\text{\AA}^2)$
Na(1)	4 <i>a</i>	0.7429(47)	0.5002(37)	0.8037(5)	1	0.002

Na(2)	4a	0.7104(30)	0.5105(42)	0.1932(8)	1	0.002
La	4a	0.2527(16)	0.9970(10)	0.0056(8)	1	0.005(1)
Ta/Ti(1)	4a	0.7546(85)	0.4818(60)	0.6124(13)	0.5/0.5	0.002
Ta/Ti(2)	4a	0.7432(73)	0.5270(58)	0.3935(13)	0.5/0.5	0.002
O(1)	4a	0.0555(24)	0.2940(24)	0.4037(10)	1	0.011(2)
O(2)	4a	0.4941(24)	0.2608(31)	0.6051(10)	1	0.011(2)
O(3)	4a	0.4838(24)	0.7473(28)	0.4211(10)	1	0.006(1)
O(4)	4a	0.0345(25)	0.7143(28)	0.5921(12)	1	0.006(1)
O(5)	4a	0.7431(26)	0.5293(31)	0.3106(6)	1	0.007(1)
O(6)	4a	0.7491(23)	0.5488(30)	0.7012(5)	1	0.007(1)
O(7)	4a	0.2657(22)	0.5507(11)	0.0078(12)	1	0.003(2)
Na₂La(TaTi)O₇ – space group <i>Pna2</i>₁ (#33) <i>a</i> = 5.4560(2) Å, <i>b</i> = 5.4753(2) Å, <i>c</i> = 20.4628(8) Å Formula weight = 525.70 g mol⁻¹, Z = 4 Radiation source: Neutron Time of Flight Temperature: 10 K wRp = 6.85%, Rp = 6.12%						

Table 7.20. Parameters from the structural refinement of Na₂La(TaTi)O₇ against NPD data collected 10 K.

Cation	Anion	Bond length (Å)	BVS
Na(1)	O(1)×1	3.07(3)	+0.985
	O(1)×1	2.58(3)	
	O(3)×1	3.02(3)	
	O(3)×1	3.15(3)	
	O(5)×1	2.58(3)	
	O(5)×1	2.66(3)	
	O(5)×1	2.90(3)	
	O(5)×1	2.81(3)	
	O(6)×1	2.115(15)	
Na(2)	O(2)×1	2.78(3)	+0.910
	O(2)×1	2.46(3)	
	O(4)×1	2.78(3)	

	O(4)×1	2.95(3)	
	O(5)×1	2.41(3)	
	O(6)×1	2.97(3)	
	O(6)×1	2.54(3)	
	O(6)×1	2.96(3)	
	O(6)×1	2.53(3)	
La	O(1)×1	2.58(3)	+3.081
	O(1)×1	3.12(3)	
	O(2)×1	2.84(3)	
	O(2)×1	2.76(3)	
	O(3)×1	2.65(3)	
	O(3)×1	2.56(3)	
	O(4)×1	2.43(3)	
	O(4)×1	2.84(3)	
	O(7)×1	2.811(15)	
	O(7)×1	3.033(9)	
	O(7)×1	2.445(9)	
	O(7)×1	2.670(15)	
Ta/Ti(1)	O(2)×1	1.87(5)	+4.669
	O(2)×1	1.87(5)	
	O(4)×1	2.09(5)	
	O(4)×1	2.03(5)	
	O(6)×1	1.85(3)	
	O(7)×1	2.15(4)	
Ta/Ti(2)	O(1)×1	2.04(4)	+4.697
	O(1)×1	2.14(4)	
	O(3)×1	1.94(4)	
	O(3)×1	1.89(4)	
	O(5)×1	1.70(3)	
	O(7)×1	2.38(4)	

Table 7.21. Selected bond lengths from the refined structure of Na₂La(TaTi)O₇ at 10 K.

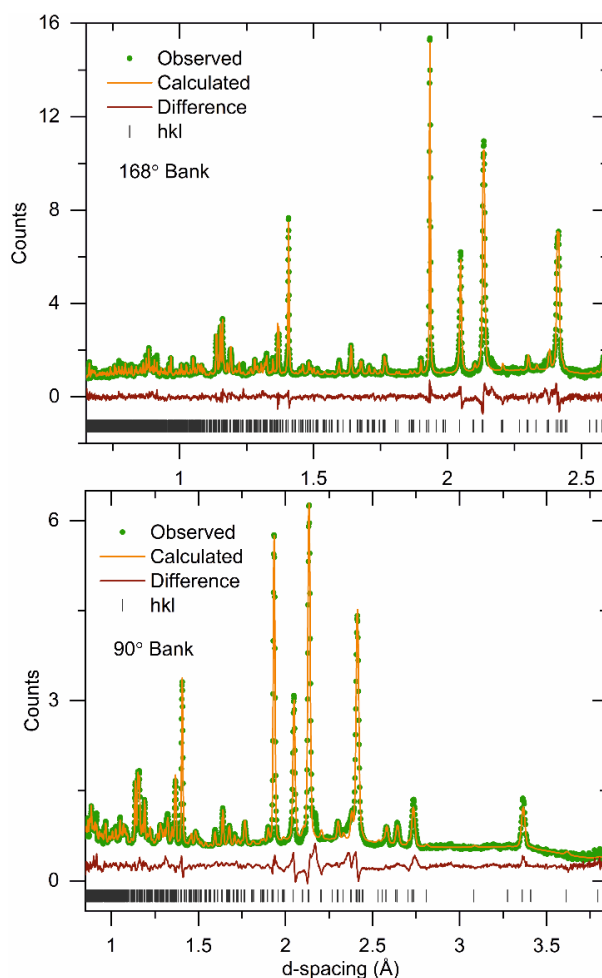


Figure 7.13. Observed, calculated and difference plots from the structural refinement of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ against NPD data collected at 10 K.

7.4 Discussion

$\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$, $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ and $\text{Na}_2\text{Li}(\text{TaTi})\text{O}_7$ adopt $n = 2$ Ruddlesden-Popper structures with polar distortions. However, the mechanism by which the inversion symmetry of the centrosymmetric aristotype $n = 2$ Ruddlesden-Popper structures is broken is qualitatively different for the Li and Na compounds.

$\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ adopt structures analogous to the room-temperature phase of $\text{Li}_2\text{SrNb}_2\text{O}_7$,⁸⁸ in which the lithium cations are located in what is often referred to as the tetrahedral coordination site in the rock salt layers of the framework. However, close inspection reveals that while the lithium cations in $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ do have four short bonds (1.99 – 2.16

Å) to the ‘apical’ O(4) oxide ions, there is a further bond of 2.362 Å to an ‘equatorial’ O(3) anion which contributes a bond valence of 0.09 out of a total lithium bond valence sum of 0.92. Similarly, the lithium cations in $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ also have four short bonds (1.87 – 2.23 Å) to the ‘apical’ O(4) oxide ions and there is a further bond of 2.438 Å to an ‘equatorial’ O(3) anion which contributes a bond valence of 0.07 out of a total lithium bond valence sum of 0.95. As a result the lithium cations in $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ should be considered to be 5-coordinate, as shown in Figure 7.14 and Figure 7.15.

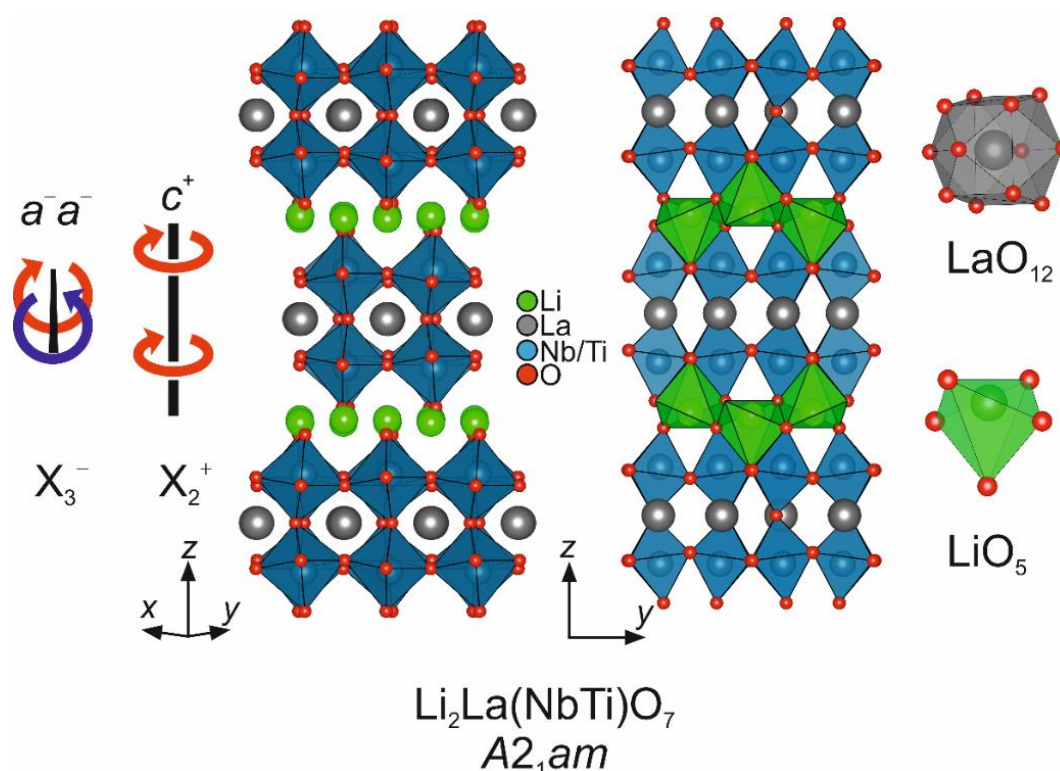


Figure 7.14. The structure and cation coordination environments of $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$.

The smaller size of the La^{3+} and Li^+ A-site cations compared to the Ta/Ti or Nb/Ti B-site cations induce a cooperative tilting distortion to the network of apex-linked (Ta/Ti) O_6 or (Nb/Ti) O_6 octahedra. As shown in Figure 7.14, the BO_6 octahedra adopt an out-of-phase $a^-a^-c^0/a^-a^-c^0$ tilting distortion in the xy-plane, described by the X_3^- irreducible representation of the $I4/mmm$ space group, and an in-phase $a^0a^0c^+/a^0a^0c^+$ distortion around the z-axis, described by the X_2^+ irreducible representation. This combination of tilting distortions ($X_3^- + X_2^+$) yields a structure that cannot be described in a centrosymmetric space group, but which retains inversion

symmetry in the arrangement of the atoms. However, the presence of these two distortion modes in combination couple to and stabilize the polar Γ_5^- distortion mode via the trilinear coupling mechanism described by Benedek and Fennie,²⁴ to yield the hybrid-improper polar structures of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$.

Table 7.22 lists the magnitudes of the distortion modes as extracted from the room temperature $A2_1am$ structures of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ with respect to their aristotype $I4/mmm$ structure. The magnitudes of X_2^+ and X_3^- distortion modes are comparable in these two phases, but the magnitude of the Γ_5^- distortion mode is significantly larger in the Nb-phase compared to the Ta-analogue. The Γ_5^- mode is responsible for the displacement of the cations in these hybrid improper polar structures along the x -axis. A larger magnitude of Γ_5^- indicates that the Nb-atoms are displaced more as a result of this polar mode in the $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$ structure than the Ta-atoms in the $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ structure; which is also consistent with the $d_{\max}$ of Nb and Ta listed in Table 7.23. The $4d$ -orbitals of Nb can hybridize more effectively with O- $2p$ orbitals than the $5d$ -orbitals of Ta. This SOJT effect although is not the reason for the polarity in this phase; it enhances the polar displacement of the B -site cations.

	$\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$		$\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$	
	A_s	A_p	A_s	A_p
Γ_1^+	0.3915	0.2768	0.4155	0.2938
Γ_5^-	0.1565	0.1107	0.5648	0.3994
X_2^+	0.1068	0.0755	0.1517	0.1073
X_3^-	0.8085	0.5717	0.7675	0.5427

Table 7.22. Distortion mode magnitudes extracted from the room temperature $A2_1am$ structures of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Li}_2\text{La}(\text{NbTi})\text{O}_7$.

Mode	A_s	A_p	$d_{\max}$
$\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$			
$[0,0,0]\Gamma_5^-[\text{Li}1:\text{d:dsp}]\text{E}(\text{a})$	0.00000	0.00000	0.00000
$[0,0,0]\Gamma_5^-[\text{La}1:\text{a:dsp}]\text{Eu}(\text{a})$	-0.00156	-0.00110	0.00110

[0,0,0] Γ_5^- [Ti1:e:dsp]E(a)	-0.00440	-0.00311	0.00220
[0,0,0] Γ_5^- [Ta1:e:dsp]E(a)	-0.00440	-0.00311	0.00220
[0,0,0] Γ_5^- [O1:b:dsp]Eu(a)	-0.12604	-0.08912	0.08912
[0,0,0] Γ_5^- [O2:g:dsp]B2(a)	0.01650	0.01167	0.00583
[0,0,0] Γ_5^- [O2:g:dsp]B1(a)	-0.07262	-0.05135	0.02568
[0,0,0] Γ_5^- [O3:e:dsp]E(a)	-0.05501	-0.03890	0.02751
[0,0,0] Γ_5^- all	0.15652	0.11068	
Li₂La(NbTi)O₇			
[0,0,0] Γ_5^- [Li1:d:dsp]E(a)	0.00000	0.00000	0.00000
[0,0,0] Γ_5^- [La1:a:dsp]Eu(a)	-0.01712	-0.01211	0.01211
[0,0,0] Γ_5^- [Ti1:e:dsp]E(a)	-0.36309	-0.25674	0.18155
[0,0,0] Γ_5^- [Nb1:e:dsp]E(a)	-0.36309	-0.25674	0.18155
[0,0,0] Γ_5^- [O1:b:dsp]Eu(a)	0.01556	0.01100	0.01100
[0,0,0] Γ_5^- [O2:g:dsp]B2(a)	0.04786	0.03384	0.01692
[0,0,0] Γ_5^- [O2:g:dsp]B1(a)	-0.04016	-0.02840	0.01420
[0,0,0] Γ_5^- [O3:e:dsp]E(a)	-0.22555	-0.15949	0.11278
[0,0,0] Γ_5^- all	0.56478	0.39936	

Table 7.23. Displacement of atoms as a result of Γ_5^- distortion mode in the $A2_{am}$ structures of Li₂La(TaTi)O₇ and Li₂La(NbTi)O₇ with respect to their respective aristotype structure.

7.4.1 Li₂La(TaTi)O₇ vs Na₂La(TaTi)O₇

The atom displacements arising from the Γ_5^- polar distortion mode, which break the inversion symmetry of the Li₂La(TaTi)O₇ framework, are shown in Figure 7.15. The displacements occur parallel to the *x*-axis and it can be seen that the direction of the displacements of the Ta/Ti cations is opposite to that of the Li and La cations. Similarly, the displacement of the ‘equatorial’ O(2) and O(3) ions oppose the O(1) bridging anion. This shows that Li₂La(TaTi)O₇ should be considered as a ferrielectric, with the overall electrical polarization of the phase arising from a series of opposed, but non-cancelling dipoles, which is a common feature of hybrid-improper ferroelectric phases.

The structure of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ shares a common $\text{La}(\text{TaTi})\text{O}_7$ core with $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$, but in contrast to the lithium phase, the Na cations reside in the ‘conventional’ 9-coordinate rock salt layer cation sites. Again the mismatch between the sizes of the La^{3+} and Na^+ A-site cations and Ta/Ti B-site cations leads to a cooperative tilting of the apex-linked $(\text{Ta/Ti})\text{O}_6$ octahedra. However, in contrast to $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$, the xy-plane $a^-a^-c^0/a^-a^-c^0$ X_3^- distortion is accompanied by an out of phase $a^0a^0c^-/a^0a^0(-c^-)$ distortion around the z-axis in $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ described by the X_1^- irreducible, as shown in Figure 7.15. This combination of tilting modes yields a centrosymmetric structure, described in space group $Pnab$, and does not couple to, or stabilize a further polar Γ -point distortion mode via the trilinear coupling mechanism. The stabilization of the Γ_3^- distortion mode, which is observed to lower the structural symmetry of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ at room temperature, must therefore arise via a different mechanism.

The atom displacements arising from the Γ_3^- polar distortion of $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ are shown in Figure 7.15. The displacements occur parallel to the z-axis and it can be seen that all the cations displace in the same direction (down), while all the anions are displaced in the opposite direction (up). This type of polar displacement is reminiscent of the polar distortions of proper ferroelectric materials, such as BaTiO_3 , where the lifting of inversion symmetry is attributed to a SOJT distortion in which the polar displacements of Ti^{4+} and O^{2-} ions allows a mixing of the empty Ti 3d and filled O 2p orbitals, leading to an overall stabilization of the phase.^{15,103–105} We propose that an analogous SOJT distortion involving the mixing of the empty Ta 5d/Ti 3d and filled oxygen 2p orbitals drives the Γ_3^- distortion in $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$.

The data above show that the inclusion of Li or Na leads to a change in the tilting distortion of the $\text{La}(\text{TaTi})\text{O}_7$ perovskite double sheets. The tilting distortions of ABO_3 perovskite phases can be generally understood with reference to the Goldschmidt tolerance factor, $t = \langle A-O \rangle / \sqrt{2} \langle B-O \rangle$,³ with the degree of distortion generally increasing as t declines. However, as noted previously, the situation is more complex in A-cation ordered Ruddlesden-Popper phases such

as $A'\text{La}(\text{TaTi})\text{O}_7$ or $A'\text{NdNb}_2\text{O}_7$,^{42,102} as the tilting of the octahedral units needs to optimize the local bonding of the two different A -cations simultaneously.

Close inspection shows that the $a^-a^-c^+/a^-a^-c^+$ tilting distortion of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ efficiently optimizes the coordination sites of the Li^+ and La^{3+} cations, as indicated by their BVS values (La^{3+} BVS = +3.051; Li^+ BVS = +0.916).^{65,106} It is clear that replacing Li^+ with Na^+ in the $A2_1am$ distorted structure would require a significant expansion of the 5-coordinate sites to accommodate the large Na^+ cations (Li^+ 4-coordinate radius = 0.59 Å; Na^+ 4-coordinate radius = 0.99 Å).⁹⁴ This expansion would require a decrease in the magnitude of the tilting distortion, which in turn would expand the 12-coordinate site, occupied by La^{3+} , from its optimum size. Thus it is no surprise that $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ adopts a different structure with Na^+ located in the larger 9-coordinate rock salt sites and an $a^-a^-c^-/a^-a^-(-c^-)$ tilting distortion which allows close to optimum local coordinations for both La^{3+} and Na^+ (La^{3+} BVS = +2.923; Na^+ BVS = +0.906/+0.905).

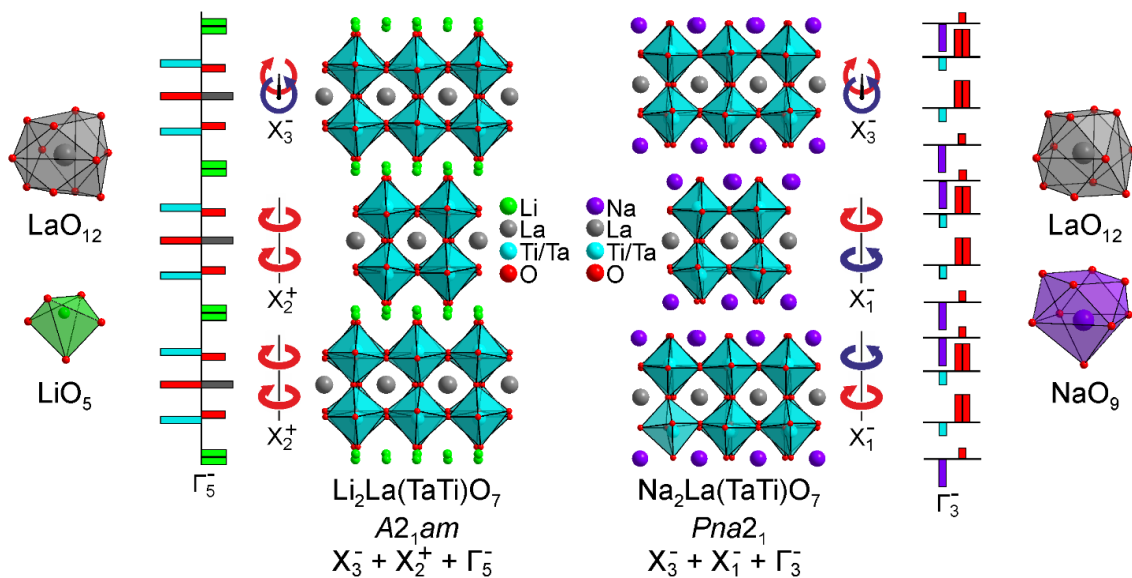


Figure 7.15. The structures of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ viewed down the $[110]$ direction, the distortion modes which relate these structures to the corresponding undistorted $I4/mmm$ symmetry aristotype structure and the local A -cation coordination polyhedra in the two structures. The lengths of the solid bars represent the magnitudes and relative directions of the displacements of ions due to the Γ -point distortion modes.

An important consequence of the change in the tilting distortion of the (Ta/Ti)O₆ octahedra on substituting Li⁺ with Na⁺ is that the $a^-a^-c^-/a^-a^-(-c^-)$ distortion, arising from a combination of X₃⁻ and X₁⁻ modes, does not stabilize a further Γ -point distortion via the trilinear-coupled hybrid-improper mechanism. This means the observed polar structure of Na₂La(TaTi)O₇ must arise via some other symmetry breaking mechanism, which we attribute to an SOJT distortion driven by the d^0 Ta⁵⁺/Ti⁴⁺ cations. Given that Li₂La(TaTi)O₇ and Na₂La(TaTi)O₇ share a common La(TaTi)O₇ block, the implication is that both A₂La(TaTi)O₇ phases are in principle unstable with respect to a symmetry lowering SOJT distortion. Two mechanisms of symmetry breaking (trilinear coupling and SOJT distortion) are in competition, with the Γ -point distortion which contributes to the ground state structures (trilinear coupling: Γ_5^- ; SOJT: Γ_3^-) controlled by the tilting distortion of the (Ta/Ti)O₆ octahedra, which in turn is directed by the relative size of the A-site cations.

Given that many of the reported hybrid-improper ferroelectric phases derived from layered perovskite oxides contain d^0 transition metals on their B-sites, it is likely that the competition between the hybrid-improper and SOJT symmetry breaking mechanisms observed for A₂La(TaTi)O₇ phases is a common feature for many hybrid-improper ferroelectrics. For example, of the A'NdNb₂O₇ (A' = Li, Na, K, Rb, Cs) series of materials, LiNdNb₂O₇, RbNdNb₂O₇ and CsNdNb₂O₇ adopt polar structures attributable to the trilinear-coupling symmetry-breaking mechanism. In contrast, the polar structure of KNdNb₂O₇ is attributed to an SOJT distortion of its constituent Nb⁵⁺O₆ units. Again, this implies the NdNb₂O₇ sheets in all the A'NdNb₂O₇ phases are unstable with respect to an SOJT distortion which competes with the trilinear-coupled polar distortions observed for LiNdNb₂O₇, RbNdNb₂O₇ and CsNdNb₂O₇.

7.5 Conclusion

The Li₂La(TaTi)O₇ and Li₂La(NbTi)O₇ phases adopt A₂1*am* structures with a $a^-a^-c^+/a^-a^-c^+$ tilting distortion of the BO₆ octahedra at room temperature as well as at 10 K. On the other

hand the $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ phase adopts a $Pna2_1$ structure with $a^-a^-c^-/a^-a^-(-c^-)$ tilting of BO_6 octahedra. The lifting of inversion symmetry in the polar structures of $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$ occurs via two different mechanisms: a trilinear coupled hybrid-improper mechanism for the Li phase and a more conventional SOJT-driven mechanism for the Na phase. The operation of these two different mechanisms in materials with a common $\text{La}(\text{TaTi})\text{O}_7$ core suggests they compete against each other, and further suggests this competition is also occurring in other hybrid-improper ferroelectric phases which contain SOJT active cations.

Chapter 8 – Synthesis and characterisation of $\text{MnCaTa}_2\text{O}_7$

8.1 Introduction

Topochemical cation exchange reactions of layered perovskites have been studied widely to synthesize metastable phases which are otherwise inaccessible via traditional high-temperature solid-state synthesis routes. In chapters 3, 4 and 5, the synthesis of metastable KNdM_2O_7 ($M = \text{Ta, Nb}$) and $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Li, Na and K}$) is demonstrated. These phases are synthesized by topochemical cation exchange reactions from thermodynamically stable precursors. Similarly, the $n = 3$ Ruddlesden-Popper phase, $\text{Na}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ is shown to undergo cation exchange reactions to yield $M^{\text{II}}\text{La}_2\text{Ta}_3\text{O}_{10}$ ($M = \text{Co, Cu, Zn}$) when reacted with the corresponding transition metal chlorides ($M\text{Cl}_2$).⁴⁴ In chapters 6 and 7, a series of polar $n = 2$ Ruddlesden-Popper phases (e.g. $\text{Li}_2\text{CaTa}_2\text{O}_7$, $\text{Li}_2\text{LaTiTaO}_7$ and $\text{Li}_2\text{LaTiNbO}_7$) are investigated which could act as potential precursors to perform cation exchange reactions to introduce paramagnetic cations in the interlayer spaces of layered perovskites. If the resulting exchanged product has a polar structure, this cation exchange pathway can act as an alternative to synthesize new magnetoelectric multiferroic materials.

8.2 Synthesis

The synthesis of $\text{MnCaTa}_2\text{O}_7$ was carried out by performing cation exchange reactions on $\text{Li}_2\text{CaTa}_2\text{O}_7$. The synthesis of polycrystalline $\text{Li}_2\text{CaTa}_2\text{O}_7$ is described in chapter 6. $\text{Li}_2\text{CaTa}_2\text{O}_7$ was ground together with anhydrous MnCl_2 in a 1:5 molar ratio using an agate pestle and mortar in an argon-filled glove box. The mixture was then placed in a pyrex tube, which was sealed using a blow torch under vacuum. The tube was heated at 375 °C for a period of 3 days. A large-scale sample (~4 g) for neutron diffraction was synthesized in flowing argon as described in chapter 2. After the final heat treatment, the reaction mixture was washed with distilled water to remove the remaining chlorides. Reaction progress was assessed by collecting X-ray powder diffraction data using a PANalytical X'Pert diffractometer.

8.3 Results

8.3.1 Optical SHG measurement

Powder SHG data collected from $\text{MnCaTa}_2\text{O}_7$ indicate that the sample is SHG active and the activity is 0.46 times that of $\alpha\text{-SiO}_2$. This observation indicates that $\text{MnCaTa}_2\text{O}_7$ adopts a non-centrosymmetric crystal structure.

8.3.2 Characterisation of $\text{MnCaTa}_2\text{O}_7$

8.3.2.1 Room temperature synchrotron X-ray diffraction data

Synchrotron X-ray diffraction (SXRD) data collected from $\text{MnCaTa}_2\text{O}_7$ at room temperature could be indexed using an orthorhombic unit cell ($a = 5.515 \text{ \AA}$, $b = 5.517 \text{ \AA}$, $c = 19.03 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Ruddlesden-Popper aristotype unit cell. Systematic absences indicate a primitive cell is required to index all the peaks in the diffraction pattern. Powder SHG measurements reveal that the sample is SHG active; hence adopts a noncentrosymmetric crystal structure. Symmetry analysis of the structural distortions of the $n = 2$ Ruddlesden-Popper framework reveals two noncentrosymmetric orthorhombic candidate structures described in the $P2_1nm$ and $P2cm$ space groups. Structural models were constructed in the $P2_1nm$ and $P2cm$ space groups and refined against the SXRD data. The $P2_1nm$ model resulted in slightly better fitting than the $P2cm$ model.

Mn^{2+} cations in the cation exchanged $\text{MnCaTa}_2\text{O}_7$ Ruddlesden-Popper phase occupy only half of the available pseudo-tetrahedral coordination sites in the framework, so can adopt either ordered or disordered arrangements. There are two $4b$ sites for Mn in the $P2_1nm$ model. The Mn-site occupancies were refined within the constraint of total occupancy being one. After refinement, the occupancy of the first $4b$ site reached 0.08 and the occupancy of the other $4b$ site reached 0.92, indicating that the Mn^{2+} ions are ordered. The second $4b$ site was fixed as fully occupied which did not change the fitting statistics. Moreover, the ordered model results

in a better fit than the disordered model as shown in Figure 8.1. The observed, calculated and difference plots from the structural refinement of the ordered $P2_1nm$ model of $MnCaTa_2O_7$ against the SXRD data collected at room temperature are shown in Figure 8.2.

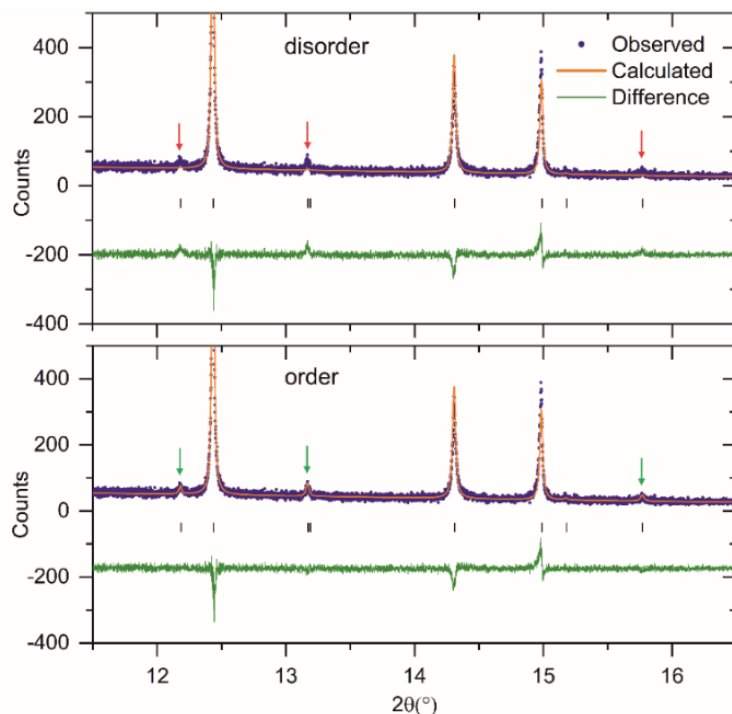


Figure 8.1. Comparison of the refinements of the disordered and ordered model of $P2_1nm$ symmetry structure of $MnCaTa_2O_7$. The arrows indicate the Mn-ordering peaks.

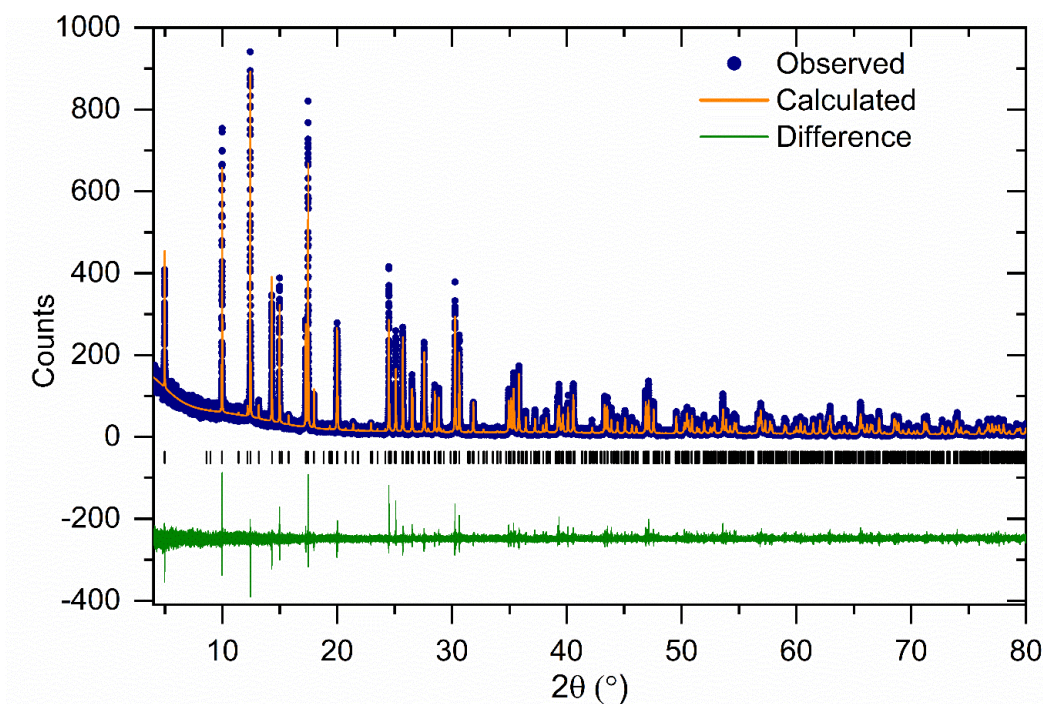


Figure 8.2. Observed, calculated and difference plots from the structural refinement of $P2_1nm$ model of $MnCaTa_2O_7$ against the SXRD data collected at room temperature.

8.3.2.2 Room temperature neutron diffraction data

Neutron powder diffraction (NPD) data collected from $\text{MnCaTa}_2\text{O}_7$ using the GEM diffractometer at ISIS Neutron and Muon Source can be indexed using an orthorhombic unit cell ($a = 5.515 \text{ \AA}$, $b = 5.517 \text{ \AA}$, $c = 19.03 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of an undistorted aristotype $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Systematic absences indicate a primitive cell is required to index all the peaks in the diffraction pattern. The noncentrosymmetric $P2_1nm$ and $P2cm$ models were constructed and refined against the NPD data collected at room temperature. A centrosymmetric tetragonal $P4_2/mnm$ model was considered as the refined a - and b -lattice parameters were close to one another. Another centrosymmetric model $Pnnm$ with $a^-b^-c^0/b^-a^-c^0$ tilting distortion was also considered to ensure the presence of c^+ tilt in $P2_1nm$ structure. An $a^-a^-c^+/a^-a^-(-c^+)$ distorted structure described in space group $Pna2_1$ (#33) was considered since this is the structure of the precursor $\text{Li}_2\text{CaTa}_2\text{O}_7$ phase. The best numerical fits to the data were achieved by the model described in space group $P2_1nm$ with an $a^-b^-c^+/b^-a^-c^+$ tilting distortion as shown in Table 8.1. Full details of the refined structure of $\text{MnCaTa}_2\text{O}_7$ in $P2_1nm$ symmetry structure are given in Table 8.2, with plots of the fitted diffraction patterns shown in Figure 8.3, Selected bond lengths are given in Table 8.3.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
$P2_1nm$ (#31)	$a^-b^-c^+/b^-a^-c^+$	178	2.879	3.088
$P2cm$ (#28)	$a^-b^-c^+/(a^-b^-)c^+$	179	8.580	5.750
$Pna2_1$ (#)	$a^-a^-c^+/a^-a^-(-c^+)$	249	5.363	4.148
$P4_2/mnm$ (#136)	$a^-b^0c^0/b^0a^-c^0$	141	3.226	3.281
$Pnnm$ (#58)	$a^-b^-c^0/b^-a^-c^0$	224	3.102	3.143

Table 8.1. Fitting statistics from the structural refinement of $\text{MnCaTa}_2\text{O}_7$ against the neutron powder diffraction data collected at room temperature.

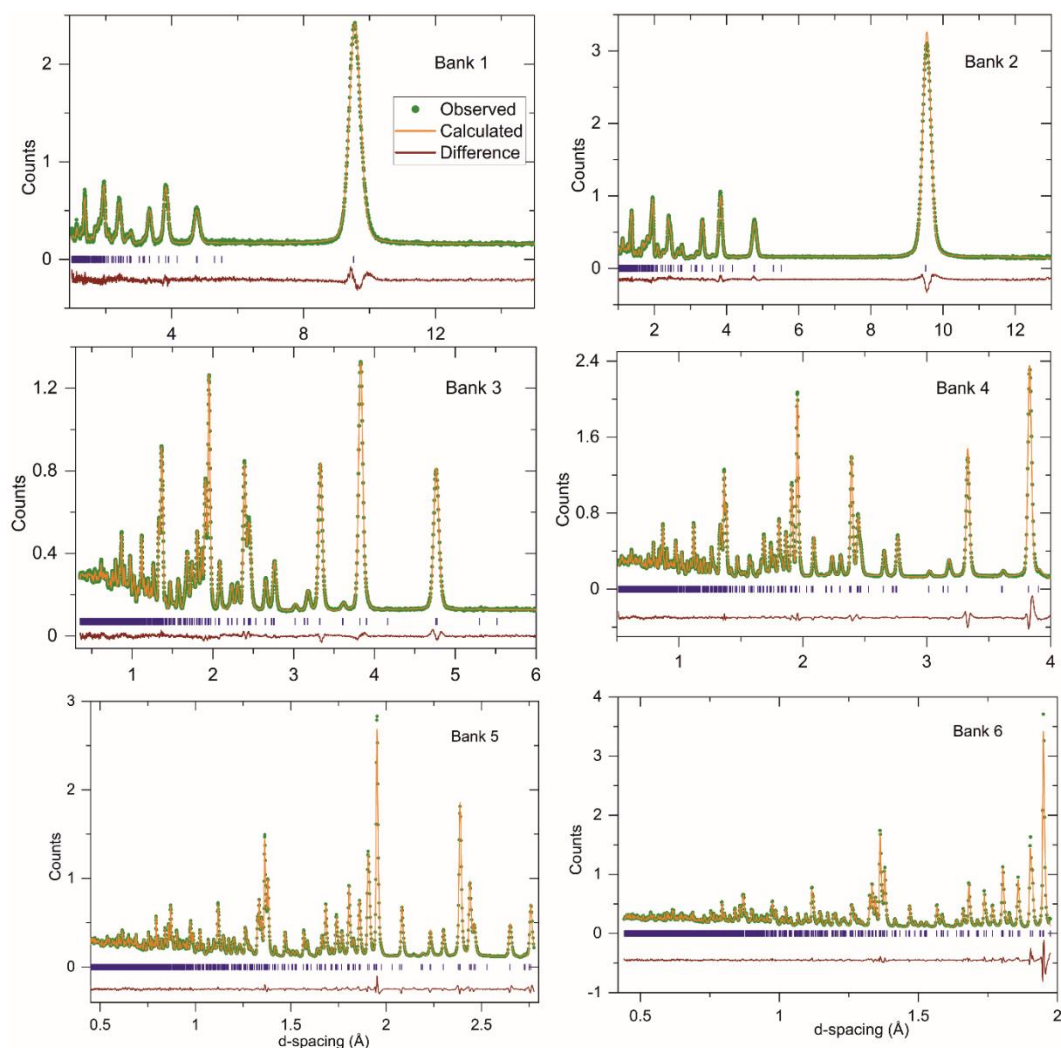


Figure 8.3. Observed, calculated and difference plots from the structural refinement of $P2_1nm$ model of $MnCaTa_2O_7$ against the NPD data collected from the GEM diffractometer at room temperature.

Atom	Site	x	y	z	Occ.	B _{iso} (Å ²)
Mn1	4b	0.2375(15)	0.2515(10)	0.7382(1)	1	0.85(3)
Ca1	2a	0.9893(11)	0.9990(10)	0	1	0.23(4)
Ca2	2a	0.5108(18)	0.5152(15)	0	1	1.69(9)
Ta1	4b	0.9966(7)	0.9964(5)	0.3940(1)	1	0.23(4)
Ta2	4b	0.5025(6)	0.4997(5)	0.3939(1)	1	0.27(4)
O1	2a	0.5463(7)	0.9313(7)	0	1	0.48(6)
O2	2a	0.9351(10)	0.5497(8)	0	1	0.68(7)
O3	4b	0.7301(8)	0.2654(6)	0.0886(1)	1	0.37(4)
O4	4b	0.2454(13)	0.7491(7)	0.0932(1)	1	1.10(5)
O5	4b	0.2599(7)	0.2359(7)	0.6213(1)	1	0.88(2)

O6	4b	0.7381(10)	0.7569(8)	0.5797(1)	1	0.62(2)
O7	4b	0.9647(6)	0.9720(7)	0.2957(3)	1	0.68(5)
O8	4b	0.5183(7)	0.5349(7)	0.2967(3)	1	0.92(6)
MnCaTa₂O₇ – space group <i>P2₁nm</i> (#31) $a = 5.5155(4) \text{ \AA}$, $b = 5.5169(4) \text{ \AA}$, $c = 19.0303(12) \text{ \AA}$, volume = 579.07(6) $\text{\AA}^3$ Formula weight = 568.91 g mol⁻¹, Z = 4 Radiation source: Neutron Time of Flight Temperature: 298 K R_p = 3.088 %, wR_p = 2.879 %						

Table 8.2. Parameters from the structural refinement of *P2₁nm* model of MnCaTa₂O₇ against the neutron powder diffraction data collected at room temperature.

Cation	Anion	Bond length ($\text{\AA}$)	BVS
Ta1	O1 $\times$ 1	2.074(3)	+5.114
	O3 $\times$ 1	1.963(6)	
	O4 $\times$ 1	1.988(7)	
	O5 $\times$ 1	1.985(6)	
	O6 $\times$ 1	2.007(7)	
	O7 $\times$ 1	1.884(7)	
Ta2	O2 $\times$ 1	2.071(3)	+5.219
	O3 $\times$ 1	2.012(6)	
	O4 $\times$ 1	1.934(8)	
	O5 $\times$ 1	1.998(6)	
	O6 $\times$ 1	1.989(7)	
	O8 $\times$ 1	1.862(7)	
Ca1	O1 $\times$ 1	2.472(8)	+1.910
	O1 $\times$ 1	3.095(8)	
	O2 $\times$ 1	2.497(8)	
	O2 $\times$ 1	3.053(8)	
	O3 $\times$ 2	2.655(6)	
	O4 $\times$ 2	2.654(7)	
	O5 $\times$ 2	2.934(5)	

	O6 × 2	2.449(7)	
Ca2	O1 × 1	2.304(10)	+2.111
	O1 × 1	3.227(10)	
	O2 × 1	2.348(12)	
	O2 × 1	3.181(12)	
	O3 × 2	2.491(8)	
	O4 × 2	2.637(9)	
	O5 × 2	3.017(7)	
	O6 × 2	2.611(9)	
Mn1	O5 × 1	2.230(3)	+1.849
	O7 × 1	2.071(8)	
	O7 × 1	2.249(8)	
	O8 × 1	2.022(8)	
	O8 × 1	2.299(8)	

Table 8.3. Selected bond lengths and cation bond valence sums from the refined structure of MnCaTa₂O₇ at room temperature.

8.3.2.3 SQUID magnetometry of MnCaTa₂O₇

Magnetisation data were collected from a sample of MnCaTa₂O₇ in an applied field of 100 Oe in the temperature range of 5 K ≤ T(K) ≤ 300 K. The ZFC and FC data are shown in Figure 8.4, which diverge below 44 K, suggesting a transition to a magnetically ordered state. The magnetisation-field isotherm collected at 300 K is a straight line that passes through the origin, but the 5 K data shows a small hysteresis (as shown in Figure 8.5) which indicates canting in the antiferromagnetic ordering of Mn²⁺ spins.

Mn₃O₄ is a ferrimagnet that shows magnetic transition around 43 K-44 K.^{107,108} Therefore, to determine whether the transition observed at 44 K is from Mn₃O₄ or from MnCaTa₂O₇, the MnCaTa₂O₇ sample was heated at 350 °C with 10 % H₂ in Ar gas flow in order to reduce the Mn₃O₄ if it is present as an impurity. The diffraction pattern remained unchanged after the heat treatment. Magnetisation data were collected from the H₂-treated sample of MnCaTa₂O₇ in an applied field of 100 Oe in the temperature range of 5 K ≤ T(K) ≤ 300 K. The ZFC-FC plots

(Figure 8.4) appear to be significantly different than the original sample. The sharp divergence around 44 K has disappeared which confirms that the $\text{MnCaTa}_2\text{O}_7$ does not order magnetically at 44 K and the transition at 44 K is because of a magnetic impurity (most probably Mn_3O_4) present in the sample. There is a small discontinuity at 56 K in the ZFC-FC magnetisation plot and the derivative of the (M/H) plot as shown in Figure 8.5 which indicates the real magnetic ordering temperature of $\text{MnCaTa}_2\text{O}_7$ that will also be confirmed later using neutron diffraction data. The magnetisation-field isotherm collected from the H_2 -treated $\text{MnCaTa}_2\text{O}_7$ sample at 300 K is a straight line that passes through the origin. The 5 K isotherm is also a straight line passing through the origin which indicates that there is no or very small canting in the antiferromagnetic order of Mn^{2+} moments.

It is possible that the $\text{MnCaTa}_2\text{O}_7$ sample inherited a very small amount of Mn_3O_4 from the oxidation of MnCl_2 during the cation-exchange reaction, although no indication of the presence of any secondary phase was observed in the diffraction measurements.

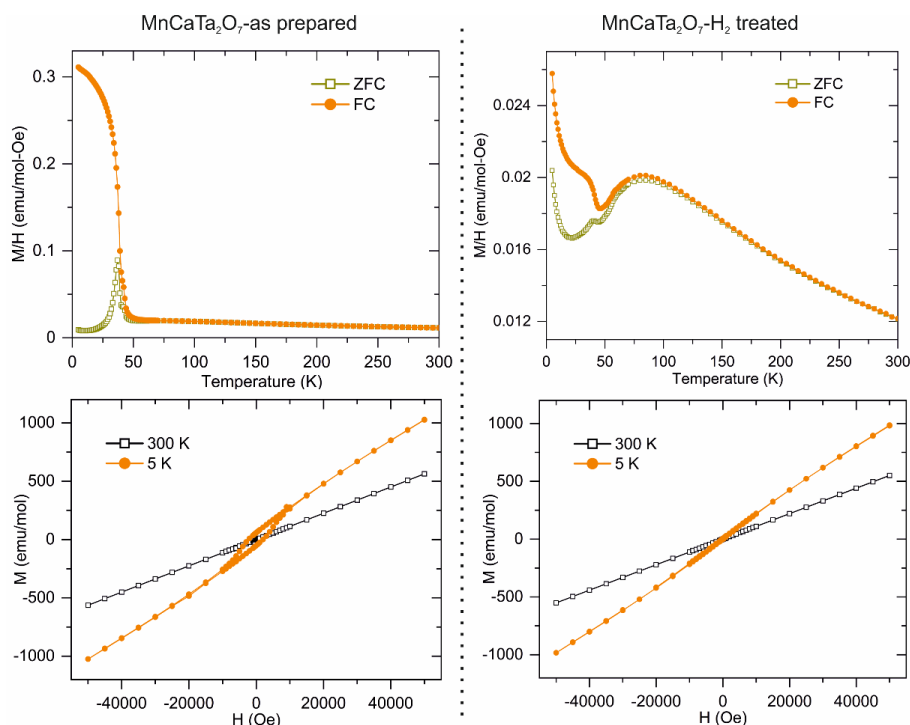


Figure 8.4. Zero field cooled (ZFC) and field cooled (FC) magnetisation data, and magnetisation-field isotherm at 300 K and 5 K collected from the as-prepared sample (left) and H_2 -treated sample (right) of $\text{MnCaTa}_2\text{O}_7$.

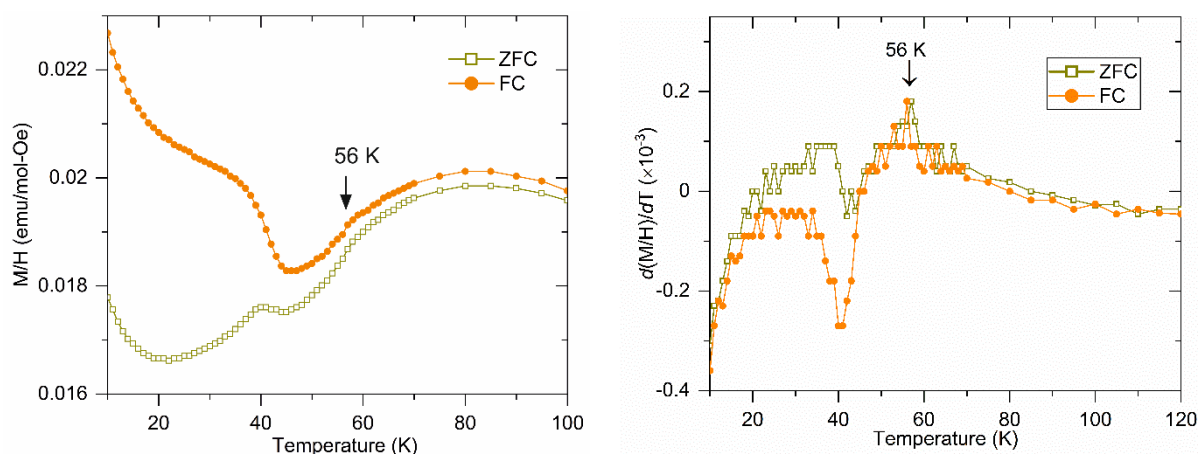


Figure 8.5. ZFC-FC magnetisation plots (left) and derivative of the ZFC-FC magnetisation data (right) collected from the H₂-treated sample of MnCaTa₂O₇.

8.3.2.4 Low temperature (5 K) neutron diffraction data

Neutron powder diffraction data were collected from a sample of 4 g MnCaTa₂O₇ at 5 K using the GEM instrument at ISIS. Comparison of the neutron powder diffraction data collected at room temperature and 5 K reveals that there are a series of additional diffraction peaks in the 5 K data as shown in Figure 8.6. The additional diffraction peaks are attributed to a magnetically ordered phase. The additional diffraction peaks can be indexed using a single magnetic propagation vector, $\mathbf{k} = (0, 0, 0)$, of the crystallographic unit cell. The room temperature $P2_1nm$ model was used to generate possible magnetic models with the help of ISOSDISTORT software. The possible models were refined against the 5 K neutron data. The best fit to the data was achieved by using the model in magnetic space group $P2_1n'm'$, in which the Mn-lattice adopts G-type antiferromagnetic order. The refinement of the magnetic moments reveals that the magnitude of the obtained moment along x -or y -direction is zero within error. Therefore, a magnetic moment only along the z -direction was considered and the refined magnetic moment was 4.496(8) μ_B . Full details of the refined structure of MnCaTa₂O₇ at 5 K are given in Table 8.4, with plots of the fitted diffraction patterns shown in Figure 8.7. Selected bond lengths are given in Table 8.5. The refined magnetic structure is shown in Figure 8.8.

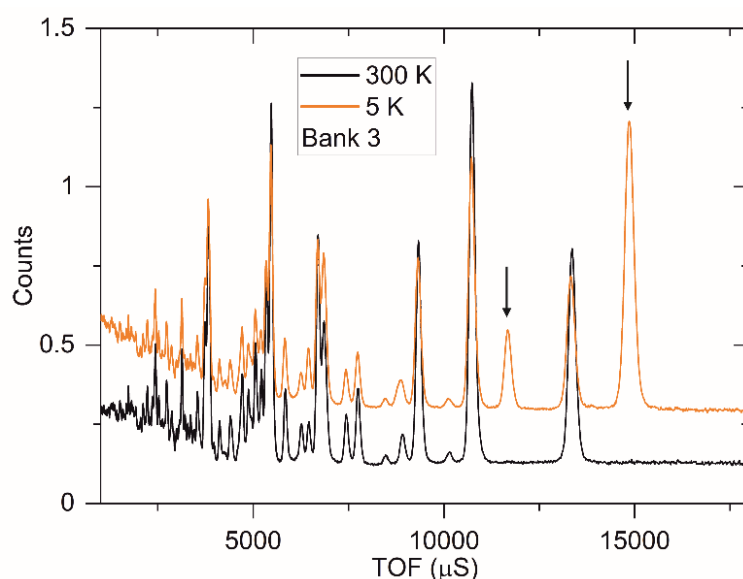


Figure 8.6. Neutron diffraction patterns collected from $\text{MnCaTa}_2\text{O}_7$ at 300 K and 5 K using bank 3 of the GEM diffractometer. Black arrows indicate the magnetic diffraction peaks.

Atom	Site	x	y	z	Occ.	B _{iso} (Å ²)
Mn1	4b	0.2411(12)	0.2530(8)	0.7377(1)	1	0.34(2)
		M _x = 0	M _y = 0	M _z = 4.496(8)		
Ca1	2a	0.9919(17)	0.9906(17)	0	1	0.12(4)
Ca2	2a	0.5060(20)	0.5110(20)	0	1	0.85(7)
Ta1	4b	0.9928(8)	0.9948(8)	0.3939(1)	1	0.12(3)
Ta2	4b	0.4996(9)	0.5015(8)	0.3938(1)	1	0.06(3)
O1	2a	0.5511(10)	0.9346(11)	0	1	0.33(5)
O2	2a	0.9442(11)	0.5627(10)	0	1	0.46(6)
O3	4b	0.7302(8)	0.2661(8)	0.0894(2)	1	0.32(5)
O4	4b	0.2571(8)	0.7378(9)	0.0914(2)	1	0.73(6)
O5	4b	0.2653(7)	0.2321(6)	0.6215(5)	1	0.57(2)
O6	4b	0.7345(8)	0.7613(8)	0.5796(1)	1	0.40(2)
O7	4b	0.9624(10)	0.9760(11)	0.2959(2)	1	0.45(5)
O8	4b	0.5207(10)	0.5336(10)	0.2955(2)	1	0.47(5)
$\text{MnCaTa}_2\text{O}_7$ – space group $P2_1n'm'$ (#31.127) $a = 5.5086(4)$ Å, $b = 5.5107(4)$ Å, $c = 18.9905(11)$ Å, volume = 576.48(6) Å³ Formula weight = 568.91 g mol⁻¹, Z = 4 Radiation source: Neutron Time of Flight						

Temperature: 5 K
$R_p = 1.991 \%$, $wR_p = 2.333 \%$

Table 8.4. Parameters from the structural refinement of $\text{MnCaTa}_2\text{O}_7$ against the neutron powder diffraction data collected at 5 K.

Cation	Anion	Bond length (Å)	BVS
Ta1	O1 $\times$ 1	2.077(3)	+5.134
	O3 $\times$ 1	1.969(7)	
	O4 $\times$ 1	1.984(7)	
	O5 $\times$ 1	2.012(6)	
	O6 $\times$ 1	1.983(7)	
	O7 $\times$ 1	1.871(5)	
Ta2	O2 $\times$ 1	2.070(3)	+5.174
	O3 $\times$ 1	1.986(7)	
	O4 $\times$ 1	1.957(7)	
	O5 $\times$ 1	1.989(6)	
	O6 $\times$ 1	1.995(7)	
	O8 $\times$ 1	1.879(5)	
Ca1	O1 $\times$ 1	2.448(11)	+2.002
	O1 $\times$ 1	3.096(11)	
	O2 $\times$ 1	2.373(11)	
	O2 $\times$ 1	3.164(11)	
	O3 $\times$ 2	2.695(9)	
	O4 $\times$ 2	2.662(9)	
	O5 $\times$ 2	2.896(10)	
	O6 $\times$ 2	2.437(9)	
Ca2	O1 $\times$ 1	2.348(13)	+2.092
	O1 $\times$ 1	3.186(13)	
	O2 $\times$ 1	2.431(13)	
	O2 $\times$ 1	3.108(13)	
	O3 $\times$ 2	2.496(10)	
	O4 $\times$ 2	2.541(10)	
	O5 $\times$ 2	3.061(11)	

	O6 $\times$ 2	2.603(10)	
Mn1	O5 $\times$ 1	2.214(10)	+1.882
	O7 $\times$ 1	2.074(8)	
	O7 $\times$ 1	2.257(8)	
	O8 $\times$ 1	2.015(8)	
	O8 $\times$ 1	2.272(8)	

Table 8.5. Selected bond lengths and cation bond valence sums from the refined structure of MnCaTa₂O₇ at 5 K.

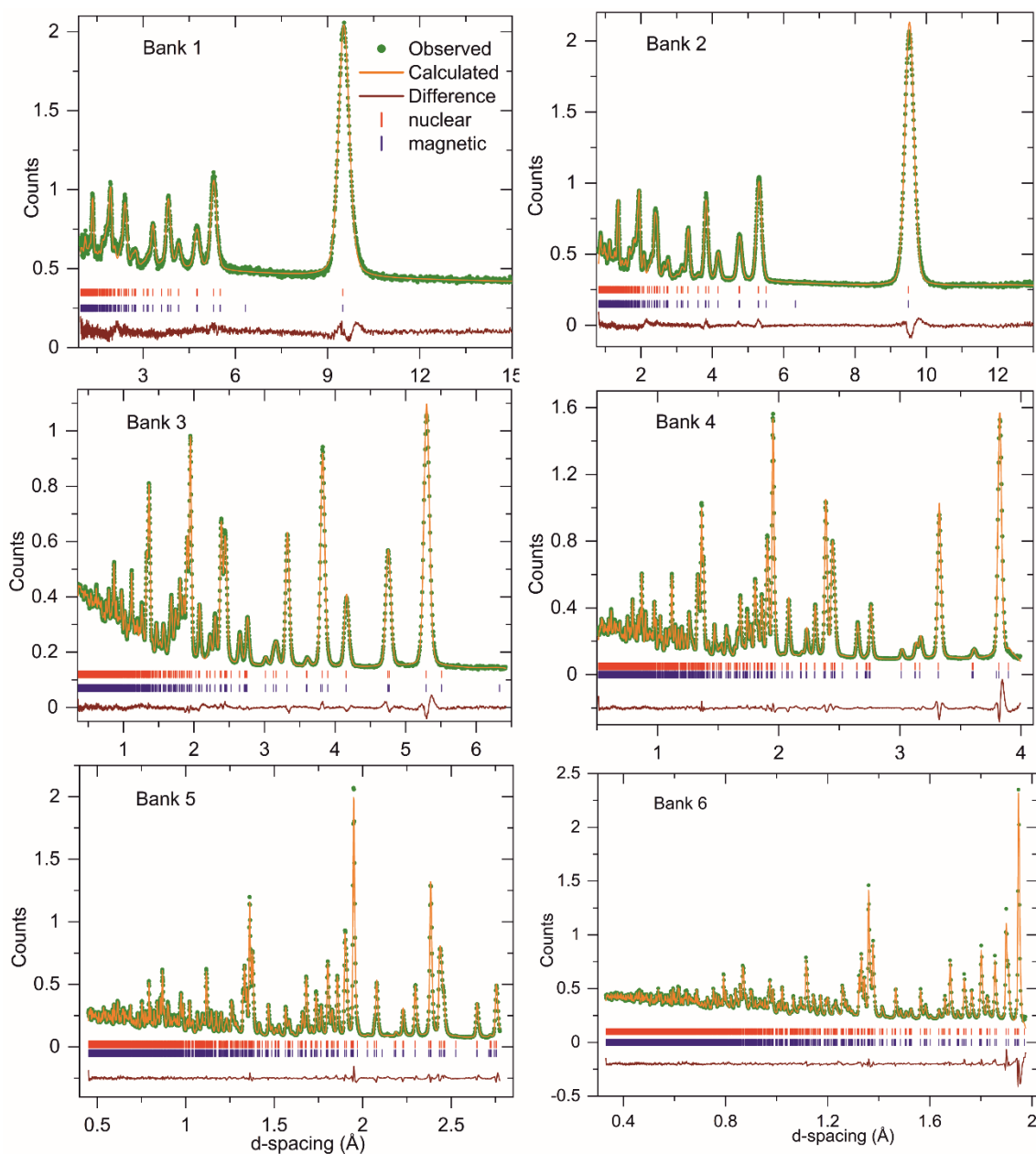


Figure 8.7. Observed, calculated and difference plots from the structural refinement of MnCaTa₂O₇ against the neutron powder diffraction data collected at 5 K.

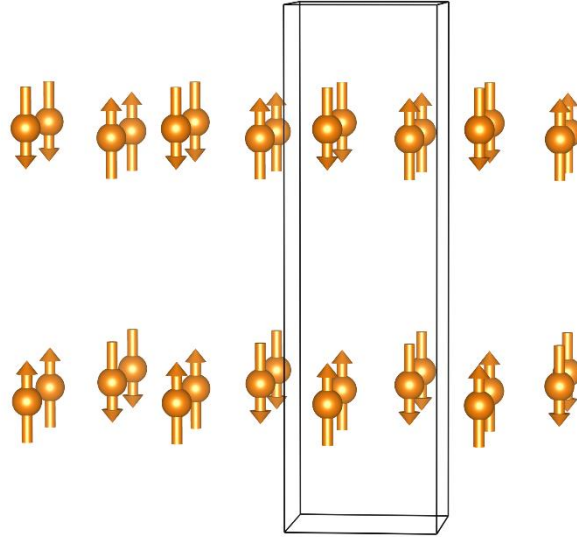


Figure 8.8. G-type antiferromagnetic order of Mn^{2+} in the 5 K structure of $\text{MnCaTa}_2\text{O}_7$.

8.3.2.5 Variable temperature neutron powder diffraction data

Neutron diffraction data were collected from $\text{MnCaTa}_2\text{O}_7$ using the WISH diffractometer at 1.5 K, 10 K, 15 K, 20 K, 25 K, 30 K, 35 K, 40 K, 42 K, 45 K, 47 K, 50 K, 52 K, 55 K, 57 K, 60 K, 62.5 K, 70 K and 100 K. The magnetic model was refined against the 1.5 K data. This model was sequentially refined against the variable temperature neutron diffraction data to extract the ordered moment and lattice parameters at different temperatures. The peak shape parameters were fixed after the first refinement. Figure 8.9 shows the evolution of neutron powder diffraction collected from $\text{MnCaTa}_2\text{O}_7$ as a function of temperature. The black arrows indicate the position of the magnetic diffraction peaks.

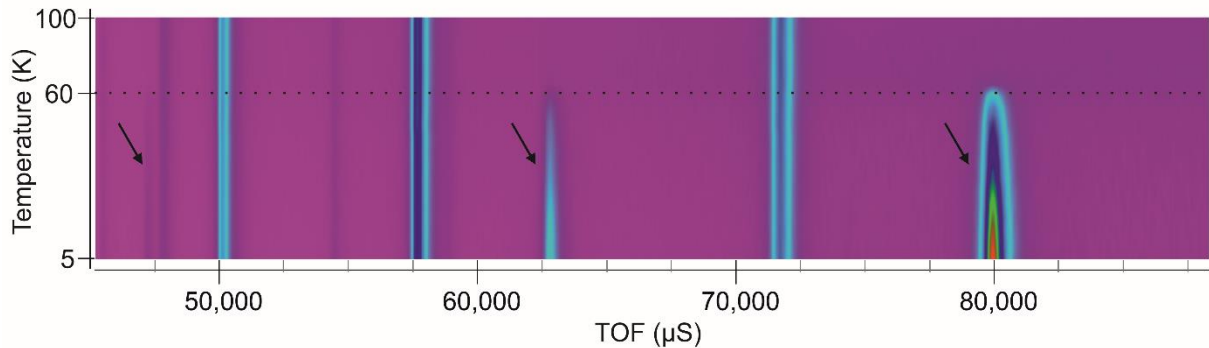


Figure 8.9. Evolution of the magnetic diffraction peaks as temperature. Magnetic peaks are indicated by black arrows. The patterns are collected from Bank 3 of the WISH diffractometer.

Figure 8.10 (left) shows the evolution of the refined magnetic moments with temperature. The magnetic moments can be fitted using a power law, $M = M_0(1 - T/T_N)^\beta$, which yields the following parameters: $M_0 = 4.89(3)$ μB , $T_N = 56.18(19)$ K and $\beta = 0.206(7)$. However, it can be seen from the data in Figure 8.10 (Right) that the magnetic scattering peaks are still present above the Neel temperature, 56.18 K. Close inspection of the data reveals that above 56 K, the magnetic scattering peaks broaden significantly as they lower in intensity as highlighted in Figure 8.10 (Right). This peak broadening and high backgrounds observed around these residual peaks can be attributed to the presence of strong magnetic interactions in the xy -plane above the T_N . The value of the exponential term obtained from the power-law fitting ($\beta = 0.206(7)$) is in good agreement with other systems that show strong 2D magnetic interactions but weak 3D coupling.¹⁰⁹

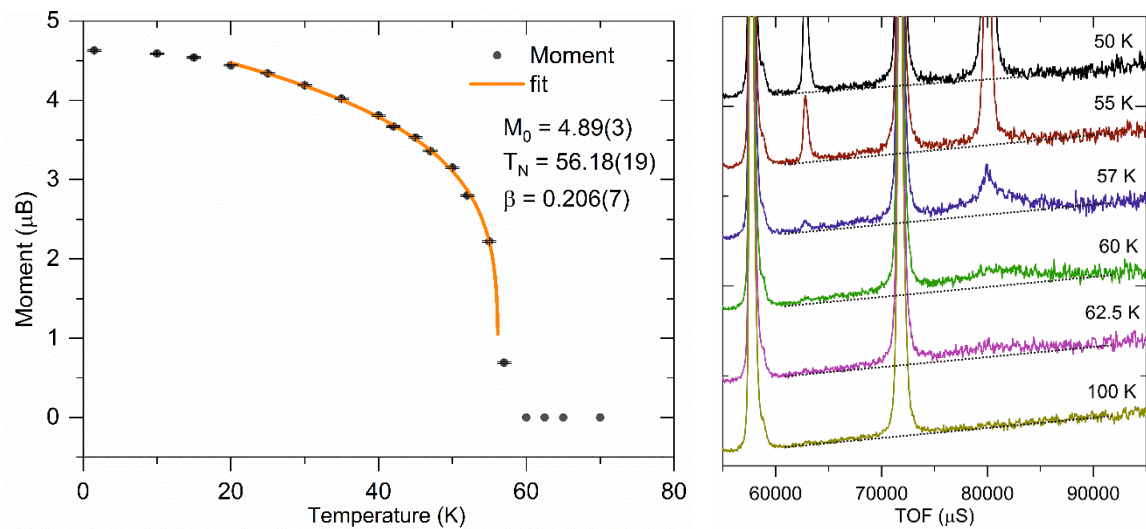


Figure 8.10. (Left) Ordered magnetic moments extracted from the refinement of variable temperature NPD data collected from $\text{MnCaTa}_2\text{O}_7$ using the WISH diffractometer. (Right) NPD data highlighting the magnetic diffuse scattering observed near and above T_N . The dotted black lines are to guide the eye.

8.4 Discussion

The successful synthesis of polar, magnetically ordered $\text{MnCaTa}_2\text{O}_7$ reveals that it is possible to exchange Li^+ cations by divalent 3d transition metal cations to introduce paramagnetic cations in the interlayer of polar layered perovskites sheets. This topochemical cation exchange

approach demonstrates possibilities to synthesize new multiferroic materials which are usually inaccessible by high-temperature synthesis routes. As a monovalent cation is substituted by a divalent cation the number of available sites in the exchanged phase is twice the number of transition metal cations available. Therefore, the metal cations in the interlayer sites can either be ordered or disordered. As demonstrated in the results section, the Mn^{2+} cations are ordered in a checkerboard pattern within the 5-coordinate sites as shown in Figure 8.11.

The parent $\text{Li}_2\text{CaTa}_2\text{O}_7$ phase adopts a polar $Pna2_1$ symmetry structure with $a^-a^-c^+/a^-a^-(-c^+)$ tilting distortion of TaO_6 octahedra. The structure of the $\text{MnCaTa}_2\text{O}_7$ phase can be analysed in terms of the distortion modes which need to be applied to get the distorted structure from the aristotype $I4/mmm$ symmetry structure. The $P2_1nm$ structure of $\text{MnCaTa}_2\text{O}_7$ can be constructed by applying two tilting distortion modes (X_2^+ and X_3^-) and a Γ_5^- polar distortion mode. The X_3^- and X_2^+ irreducible representations describe the $a^-b^-c^0/b^-a^-c^0$ and the $a^0a^0c^+/a^0a^0c^+$ tilting distortions respectively as shown in Figure 8.11.

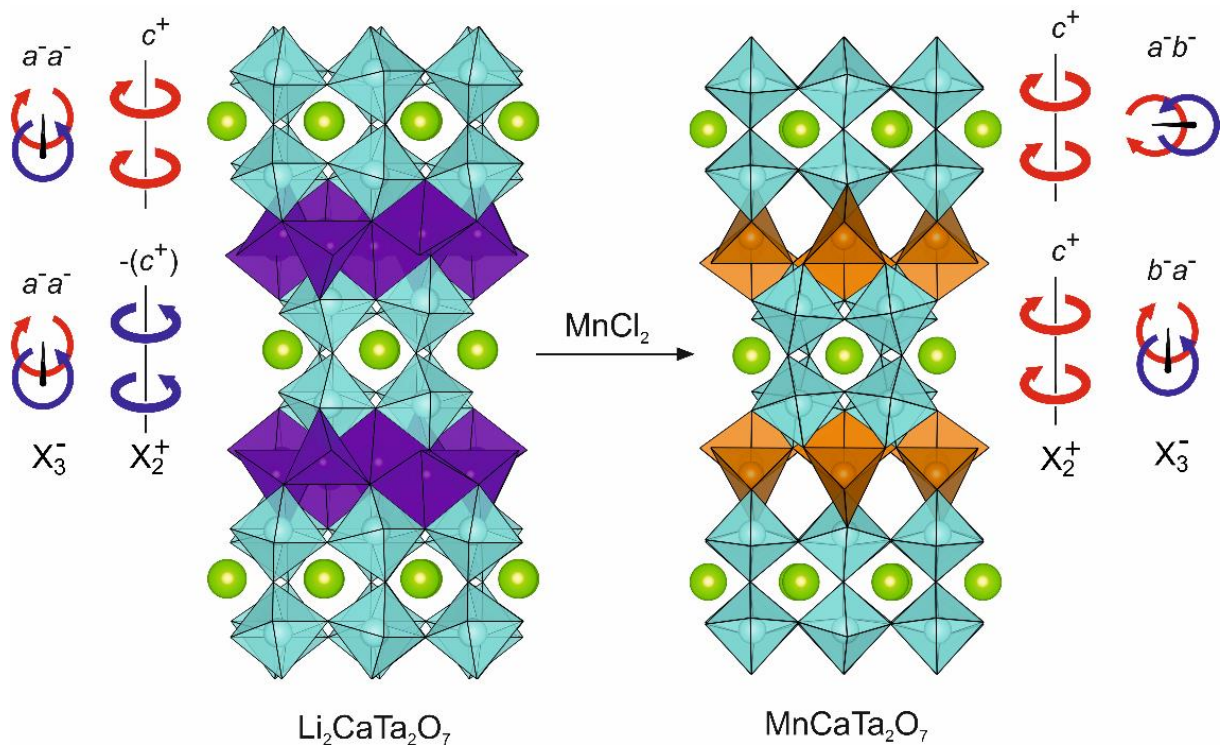


Figure 8.11. Topochemical cation exchange reaction to synthesize $\text{MnCaTa}_2\text{O}_7$.

MnSrTa₂O₇ adopts an incommensurately modulated structure which can be described in the superspace group $A2_1am(0\beta0)000$ with a propagation vector $\mathbf{q} = (0, 0.86, 0)$.⁹⁰ The modulation is consistent with the checkerboard ordering arrangement of Mn²⁺ cations. The $A2_1am$ structure of MnSrTa₂O₇ can also be constructed by applying two tilting distortion modes (X_2^+ and X_3^-) and a Γ_5^- polar distortion mode. In this case, the X_3^- and X_2^+ irreducible representations describe the $a^-a^-c^0/a^-a^-c^0$ and the $a^0a^0c^+/a^0a^0c^+$ tilting distortions respectively. The precursor to synthesise the MnSrTa₂O₇ phase is the Li₂SrTa₂O₇ phase which also adopts the same $A2_1am$ symmetry structure with the same $a^-a^-c^+/a^-a^-c^+$ tilting distortion.

Therefore, it is established that during the cation exchange reaction from Li₂SrTa₂O₇ to MnSrTa₂O₇ the tilting distortion ($a^-a^-c^+/a^-a^-c^+$) remains unchanged, whereas, during the reaction from Li₂CaTa₂O₇ to MnCaTa₂O₇ there is a change in tilting distortion from $a^-a^-c^+/a^-a^-(-c^+)$ to $a^-b^-c^+/b^-a^-c^+$.

Although the irreducible representations describing the $A2_1am$ structure of MnSrTa₂O₇ and the $P2_1nm$ structure of MnCaTa₂O₇ are the same (X_3^- and X_2^+), the order parameters describing the irreducible representations are different. The irreducible representations with the order parameters for the $A2_1am$ and $P2_1nm$ structure would be $X_2^+ \oplus X_3^-$ (0, a ; 0, b) and $X_2^+ \oplus X_3^-$ (0, a ; b , c) respectively.

Mn²⁺ cations in both MnSrTa₂O₇ and MnCaTa₂O₇ structures are ordered in checkerboard arrangement. As discussed in chapter 4, this arrangement minimizes the interionic repulsion. In both the structures the Mn-sites are slightly under-bonded, which highlights the fact that the structures prefer to minimize the strong Coulombic repulsion among the Mn²⁺ ions by arranging them in a checkerboard pattern even though that makes the coordination sites slightly under bonded.

The magnetic ordering temperature (T_N) of MnCaTa₂O₇ ($T_N = 56$ K) is higher than the ordering temperature of MnSrTa₂O₇ ($T_N = 43$ K) which indicates that the interactions between the Mn²⁺

moments is stronger in the Ca-phase than in the Sr-phase. The ionic radius of Ca^{2+} is significantly smaller than the ionic radius of Sr^{2+} (1.34 Å for Ca^{2+} and 1.44 Å for Sr^{2+} in 12 coordinate site). Consequently, the unit cell volume of $\text{MnCaTa}_2\text{O}_7$ is smaller than that of $\text{MnSrTa}_2\text{O}_7$. As a result, the average nearest neighbour Mn-Mn distance in $\text{MnCaTa}_2\text{O}_7$ (3.926 Å at 298 K) is shorter than the same Mn-Mn distance in the checkerboard of $\text{MnSrTa}_2\text{O}_7$ (3.954 Å at 298 K). This leads to a stronger interaction among Mn^{2+} and therefore the higher transition temperature in $\text{MnCaTa}_2\text{O}_7$.

The antiferromagnetic Mn^{2+} moments in the $\text{MnSrTa}_2\text{O}_7$ phase are slightly canted as evidenced from the hysteresis observed below the magnetic transition temperature.⁹⁰ In contrast, the M-H isotherm of $\text{MnCaTa}_2\text{O}_7$ at 5 K is a straight line which passes through the origin (Figure 8.4) indicating no (or very small) canting among the Mn^{2+} moments.

The refined lattice parameters of $\text{MnCaTa}_2\text{O}_7$ are plotted as a function of temperature as shown in Figure 8.12. A clear anomaly can be observed at temperature $T_A = 50$ K, with the b - and c -lattice parameters exhibiting a sharp minimum at this temperature. The a -lattice parameter remains almost temperature-independent during the transition.

The magnitudes of the tilting distortion modes X_2^+ and X_3^- and the polar Γ_5^- distortion modes also demonstrate anomalies (Figure 8.12) at and around T_A and T_N . Below T_A the magnitude of the polar distortion mode, Γ_5^- remains largely temperature independent. The magnitude of Γ_5^- increases sharply at T_A . From T_A to T_N the magnitude decreases linearly, reaching the initial value at T_N . In contrast, the magnitude of the X_2^+ distortion mode decreases sharply at T_A . The change in the magnitude of X_3^- distortion mode is small compared to the changes in X_2^+ and Γ_5^- distortion modes, considering the errors bound to them.

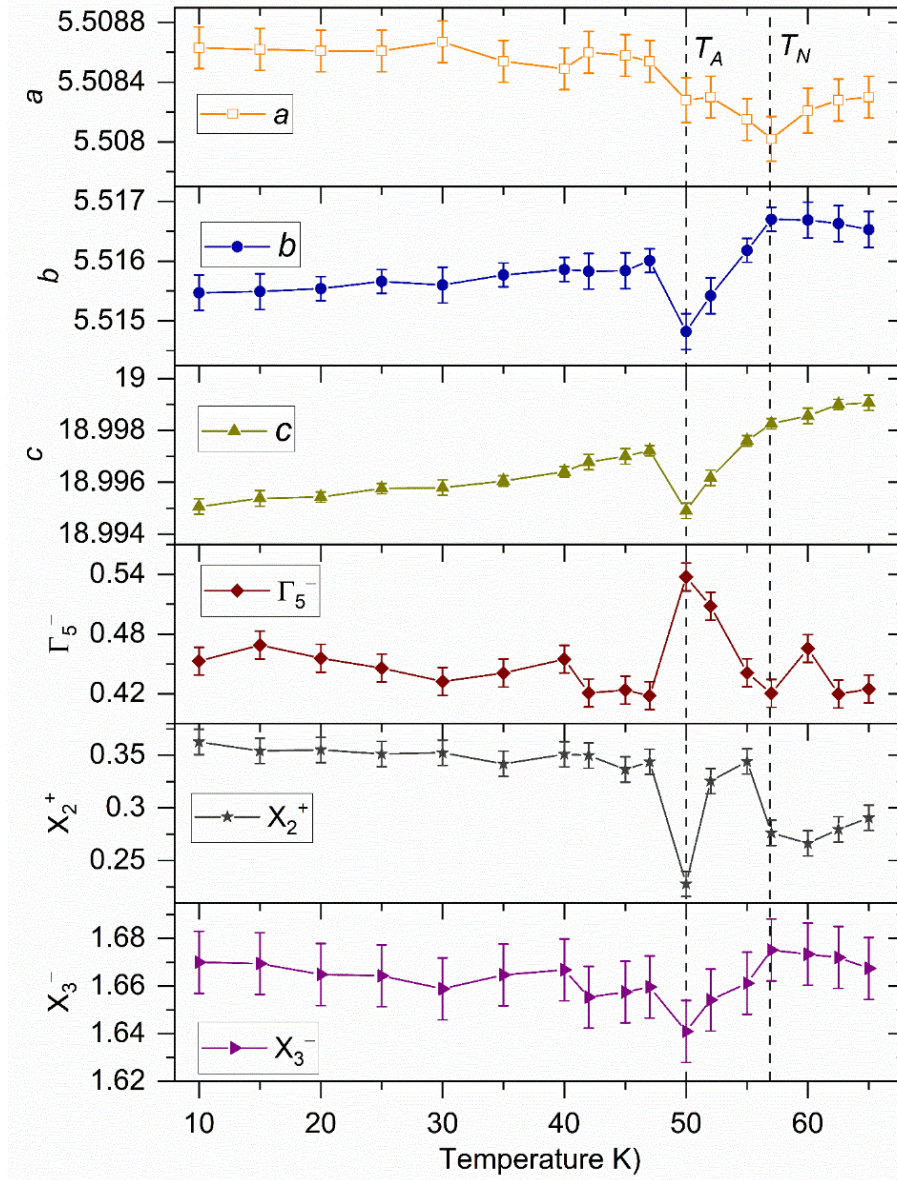


Figure 8.12. Evolution of a -, b - and c -lattice parameters, Γ_5^- , X_2^+ and X_3^- distortion mode magnitudes of $\text{MnCaTa}_2\text{O}_7$ with temperature.

Similar discontinuities in the lattice parameters are also observed in the magnetoelectric phase $\text{MnSrTa}_2\text{O}_7$ at $T_A = 38$ K.⁹⁰ The magnetisation-field isotherms collected from $\text{MnSrTa}_2\text{O}_7$ at 35 K and 30 K show significant increase in remnant magnetisation and coercive field consistent with a sharp increase in the ferromagnetic component of the magnetic state. Further the magnitudes of the Γ_5^- , mX_3^+ , and X_3^- distortions undergo a step change at T_A , coincident with a sharp increase in the weak ferromagnetic moment ($m\Gamma_5^+$) of $\text{MnSrTa}_2\text{O}_7$, consistent with magnetoelectric coupling. In contrast, the signatures of the distortion modes at $T_A = 50$ K for

the $\text{MnCaTa}_2\text{O}_7$ phase are significantly different to that of $\text{MnSrTa}_2\text{O}_7$. Most importantly, there is no ferromagnetic moment observed at T_A or even at lower temperatures. Therefore, the coupling mechanism relating the electrical polarisation of $\text{MnSrTa}_2\text{O}_7$ with ferromagnetic moment of Mn^{2+} does not take place in the $\text{MnCaTa}_2\text{O}_7$ phase. It is likely that the slight changes in the order parameters of the associated distortion modes in the $\text{MnCaTa}_2\text{O}_7$ phase compared to the order parameters of the distortion modes in $\text{MnSrTa}_2\text{O}_7$ destroys the possibility of any strong magnetoelectric coupling.

8.5 Conclusion

Synthesis of $\text{MnCaTa}_2\text{O}_7$ is possible by a topochemical cation exchange reaction from $\text{Li}_2\text{CaTa}_2\text{O}_7$ phase. $\text{MnCaTa}_2\text{O}_7$ adopts a polar $P2_1nm$ structure where the Mn^{2+} cations are ordered in checkerboard arrangement within the 5-coordinate sites. SQUID magnetometry and neutron diffraction data reveals that the Mn^{2+} moments antiferromagnetically order below 56 K. The successful synthesis of the Mn-phase from the corresponding Li-phase suggests that the low-temperature cation exchange chemistry could be utilized to prepare new magnetoelectric materials.

An obvious subsequent question would be: is it possible to incorporate other divalent 3d transition metal cations e.g. Co^{2+} or Fe^{2+} by performing similar cation exchange reactions? The answer to this question is explored in the next chapters.

Chapter 9 – Synthesis and characterisation of $\text{MnLa}(\text{TiNb})\text{O}_7$ and $\text{MnLa}(\text{TiTa})\text{O}_7$

9.1 Introduction

In chapter 8, the synthesis and characterisation of metastable $\text{MnCaTa}_2\text{O}_7$ are demonstrated. This phase is synthesized by a topochemical cation exchange reaction from the thermodynamically stable precursor, $\text{Li}_2\text{CaTa}_2\text{O}_7$. In chapter 7, synthesis of polar $\text{Li}_2\text{LaB}_2\text{O}_7$ ($B = \text{TiNb}/\text{TiTa}$) phases are described. Therefore, it is of interest to find out if these two Li-phases also undergo topochemical cation exchange reactions to incorporate magnetic cations in the interlayer of double perovskite sheets. If the resulting exchanged products adopt polar structures, then this cation exchange pathway can act as an alternative to synthesize new magnetoelectric multiferroic materials.

9.2 Synthesis

The synthesis of $\text{MnLa}(\text{TiNb})\text{O}_7$ and $\text{MnLa}(\text{TiTa})\text{O}_7$ was carried out by performing cation exchange reactions from $\text{Li}_2\text{La}(\text{TiNb})\text{O}_7$ and $\text{Li}_2\text{La}(\text{TiTa})\text{O}_7$ respectively. The synthesis of polycrystalline $\text{Li}_2\text{La}(\text{TiNb})\text{O}_7$ and $\text{Li}_2\text{La}(\text{TiTa})\text{O}_7$ ¹⁰² is described in chapter 7. The precursor Li-phases were ground together with anhydrous MnCl_2 in a 1:5 molar ratio using an agate pestle and mortar in an argon-filled glove box. The mixture was then placed in a pyrex tube, which was sealed using a blow torch under vacuum. The tube was heated at 375 °C for a period of 3 days. Large scale samples (~ 4 g) for neutron diffraction were synthesized in flowing argon as described in chapter 2. After the heat treatment, the reaction mixtures were washed with distilled water to remove the remaining chlorides. Reaction progress was assessed by collecting X-ray powder diffraction using a PANalytical X'Pert diffractometer.

9.3 Results

9.3.1 Optical SHG measurement

Powder SHG data collected from $\text{MnLa}(\text{TiNb})\text{O}_7$ indicate that the sample is SHG active and the activity is 0.51 times that of $\alpha\text{-SiO}_2$. This observation indicates that $\text{MnLa}(\text{TiNb})\text{O}_7$ adopts a non-centrosymmetric crystal structure.

9.3.2 Characterisation of $\text{MnLa}(\text{TiNb})\text{O}_7$

9.3.2.1 Room temperature synchrotron X-ray diffraction data

Synchrotron X-ray diffraction (SXRD) data collected from $\text{MnLa}(\text{TiNb})\text{O}_7$ at room temperature could be indexed using an orthorhombic unit cell ($a = 5.492 \text{ \AA}$, $b = 5.494 \text{ \AA}$, $c = 19.13 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Ruddlesden-Popper aristotype unit cell. Systematic absences indicate a primitive cell is required to index all the peaks in the diffraction pattern. Powder SHG measurement reveals that the sample is SHG active, hence adopts a noncentrosymmetric crystal structure. Symmetry analysis of the $n = 2$ Ruddlesden-Popper framework,^{42,79} in combination with the observation that the $\text{MnLa}(\text{TiNb})\text{O}_7$ is SHG active (activity 0.51 times $\alpha\text{-SiO}_2$) suggests an $a^-b^-c^+/b^-a^-c^+$ distorted structure described in space group $P2_1nm$ (#31), analogous to the room temperature structure of $\text{MnCaTa}_2\text{O}_7$ as described in chapter 8. There is no evidence for any Ti/Nb ordering. A model based on the room temperature structure of $\text{MnCaTa}_2\text{O}_7$, but with Ca replaced by La and Ta replaced by a 1:1 disordered mixture of Ti:Nb was constructed and refined against the SXRD data to achieve a good fit as shown in Figure 9.2. The Mn^{2+} cations are also ordered in chequerboard pattern in the 5-coordinate interlayer sites similar to the $\text{MnCaTa}_2\text{O}_7$ phase as indicated by a better fit to the data for the ordered Mn^{2+} model than the disordered model as shown in Figure 9.1.

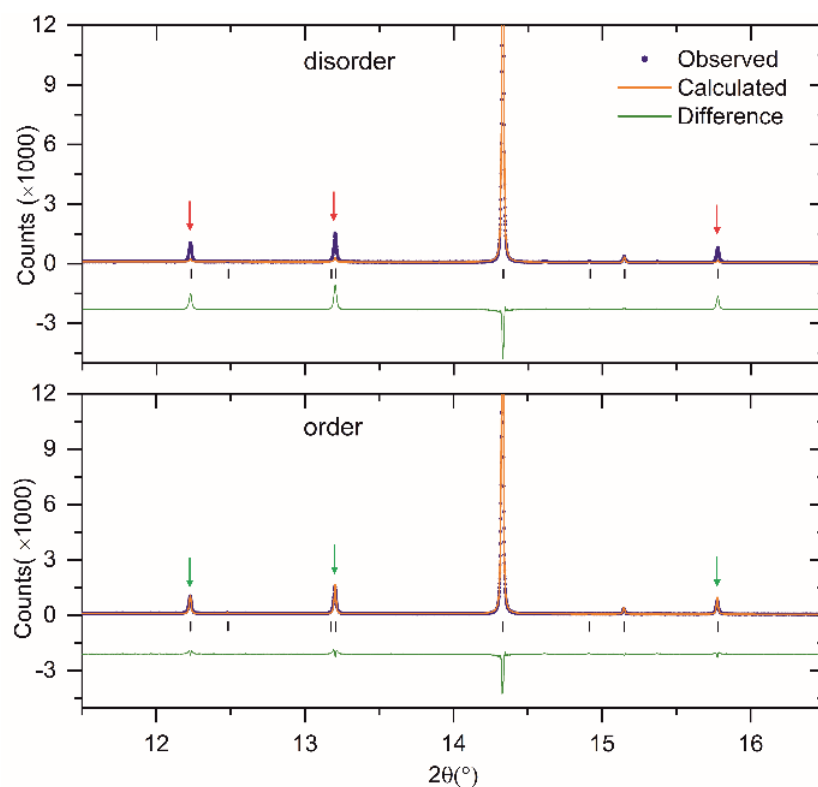


Figure 9.1. Comparison of the refinements of the disordered and ordered model of $P2_1nm$ symmetry structure of $MnLa(TiNb)O_7$. The arrows indicate the Mn-ordering peaks.

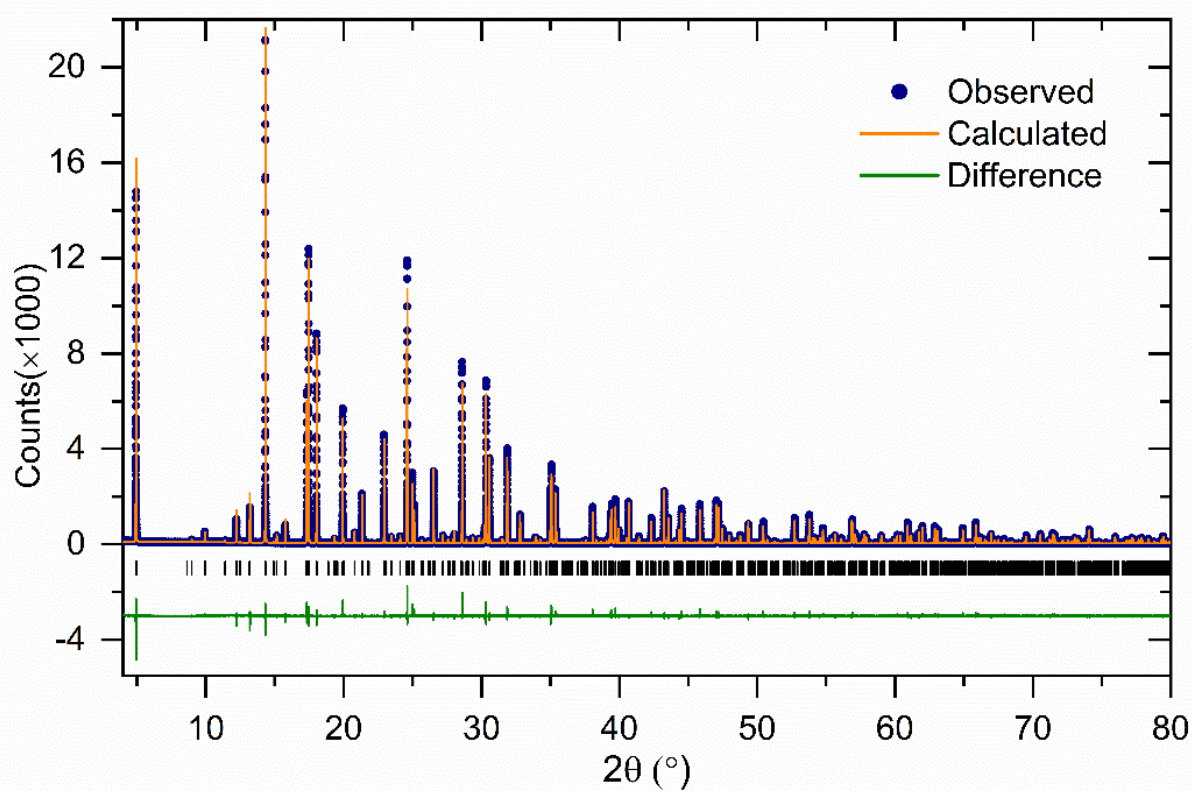


Figure 9.2. Observed, calculated and difference plots from the structural characterisation of $MnLa(TiNb)O_7$ against the SXRD data collected at room temperature.

9.3.2.2 Room temperature neutron diffraction data

Neutron powder diffraction (NPD) data collected from $\text{MnLa}(\text{TiNb})\text{O}_7$ using the GEM diffractometer at ISIS, can be indexed using an orthorhombic unit cell ($a = 5.492 \text{ \AA}$, $b = 5.494 \text{ \AA}$, $c = 19.13 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of an undistorted aristotype $I4/mmm$ symmetry unit cell of an $n = 2$ Ruddlesden-Popper phase. Systematic absences indicate a primitive cell is required to index all the peaks in the diffraction pattern. The noncentrosymmetric $P2_1nm$ and $P2cm$ models were constructed and refined against the NPD data collected at room temperature. A centrosymmetric tetragonal $P4_2/mnm$ model was considered as the refined a - and b -lattice parameters were close to one another. Another centrosymmetric model $Pnnm$ with $a^-b^-c^0/b^-a^-c^0$ tilting distortion was also considered to ensure the presence of c^+ tilt in $P2_1nm$ structure. The best numerical fits to the data were achieved by the model described in noncentrosymmetric space group $P2_1nm$ with an $a^-b^-c^+/b^-a^-c^+$ tilting distortion, as shown in Table 9.1, which is consistent with the observed SHG intensity. Full details of the refined structure of $\text{MnLa}(\text{TiNb})\text{O}_7$ in $P2_1nm$ symmetry structure are given in Table 9.2, with plots of the fitted diffraction patterns shown in Figure 9.3. Selected bond lengths are given in Table 9.3.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
$P2_1nm$ (#31)	$a^-b^-c^+/b^-a^-c^+$	177	2.103	2.433
$P2cm$ (#28)	$a^-b^-c^+/(a^-b^-)c^+$	176	7.109	4.664
$P4_2/mnm$ (#136)	$a^-b^0c^0/b^0a^-c^0$	141	2.150	2.462
$Pnnm$ (#58)	$a^-b^-c^0/b^-a^-c^0$	224	4.579	3.399

Table 9.1. Fitting statistics from the structural refinement of $\text{MnLa}(\text{TiNb})\text{O}_7$ against the neutron powder diffraction data collected at room temperature.

Atom	Site	x	y	z	Occ.	B_{iso} ($\text{\AA}^2$)
Mn1	4b	0.2233(20)	0.2565(15)	0.7371(1)	1	0.98(3)
La1	2a	0.9646(7)	0.9882(7)	0	1	0.34(5)

La2	2a	0.4696(8)	0.5072(9)	0	1	0.69(6)
Ti/Nb(1)	4b	0.9676(27)	0.0004(21)	0.3882(5)	0.5/0.5	0.20(3)
Ti/Nb(2)	4b	0.4589(19)	0.5102(19)	0.3841(5)	0.5/0.5	0.20(3)
O1	2a	0.5021(11)	0.9615(10)	0	1	0.40(6)
O2	2a	0.9203(10)	0.5562(11)	0	1	0.80(6)
O3	4b	0.7170(14)	0.2482(10)	0.0903(1)	1	0.53(3)
O4	4b	0.2195(13)	0.7459(10)	0.0950(1)	1	0.51(3)
O5	4b	0.2182(13)	0.2496(10)	0.6173(1)	1	0.78(1)
O6	4b	0.7158(13)	0.7487(11)	0.5839(1)	1	0.55(1)
O7	4b	0.9404(8)	0.9732(8)	0.2934(3)	1	0.80(6)
O8	4b	0.4799(7)	0.5323(7)	0.2938(3)	1	0.94(7)
MnLa(TiNb)O ₇ – space group <i>P2₁nm</i> (#31) $a = 5.4928(2) \text{ \AA}$, $b = 5.4942(2) \text{ \AA}$, $c = 19.1295(7) \text{ \AA}$, volume = $577.30(6) \text{ \AA}^3$ Formula weight = $446.61 \text{ g mol}^{-1}$, $Z = 4$ Radiation source: Neutron Time of Flight Temperature: 298 K $R_p = 2.433 \%$, $wR_p = 2.103 \%$						

Table 9.2. Parameters from the structural refinement of *P2₁nm* model of MnLa(TiNb)O₇ against the neutron powder diffraction data collected at room temperature.

Cation	Anion	Bond length (Å)	BVS
Ti/Nb(1)	O1 × 1	2.157(10)	+4.472
	O3 × 1	1.978(15)	
	O4 × 1	1.976(15)	
	O5 × 1	1.944(15)	
	O6 × 1	2.027(15)	
	O7 × 1	1.826(12)	
Ti/Nb(2)	O2 × 1	2.257(10)	+4.621
	O3 × 1	1.941(13)	
	O4 × 1	2.047(13)	
	O5 × 1	1.949(13)	
	O6 × 1	2.021(13)	

	O8 × 1	1.735(12)	
La1	O1 × 1	2.545(8)	+3.214
	O1 × 1	2.956(8)	
	O2 × 1	2.386(8)	
	O2 × 1	3.130(8)	
	O3 × 2	2.622(6)	
	O4 × 2	2.652(6)	
	O5 × 2	2.928(6)	
	O6 × 2	2.563(7)	
La2	O1 × 1	2.502(8)	+3.186
	O1 × 1	3.003(8)	
	O2 × 1	2.490(8)	
	O2 × 1	3.029(8)	
	O3 × 2	2.618(7)	
	O4 × 2	2.629(6)	
	O5 × 2	2.947(6)	
	O6 × 2	2.549(7)	
Mn1	O5 × 1	2.292(3)	+1.868
	O7 × 1	2.043(10)	
	O7 × 1	2.275(11)	
	O8 × 1	2.076(10)	
	O8 × 1	2.152(11)	

Table 9.3. Selected bond lengths and cation bond valence sums from the refined structure of MnLa(TiNb)O₇ at room temperature.

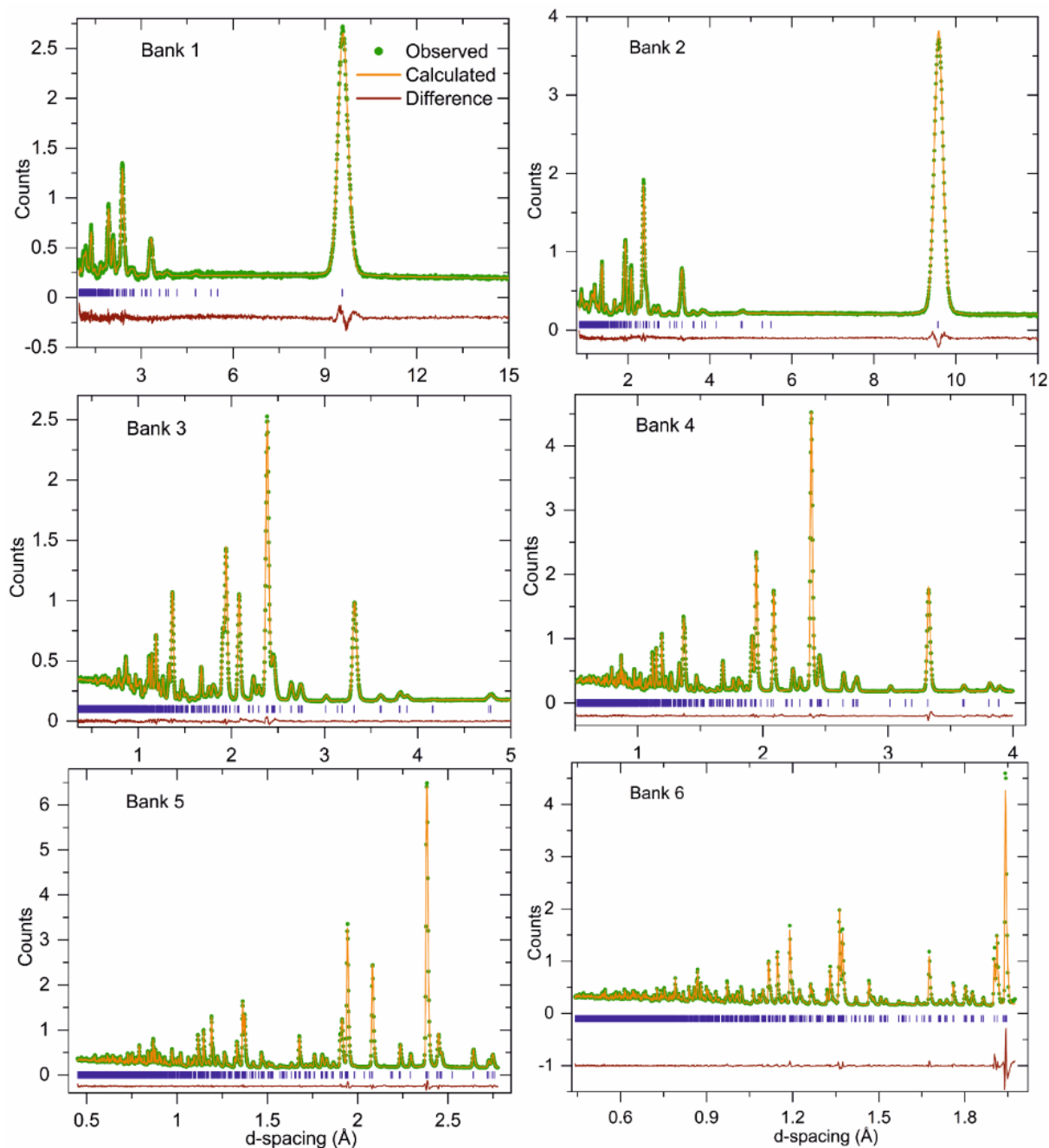


Figure 9.3. Observed, calculated and difference plots from the structural refinement of $\text{MnLa}(\text{TiNb})\text{O}_7$ against the neutron powder diffraction data collected at room temperature.

9.3.2.3 Magnetic characterisation of $\text{MnLa}(\text{TiNb})\text{O}_7$

Magnetisation data were collected from a sample of $\text{MnLa}(\text{TiNb})\text{O}_7$ in an applied field of 100 Oe in the temperature range of $5 \text{ K} \leq T(\text{K}) \leq 300 \text{ K}$. The ZFC and FC data are shown in Figure 9.4, which diverge below 44 K, suggesting a transition to a magnetically ordered state. The magnetisation-field isotherm collected at 300 K is a straight line that passes through the origin. But the 5 K data shows a small hysteresis as shown in Figure 9.4; which indicates canting in

the antiferromagnetic ordering of Mn^{2+} spins. From the analysis of $\text{MnCaTa}_2\text{O}_7$ sample, it was observed that the transition at 44 K is because of the presence of a small amount of Mn_3O_4 , undetectable by diffraction methods. Hence, the $\text{MnLa}(\text{TiNb})\text{O}_7$ sample was also treated with 10 % H_2 in Ar flow at 350 °C for 24 h to remove the Mn_3O_4 . After this heat treatment, magnetisation data were collected. The ZFC-FC plots (Figure 9.4) appear to be significantly different than the original sample. The sharp divergence around 44 K has disappeared which confirms that $\text{MnLa}(\text{TiNb})\text{O}_7$ does not order magnetically at 44 K and the transition at 44 K is because of a magnetic impurity (most probably Mn_3O_4) present in the sample. The magnetisation-field isotherm collected at 300 K is a straight line that passes through the origin. The 5 K isotherm is also a straight line passing through the origin which indicates that there is no or very small canting in the antiferromagnetic order of Mn^{2+} moments.

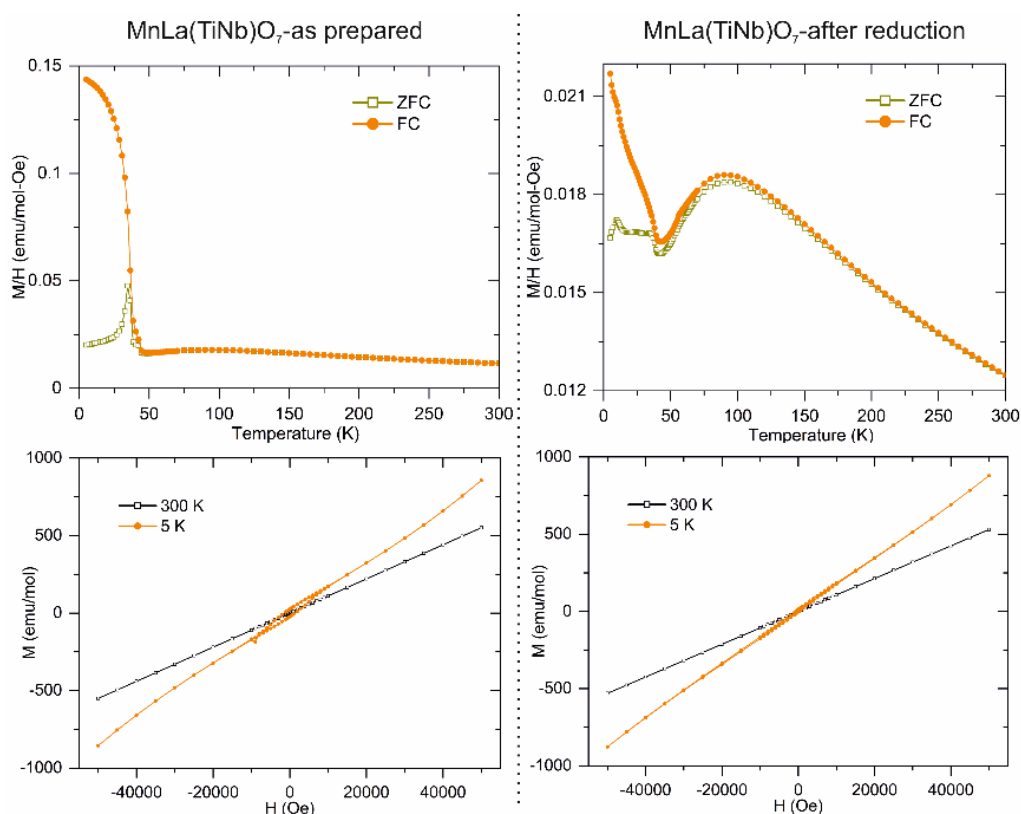


Figure 9.4. (Left) Zero field cooled (ZFC) and field cooled (FC) magnetisation data, and magnetisation-field isotherm at 300 K and 5 K collected from the as-prepared sample of $\text{MnLa}(\text{TiNb})\text{O}_7$. (Right) Zero field cooled (ZFC) and field cooled (FC) magnetisation data, and magnetisation-field isotherm at 300 K and 5 K collected from the H_2 -treated sample of $\text{MnLa}(\text{TiNb})\text{O}_7$.

9.3.2.4 Low temperature (5 K) neutron diffraction data

Neutron powder diffraction data were collected from a sample of 4 g $\text{MnLa}(\text{TiNb})\text{O}_7$ at 5 K using the GEM instrument at ISIS. Comparison of the neutron powder diffraction data collected at room temperature and 5 K reveals that there are a series of additional diffraction peaks in the 5 K data as shown in Figure 9.5. The additional diffraction peaks are attributed to a magnetically ordered phase. The additional diffraction peaks can be indexed using a single magnetic propagation vector, $\mathbf{k} = (0, 0, 0)$, of the crystallographic unit cell. The room temperature $P2_1nm$ model was used to generate possible magnetic models with the help of ISOSDISTORT software. The possible models were refined against the 5 K neutron data. The best fit to the data was achieved by using the model in magnetic space group $P2_1n'm'$, in which the Mn-lattice adopts G-type antiferromagnetic order. The refinement of the magnetic moments reveals that the magnitude of the obtained moment along x-or y-direction is zero within error. Therefore, the magnetic moment only along z-direction was considered and the refined magnetic moment is $4.49(1) \mu\text{B}$. Full details of the refined structure of $\text{MnLa}(\text{TiNb})\text{O}_7$ at 5 K are given in Table 9.4, with plots of the fitted diffraction patterns shown in Figure 9.6. Selected bond lengths are given in Table 9.5.

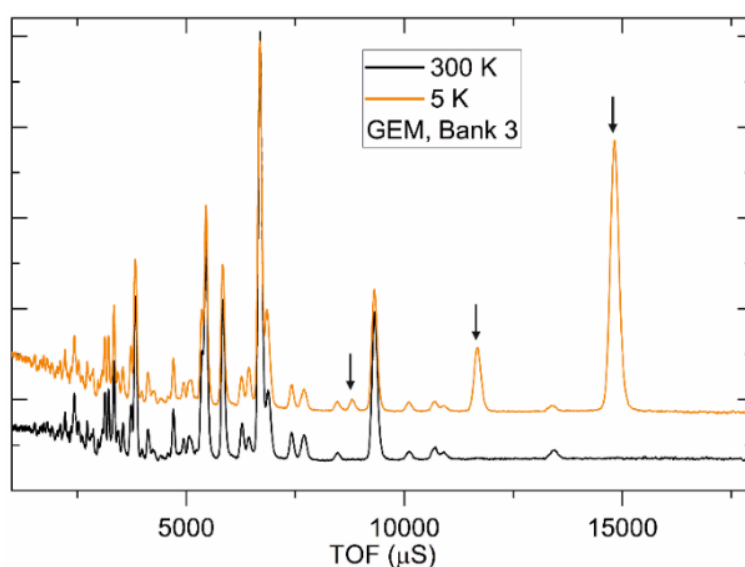


Figure 9.5. Neutron diffraction patterns collected from $\text{MnLa}(\text{TiNb})\text{O}_7$ at 300 K and 5 K using bank 3 of the GEM diffractometer. Black arrows indicate the magnetic diffraction peaks.

Atom	Site	x	y	z	Occ.	B _{iso} (Å ²)
Mn1	4b	0.2460(18)	0.7517(14)	0.7366(1)	1	0.50(2)
		M _x = 0	M _y = 0	M _z = 4.49(1)		
La1	2a	0.5102(7)	0.4952(10)	0	1	0.16(5)
La2	2a	0.9898(6)	0.0027(8)	0	1	0.26(6)
Ti/Nb(1)	4b	0.0038(21)	0.5005(30)	0.8873(9)	0.5/0.5	0.09(2)
Ti/Nb(2)	4b	0.5040(20)	0.9965(28)	0.1146(9)	0.5/0.5	0.09(2)
O1	2a	0.9609(10)	0.4636(13)	0	1	0.22(4)
O2	2a	0.5597(12)	0.0483(10)	0	1	0.32(4)
O3	4b	0.2536(12)	0.7515(13)	0.6178(1)	1	0.44(1)
O4	4b	0.2517(16)	0.2508(16)	0.4063(2)	1	0.39(3)
O5	4b	0.7514(13)	0.2506(12)	0.5836(1)	1	0.32(1)
O6	4b	0.7513(15)	0.7516(15)	0.4086(1)	1	0.27(3)
O7	4b	0.0327(7)	0.5215(9)	0.7928(3)	1	0.49(6)
O8	4b	0.4793(8)	0.9742(11)	0.2064(4)	1	0.58(6)
MnLa(TiNb)O ₇ – space group <i>P2₁n</i> 'm' (#31.127) <i>a</i> = 5.4900(2) Å, <i>b</i> = 5.4910(2) Å, <i>c</i> = 19.0722(6) Å, volume = 574.94(6) Å ³ Formula weight = 446.61 g mol ⁻¹ , Z = 4 Radiation source: Neutron Time of Flight Temperature: 5 K R _p = 1.738 %, wR _p = 1.809 %						

Table 9.4. Parameters from the structural refinement of MnLa(TiNb)O₇ against the neutron powder diffraction data collected at 5 K.

Cation	Anion	Bond length (Å)	BVS
Ti/Nb(1)	O1 × 1	2.172(14)	+4.503
	O3 × 1	1.952(16)	
	O4 × 1	1.978(17)	
	O5 × 1	2.006(16)	
	O6 × 1	1.982(17)	
	O7 × 1	1.813(15)	
Ti/Nb(2)	O2 × 1	2.225(18)	+4.568

	O3 × 1	1.948(16)	
	O4 × 1	1.963(17)	
	O5 × 1	2.028(16)	
	O6 × 1	2.008(16)	
	O8 × 1	1.760(19)	
La1	O1 × 1	2.480(7)	+3.215
	O1 × 1	3.021(7)	
	O2 × 1	2.469(8)	
	O2 × 1	3.049(8)	
	O3 × 2	2.944(6)	
	O4 × 2	2.626(8)	
	O5 × 2	2.551(7)	
	O6 × 2	2.626(8)	
La2	O1 × 1	2.536(9)	+3.294
	O1 × 1	2.964(9)	
	O2 × 1	2.374(8)	
	O2 × 1	3.139(8)	
	O3 × 2	2.924(6)	
	O4 × 2	2.615(8)	
	O5 × 2	2.557(7)	
	O6 × 2	2.631(7)	
Mn1	O3 × 1	2.266(3)	+1.903
	O7 × 1	2.029(9)	
	O7 × 1	2.245(10)	
	O8 × 1	2.077(10)	
	O8 × 1	2.177(11)	

Table 9.5. Selected bond lengths and cation bond valence sums from the refined structure of MnLa(TiNb)O₇ at 5 K.

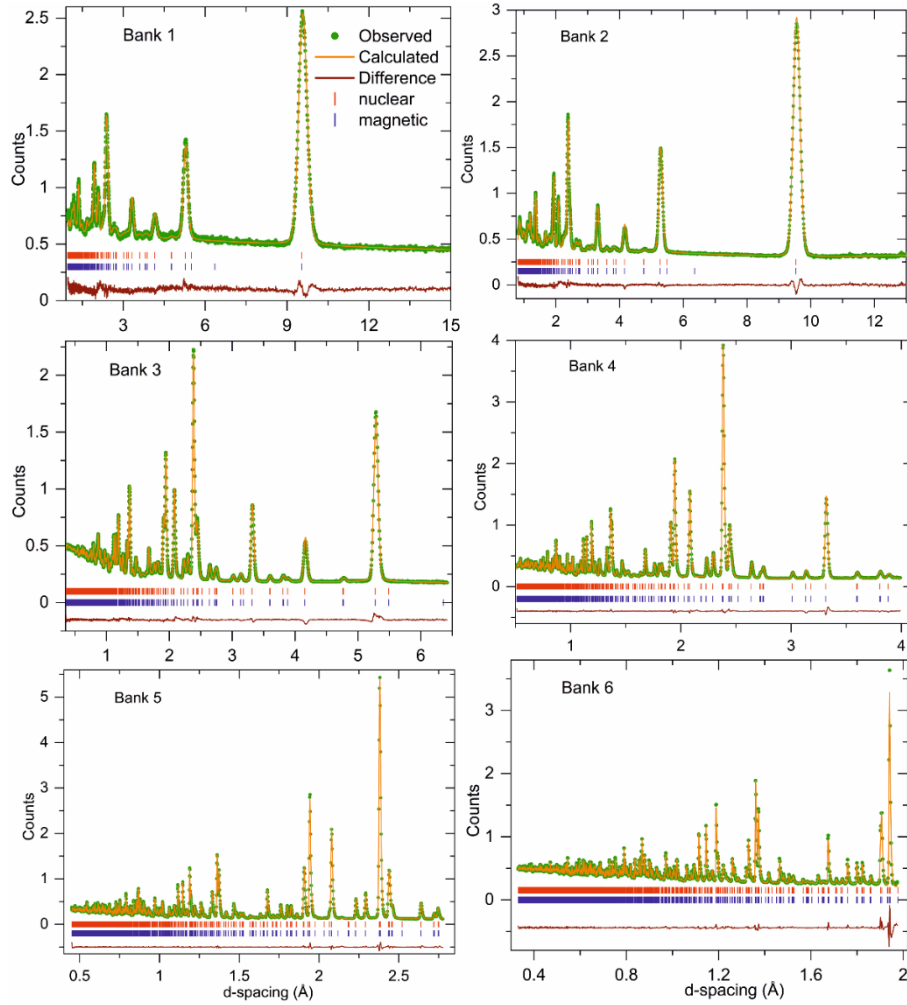


Figure 9.6. Observed, calculated and difference plots from the structural refinement of MnLa(TiNb)O₇ against the NPD data collected at 5 K.

9.3.2.5 Variable temperature neutron diffraction data

Neutron diffraction data were collected from MnLa(TiNb)O₇ sample using the GEM diffractometer at temperatures $5 \leq T(\text{K}) \leq 60$. The progression of the magnetic scattering peaks indicates that the magnetic transition occurs at a temperature between 50 K and 60 K as shown in Figure 9.7. There is a discontinuity in the derivative of the ZFC-FC plot collected from the H₂-treated MnLa(TiNb)O₇ sample at 56 K as shown in Figure 9.7, which indicates the magnetic ordering temperature.

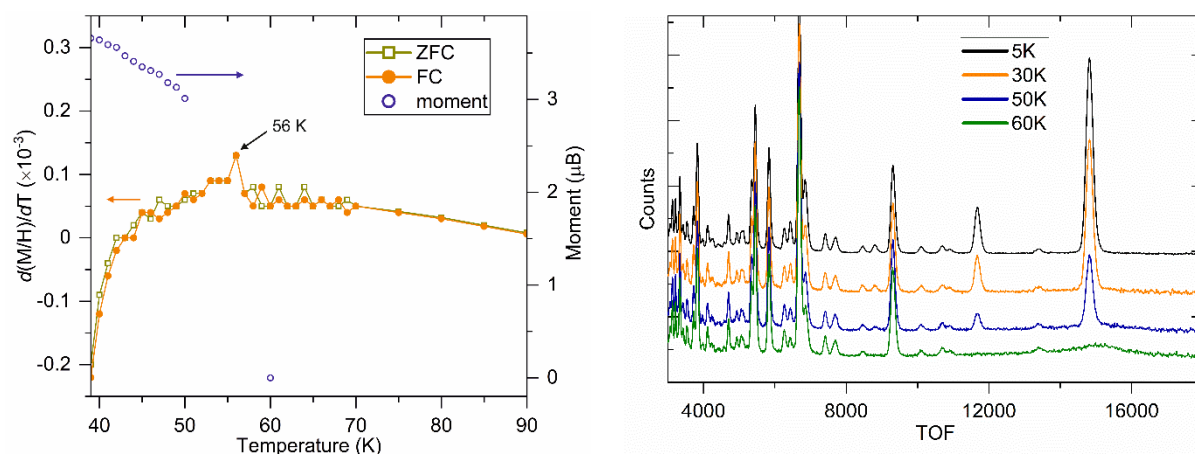


Figure 9.7. (Left) derivative of the ZFC-FC magnetisation data collected from the H₂-treated sample of MnLa(TiNb)O₇ along with the progress of magnetic moment with temperature extracted from the GEM data. (Right) Neutron diffraction data collected from MnLa(TiNb)O₇ using the GEM diffractometer (Bank 3).

9.3.3 Characterisation of MnLa(TiTa)O₇

9.3.3.1 Room temperature synchrotron and neutron diffraction data

Synchrotron X-ray diffraction (SXRD) and neutron powder diffraction (NPD) data collected from MnLa(TiTa)O₇ at room temperature could be indexed using an orthorhombic unit cell ($a = 5.488 \text{ \AA}$, $b = 5.489 \text{ \AA}$, $c = 19.16 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Ruddlesden-Popper aristotype unit cell. Systematic absences indicate a primitive cell is required to index all the peaks in the diffraction pattern. There was no evidence for any Ti/Ta ordering. A model based on the room temperature $P2_1nm$ structure of MnLa(TiNb)O₇, but with Nb replaced by Ta, was constructed and refined against the SXRD data to achieve a good fit as shown in Figure 9.9. The Mn²⁺ cations are also ordered in a checkerboard pattern in the 5-coordinate interlayer sites similar to the MnCaTa₂O₇ and MnLa(TiNb)O₇ phases as indicated by a better fit to the data for the ordered Mn²⁺ model than the disordered model as shown in Figure 9.8.

The noncentrosymmetric $P2_1nm$ model was refined against the NPD data collected at room temperature. No SHG activity was observed from the MnLa(TiTa)O₇ sample but that is probably because of the dark colour of the sample. The presence of a small amount of Mn₃O₄

in the $\text{MnLa}(\text{TiTa})\text{O}_7$ sample, as will be established later, can cause this dark colour. A centrosymmetric tetragonal $P4_2/mnm$ model was considered as the refined a - and b -lattice parameters were close to one another. Another centrosymmetric model $Pnmm$ with $a^-b^-c^0/b^-a^-c^0$ tilting distortion was also considered to ensure the presence of c^+ tilt in $P2_1nm$ structure. The best numerical fits to the data were achieved by the model described in $P2_1nm$ space group with an $a^-b^-c^+/b^-a^-c^+$ tilting distortion, as shown in Table 9.6. Full details of the refined structure of $\text{MnLa}(\text{TiTa})\text{O}_7$ in $P2_1nm$ symmetry structure are given in Table 9.7, with plots of the fitted diffraction patterns shown in Figure 9.10. Selected bond lengths are given in Table 9.8.

Space group	Glazer tilt notation	No. of independent parameters	wR_p (%)	R_p (%)
$P2_1nm$ (#31)	$a^-b^-c^+/b^-a^-c^+$	177	2.183	2.500
$P4_2/mnm$ (#136)	$a^-b^0c^0/b^0a^-c^0$	141	2.292	2.571
$Pnmm$ (#58)	$a^-b^-c^0/b^-a^-c^0$	153	2.209	2.530

Table 9.6. Fitting statistics from the structural refinement of $\text{MnLa}(\text{TiTa})\text{O}_7$ against the neutron powder diffraction data collected at room temperature.

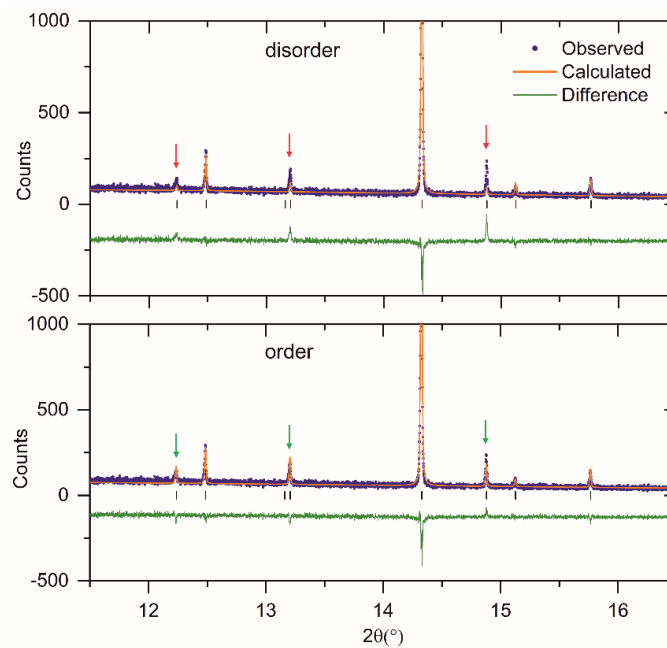


Figure 9.8. Comparison of the refinements of the disordered and ordered model of $P2_1nm$ symmetry structure of $\text{MnLa}(\text{TiTa})\text{O}_7$. The arrows indicate the Mn-ordering peaks.

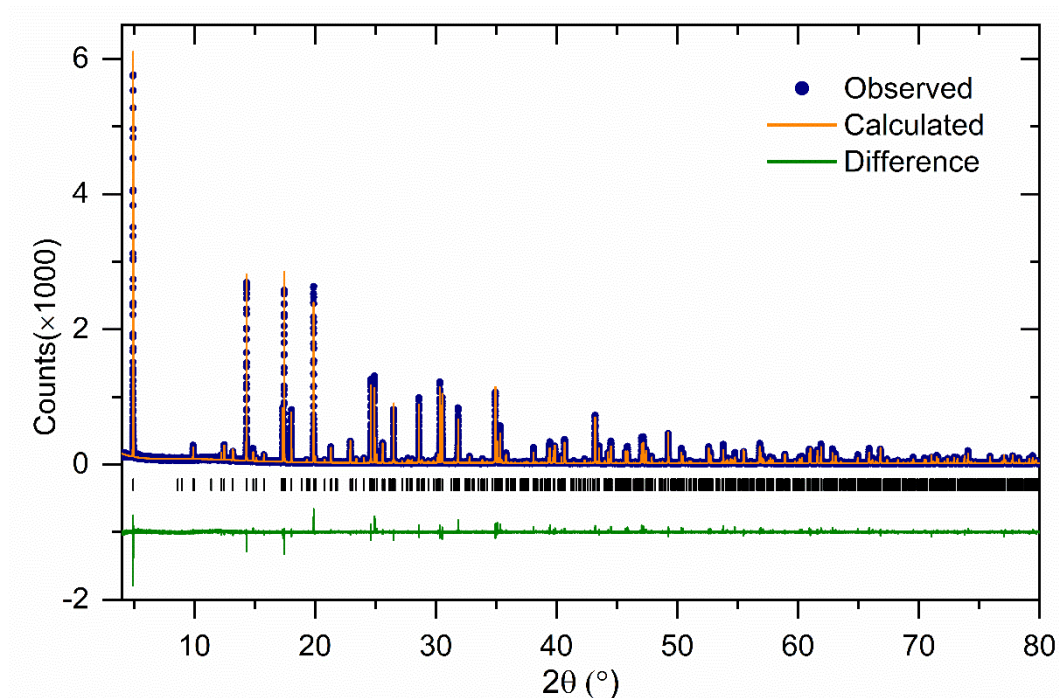


Figure 9.9. Observed, calculated and difference plots from the structural refinement of $\text{MnLa}(\text{TiTa})\text{O}_7$ against the SXRD data collected at room temperature.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
Mn1	4b	0.2195(14)	0.2548(19)	0.7377(1)	1	0.77(2)
La1	2a	0.9663(6)	0.9896(8)	0	1	0.52(6)
La2	2a	0.4733(6)	0.5084(8)	0	1	0.52(6)
Ti/Ta(1)	4b	0.9566(19)	0.0004(25)	0.3898(5)	0.5/0.5	0.13(3)
Ti/Ta(2)	4b	0.4646(18)	0.4951(23)	0.3861(5)	0.5/0.5	0.13(3)
O1	2a	0.5054(8)	0.9585(11)	0	1	0.32(6)
O2	2a	0.9277(8)	0.5537(11)	0	1	0.90(7)
O3	4b	0.7176(12)	0.2491(14)	0.0910(1)	1	0.42(3)
O4	4b	0.2181(13)	0.7455(14)	0.0940(1)	1	0.66(4)
O5	4b	0.2147(12)	0.2505(13)	0.6169(1)	1	0.72(1)
O6	4b	0.7168(12)	0.7504(12)	0.5841(1)	1	0.52(1)
O7	4b	0.9317(5)	0.9834(7)	0.2930(3)	1	0.80(5)
O8	4b	0.4833(5)	0.5274(7)	0.2942(3)	1	0.80(5)
$\text{MnLa}(\text{TiTa})\text{O}_7$ – space group $P2_1nm$ (#31) $a = 5.4884(2) \text{ \AA}$, $b = 5.4891(2) \text{ \AA}$, $c = 19.1644(6) \text{ \AA}$, volume = $577.35(6) \text{ \AA}^3$ Formula weight = $534.65 \text{ g mol}^{-1}$, $Z = 4$						

Radiation source: Neutron Time of Flight
Temperature: 298 K
$R_p = 2.509 \%$, $wR_p = 2.183 \%$

Table 9.7. Parameters from the structural refinement of $P2_1nm$ model of $MnLa(TiTa)O_7$ against the neutron powder diffraction data collected at room temperature.

Cation	Anion	Bond length (Å)	BVS
Ti/Ta(1)	O1 × 1	2.141(10)	+4.499
	O3 × 1	2.016(14)	
	O4 × 1	1.938(15)	
	O5 × 1	1.977(14)	
	O6 × 1	1.966(14)	
	O7 × 1	1.862(13)	
Ti/Ta(2)	O2 × 1	2.209(10)	+4.651
	O3 × 1	2.000(14)	
	O4 × 1	1.956(14)	
	O5 × 1	1.920(14)	
	O6 × 1	2.051(14)	
	O8 × 1	1.773(13)	
La1	O1 × 1	2.535(6)	+3.215
	O1 × 1	2.964(6)	
	O2 × 1	2.402(9)	
	O2 × 1	3.104(9)	
	O3 × 2	2.633(7)	
	O4 × 2	2.636(7)	
	O5 × 2	2.943(6)	
	O6 × 2	2.554(7)	
La2	O1 × 1	2.477(8)	+3.179
	O1 × 1	3.024(8)	
	O2 × 1	2.506(6)	
	O2 × 1	3.005(6)	
	O3 × 2	2.620(7)	
	O4 × 2	2.627(7)	

Mn1	O5 × 2	2.920(6)	+1.858
	O6 × 2	2.569(7)	
	O5 × 1	2.315(3)	
	O7 × 1	2.047(10)	
	O7 × 1	2.250(10)	
	O8 × 1	2.069(10)	
	O8 × 1	2.170(10)	

Table 9.8. Selected bond lengths and cation bond valence sums from the refined structure of MnLa(TiTa)O₇ at room temperature.

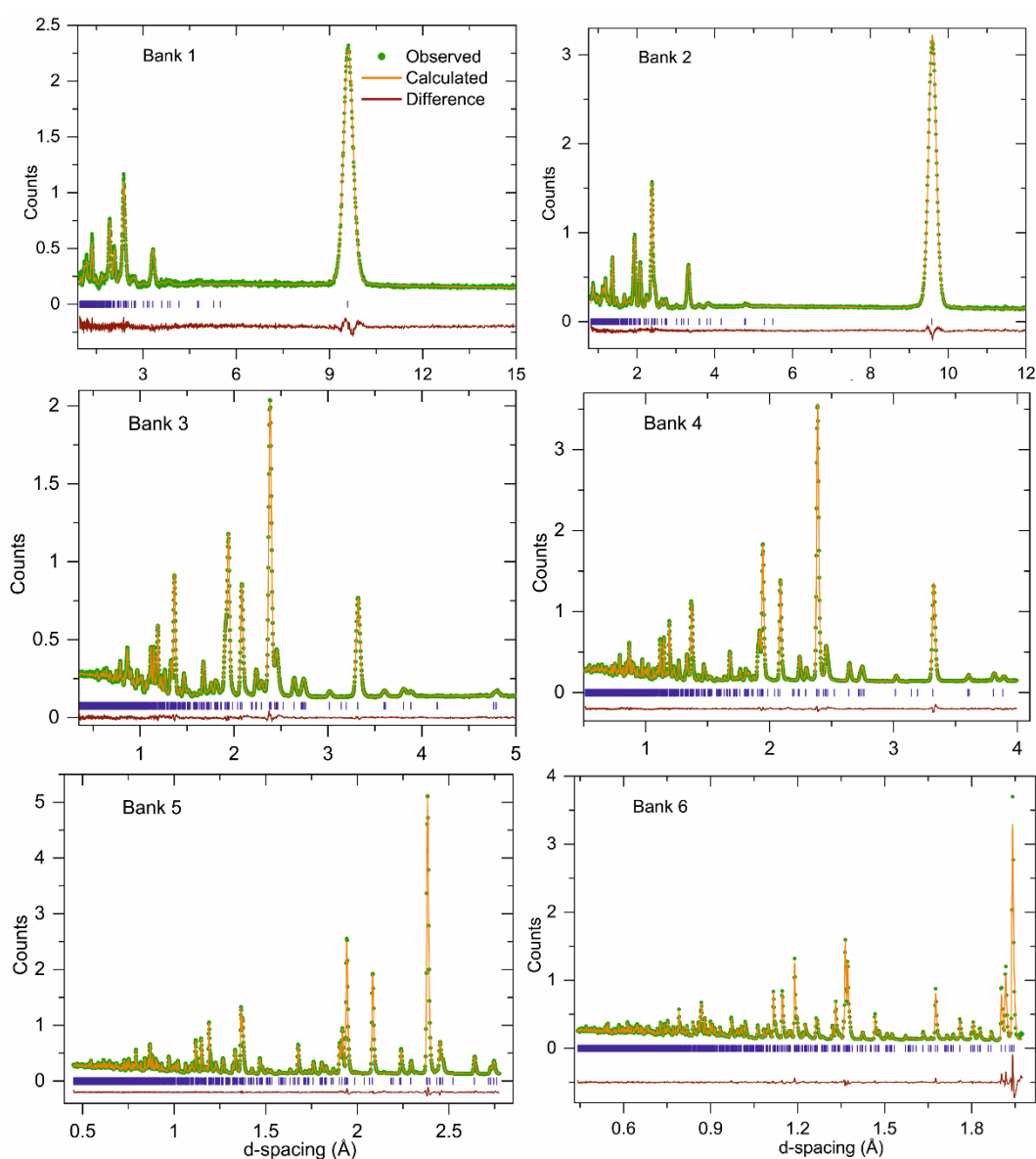


Figure 9.10. Observed, calculated and difference plots from the structural refinement of MnLa(TiTa)O₇ against the NPD data collected at room temperature.

9.3.3.2 Magnetic characterisation of $\text{MnLa}(\text{TiTa})\text{O}_7$

Magnetisation data were collected from a sample of $\text{MnLa}(\text{TiTa})\text{O}_7$ in an applied field of 100 Oe in the temperature range of $5 \text{ K} \leq T(\text{K}) \leq 300 \text{ K}$. The ZFC and FC data are shown in Figure 9.11, which diverge below 44 K, suggesting a transition to a magnetically ordered state. The magnetisation-field isotherm collected at 300 K is a straight line that passes through the origin. But the 5 K data shows a small hysteresis as shown in Figure 9.11, which indicates canting in the antiferromagnetic ordering of Mn^{2+} spins. From the analysis of $\text{MnCaTa}_2\text{O}_7$ and $\text{MnLa}(\text{TiNb})\text{O}_7$ samples, it was observed that the transition at 44 K is because of the presence of a small amount of Mn_3O_4 , undetectable by diffraction methods. Hence, the $\text{MnLa}(\text{TiTa})\text{O}_7$ sample was also treated with 10 % H_2 in Ar flow at 350 °C for 24 h to remove the Mn_3O_4 . After this heat treatment, magnetisation data were collected. The ZFC-FC plots (Figure 9.11) appear to be significantly different than the original sample. The sharp divergence around 44 K has disappeared which confirms that the $\text{MnLa}(\text{TiTa})\text{O}_7$ does not order magnetically at 44 K and the transition at 44 K is because of a magnetic impurity (most probably Mn_3O_4) present in the sample. The magnetisation-field isotherm collected at 300 K is a straight line that passes through the origin. The 5 K isotherm is also a straight line passing through the origin which indicates that there is no or very small canting in the antiferromagnetic order of Mn^{2+} moments.

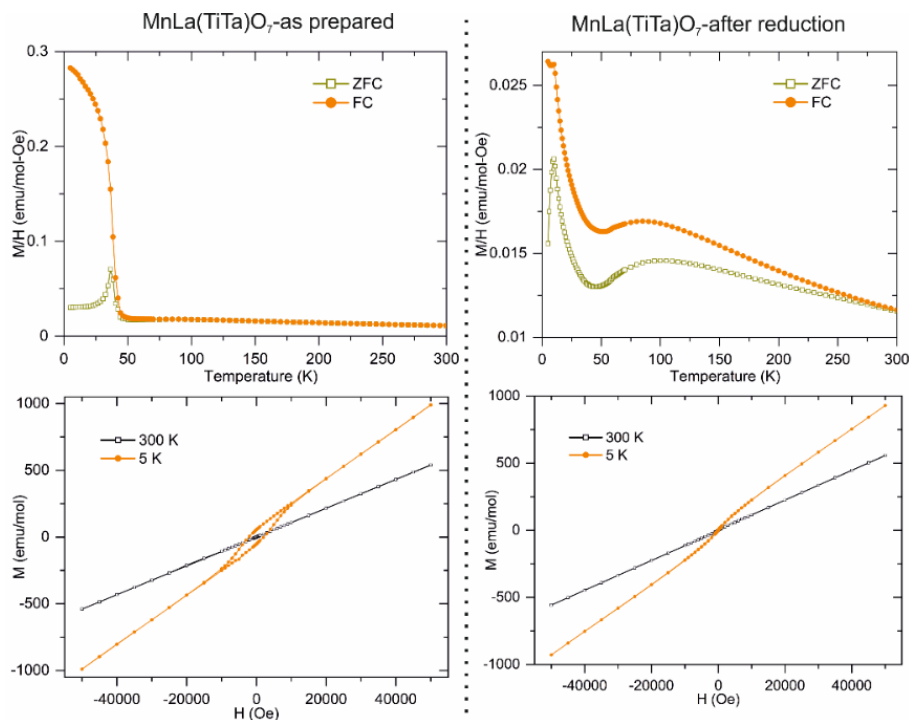


Figure 9.11. (Left) Zero field cooled (ZFC) and field cooled (FC) magnetisation data, and magnetisation-field isotherm at 300 K and 5 K collected from the as-prepared sample of $\text{MnLa}(\text{TiTa})\text{O}_7$. (Right) Zero field cooled (ZFC) and field cooled (FC) magnetisation data, and magnetisation-field isotherm at 300 K and 5 K collected from the H_2 -treated sample of $\text{MnLa}(\text{TiTa})\text{O}_7$.

9.3.3.3 Low temperature (5 K) neutron diffraction data

Neutron powder diffraction data were collected from a sample of 4 g $\text{MnLa}(\text{TiTa})\text{O}_7$ at 5 K using the GEM instrument at ISIS. Comparison of the neutron powder diffraction data collected at room temperature and 5 K reveals that there are a series of additional diffraction peaks in the 5 K data as shown in Figure 9.12. The additional diffraction peaks are attributed to a magnetically ordered phase. The additional diffraction peaks can be indexed using a single magnetic propagation vector, $\mathbf{k} = (0, 0, 0)$, of the crystallographic unit cell. The room temperature $P2_1nm$ model was used to generate possible magnetic models with the help of ISOSDISTORT software. The possible models were refined against the 5 K neutron data. The best fit to the data was achieved by using the model in magnetic space group $P2_1n'm'$, in which the Mn-lattice adopts G-type antiferromagnetic order. The refinement of magnetic moments reveals that the magnitude of the obtained moment along x-or y-direction is zero within error.

Therefore, the magnetic moment only along z-direction was considered and the refined magnetic moment is 4.57(1) μB . Full details of the refined structure of $\text{MnLa}(\text{TiTa})\text{O}_7$ at 5 K are given in Table 9.9, with plots of the fitted diffraction patterns shown in Figure 9.13. Selected bond lengths are given in Table 9.10.

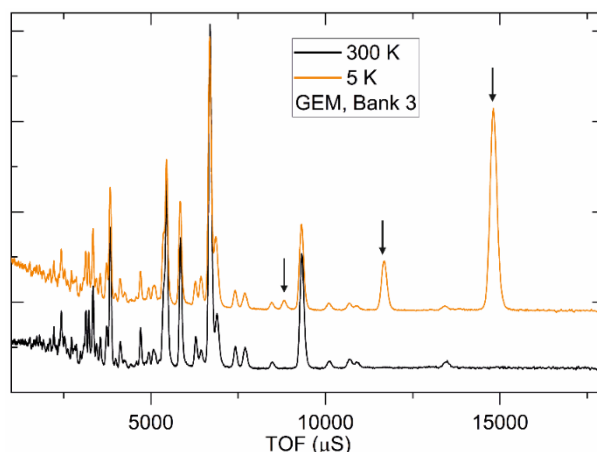


Figure 9.12. Neutron diffraction patterns collected from $\text{MnLa}(\text{TiTa})\text{O}_7$ at 300 K and 5 K using bank 3 of the GEM diffractometer. Black arrows indicate the magnetic diffraction peaks.

Atom	Site	x	y	z	Occ.	$B_{\text{iso}} (\text{\AA}^2)$
Mn1	4b	0.2357(15)	0.7494(10)	0.7370(1)	1	0.30(2)
		$M_x = 0$	$M_y = 0$	$M_z = 4.575(8)$		
La1	2a	0.5024(7)	0.4956(8)	0	1	0.17(4)
La2	2a	0.9799(6)	0.0030(7)	0	1	0.38(5)
Ti/Ta(1)	4b	0.9933(21)	0.5028(24)	0.8871(7)	0.5/0.5	0.07(2)
Ti/Ta(2)	4b	0.4978(21)	0.9952(27)	0.1111(7)	0.5/0.5	0.07(2)
O1	2a	0.9537(11)	0.4652(11)	0	1	0.24(4)
O2	2a	0.5534(10)	0.0467(9)	0	1	0.28(4)
O3	4b	0.2461(11)	0.7513(13)	0.6171(1)	1	0.44(1)
O4	4b	0.2418(15)	0.2529(11)	0.4068(1)	1	0.40(3)
O5	4b	0.7421(13)	0.2487(10)	0.5836(1)	1	0.33(1)
O6	4b	0.7438(15)	0.7498(13)	0.4086(1)	1	0.28(3)
O7	4b	0.0222(7)	0.5228(9)	0.7930(3)	1	0.63(6)
O8	4b	0.4751(7)	0.9741(8)	0.2066(3)	1	0.44(6)
MnLa(TiTa)O ₇ – Nuclear space group $P2_1nm$ (#31)						
Magnetic space group $P2_1n'm'$ (#31.127)						

$a = 5.4860(2) \text{ \AA}, b = 5.4877(2) \text{ \AA}, c = 19.1102(7) \text{ \AA},$ $\text{volume} = 575.32(6) \text{ \AA}^3$ $\text{Formula weight} = 534.65 \text{ g mol}^{-1}, Z = 4$ $\text{Radiation source: Neutron Time of Flight}$ Temperature: 5 K $R_p = 1.751 \%, wR_p = 1.875 \%$

Table 9.9. Parameters from the structural refinement of $P2_1nm$ model of $\text{MnLa}(\text{TiTa})\text{O}_7$ against the neutron powder diffraction data collected at 5 K.

Cation	Anion	Bond length ($\text{\AA}$)	BVS
Ti/Ta(1)	O1 $\times$ 1	2.178(14)	+4.581
	O3 $\times$ 1	1.947(15)	
	O4 $\times$ 1	1.960(15)	
	O5 $\times$ 1	2.009(14)	
	O6 $\times$ 1	1.995(15)	
	O7 $\times$ 1	1.809(15)	
Ti/Ta(2)	O2 $\times$ 1	2.163(14)	+4.532
	O3 $\times$ 1	1.950(15)	
	O4 $\times$ 1	1.940(16)	
	O5 $\times$ 1	2.009(15)	
	O6 $\times$ 1	2.010(16)	
	O8 $\times$ 1	1.833(15)	
La1	O1 $\times$ 1	2.481(80)	+3.226
	O1 $\times$ 1	3.015(8)	
	O2 $\times$ 1	2.479(7)	
	O2 $\times$ 1	3.037(7)	
	O3 $\times$ 2	2.938(6)	
	O4 $\times$ 2	2.608(7)	
	O5 $\times$ 2	2.561(7)	
	O6 $\times$ 2	2.622(7)	
La2	O1 $\times$ 1	2.540(80)	+3.316
	O1 $\times$ 1	2.955(8)	
	O2 $\times$ 1	2.352(7)	

	O2 × 1	3.155(7)	
	O3 × 2	2.910(6)	
	O4 × 2	2.617(6)	
	O5 × 2	2.555(6)	
	O6 × 2	2.643(7)	
Mn1	O3 × 1	2.292(3)	+1.892
	O7 × 1	2.016(8)	
	O7 × 1	2.243(9)	
	O8 × 1	2.099(8)	
	O8 × 1	2.164(8)	

Table 9.10. Selected bond lengths and cation bond valence sums from the refined structure of MnLa(TiTa)O₇ at 5 K.

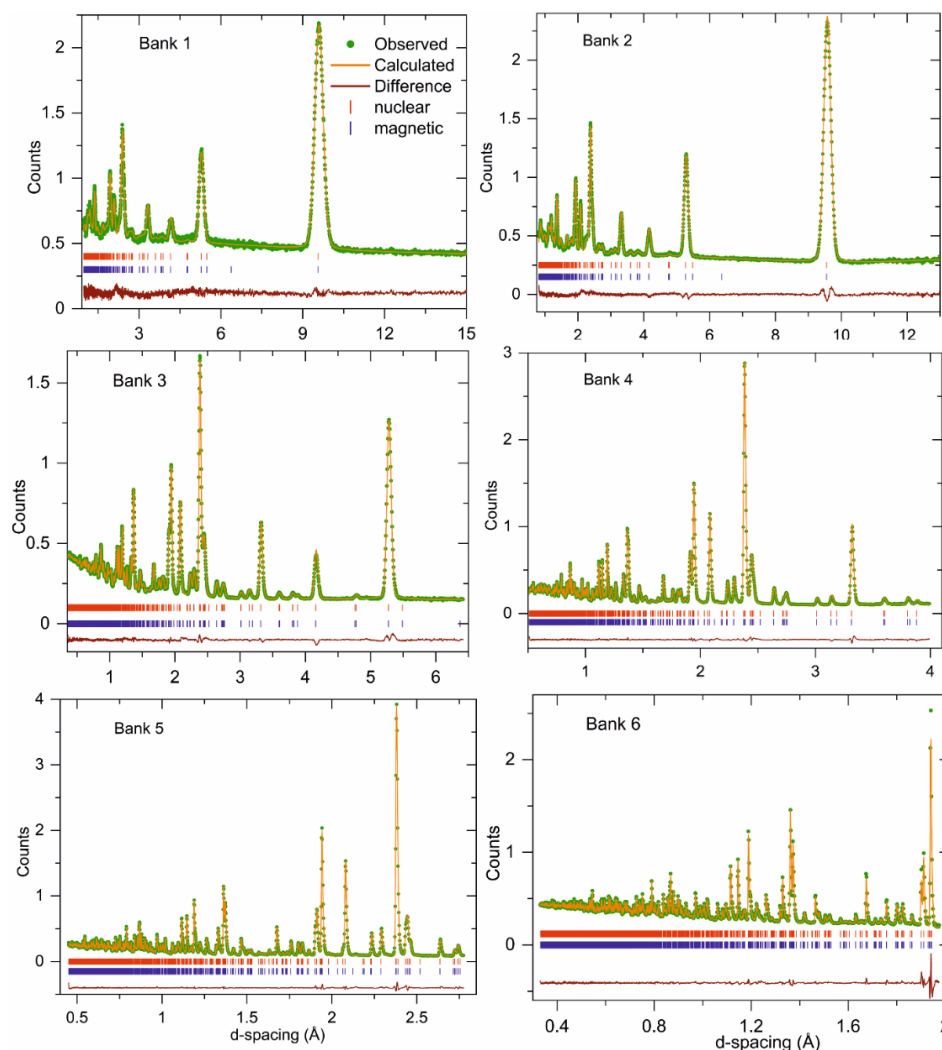


Figure 9.13. Observed, calculated and difference plots from the structural refinement of MnLa(TiTa)O₇ against the NPD data collected at 5 K.

9.3.3.4 Variable temperature neutron diffraction data

Neutron diffraction data were collected from $\text{MnLa}(\text{TiTa})\text{O}_7$ sample using the GEM diffractometer at temperatures $5 \leq T(\text{K}) \leq 60$. The progression of the magnetic scattering peaks indicates that the magnetic transition occurs at a temperature between 50 K and 60 K as shown in Figure 9.14. There is a clear anomaly at 59 K in the $d(M/H)/dT$ vs temperature plot collected from the H_2 -treated $\text{MnLa}(\text{TiTa})\text{O}_7$ sample as shown in Figure 9.14 which indicates the magnetic ordering temperature.

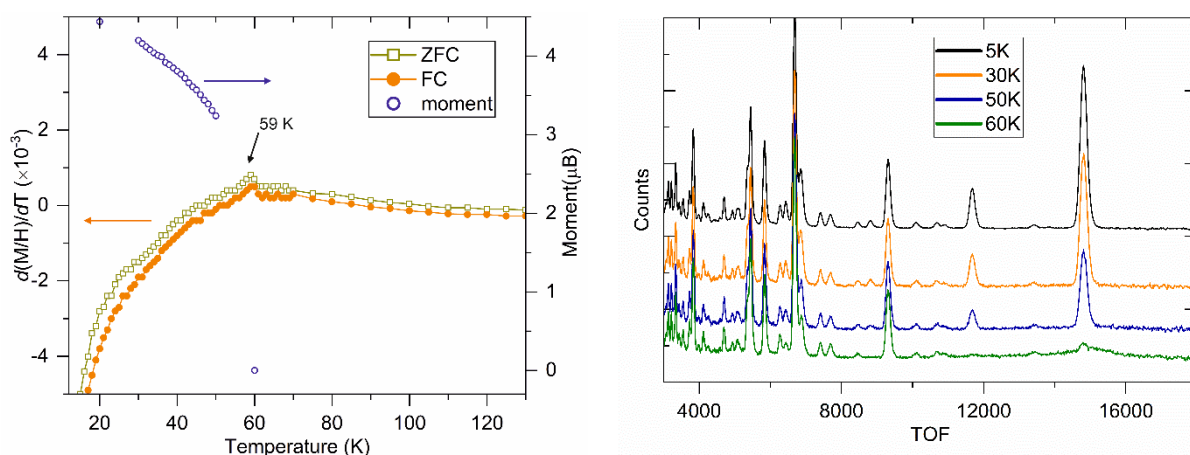


Figure 9.14. (Left) derivative of the ZFC-FC magnetisation data collected from the H_2 -treated sample of $\text{MnLa}(\text{TiTa})\text{O}_7$ along with the change of magnetic moment with temperature extracted from the GEM data. (Right) Neutron diffraction data collected from $\text{MnLa}(\text{TiTa})\text{O}_7$ using the GEM diffractometer (Bank 3).

9.4 Discussion

The successful synthesis of polar and magnetically ordered $\text{MnLa}(\text{TiNb})\text{O}_7$ and $\text{MnLa}(\text{TiTa})\text{O}_7$ reveals that it is possible to exchange Li^+ cations by divalent 3d transition metal cations to introduce paramagnetic cations in the interlayer of polar layered perovskites sheets. This topochemical cation exchange approach demonstrates possibilities to synthesize new multiferroic materials which are usually inaccessible by high-temperature synthesis routes. As a monovalent cation is substituted by a divalent cation the number of available sites in the exchanged phase is twice the number of transition metal cations available. Therefore, the metal cations in the interlayer sites can either be ordered or disordered. As demonstrated in the results section, the Mn^{2+} cations are ordered in a chequerboard pattern within the 5-coordinate sites.

The parent $\text{Li}_2\text{La}(\text{TiNb})\text{O}_7$ and $\text{Li}_2\text{La}(\text{TiTa})\text{O}_7$ phases adopt a polar $A2_1am$ symmetry structure with $a^-a^-c^+/a^-a^-c^+$ tilting distortion of BO_6 octahedra. The structure of the MnLaB_2O_7 ($B = \text{TiNb}/\text{TiTa}$) phase can be analysed in terms of the distortion modes which need to be applied to get the distorted structure from the aristotype $I4/mmm$ symmetry structure. The $P2_1nm$ structure of MnLaB_2O_7 can be constructed by applying two tilting distortion modes (X_2^+ and X_3^-) and a Γ_5^- polar distortion mode. The X_3^- and X_2^+ irreducible representations describe the $a^-b^-c^0/b^-a^-c^0$ and the $a^0a^0c^+/a^0a^0c^+$ tilting distortions respectively as shown in Figure 9.15.

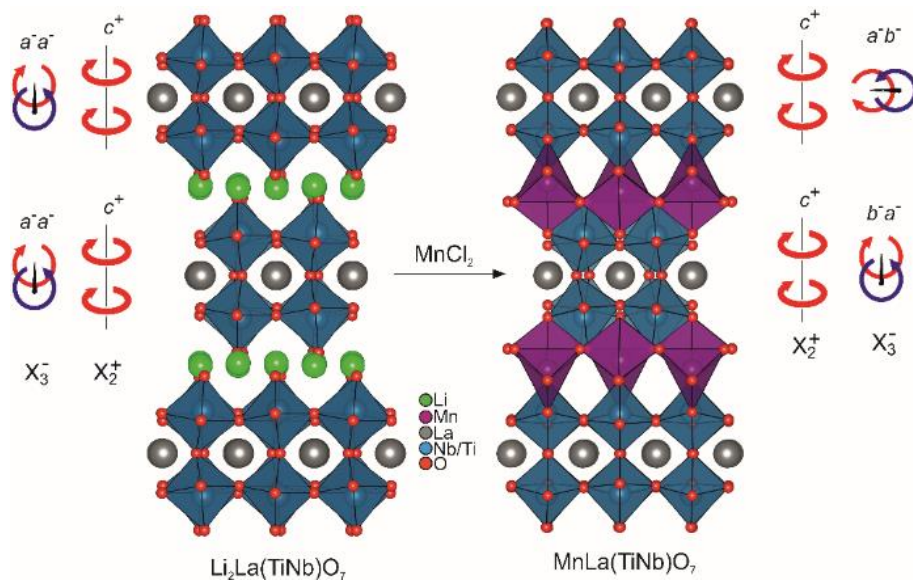


Figure 9.15. Topochemical cation exchange reaction to synthesize $\text{MnLa}(\text{TiNb})\text{O}_7$.

Mn^{2+} cations in both $\text{MnLa}(\text{TiNb})\text{O}_7$ and $\text{MnLa}(\text{TiTa})\text{O}_7$ structures are ordered in checkerboard arrangement. As discussed in chapter 4, this arrangement minimizes the interionic repulsion. In both the structures the Mn-sites are slightly under-bonded, which highlights the fact that the structures prefer to minimize the strong Coulombic repulsion among the Mn^{2+} ions by arranging them in a checkerboard pattern even though that makes the coordination sites slightly under bonded. Close inspection of the data reveals that above T_N , the magnetic scattering peaks broaden significantly as they lower in intensity as shown in Figure 9.7 and Figure 9.14. This peak broadening and high backgrounds observed around these residual peaks can be attributed to the presence of strong magnetic interactions in the xy -plane

above the T_N similar to the observed 2D magnetic interactions in $\text{MnSrTa}_2\text{O}_7$ ⁹⁰ and $\text{MnCaTa}_2\text{O}_7$.

9.5 Conclusion

Synthesis of MnLaB_2O_7 is possible by topochemical cation exchange reaction from $\text{Li}_2\text{LaB}_2\text{O}_7$ ($B = \text{TiNb}/\text{TiTa}$) phases. MnLaB_2O_7 phases adopt polar $P2_1nm$ structures where the Mn^{2+} cations are ordered in a chequerboard arrangement within the 5-coordinate sites, similar to $\text{MnCaTa}_2\text{O}_7$. The successful synthesis of the Mn-phase from the corresponding Li-phase suggests that the low-temperature cation exchange chemistry could be utilized to prepare new magnetoelectric materials.

Chapter 10 – Synthesis and characterisation of $M^{\text{II}}\text{CaTa}_2\text{O}_7$ ($M = \text{Fe, Co, Zn}$)

10.1 Introduction

The synthesis of polar magnetically ordered $\text{MnCaTa}_2\text{O}_7$ was achieved by a topochemical cation exchange reaction from the thermodynamically stable precursor $\text{Li}_2\text{CaTa}_2\text{O}_7$ as demonstrated in chapter 8. Hence it is interesting to investigate if other 3d transition metal cations can also be incorporated in the interlayer sites in this material. Therefore, similar cation exchange reactions were performed with $M^{\text{II}}\text{Cl}_2$ ($M = \text{Fe, Co, Ni, Cu, Zn}$). The size of these M^{II} -cations is similar to that of Li^+ cation in a tetrahedral coordination geometry (Table 10.1).

Ion	Li^+	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic radius (Å)	0.59	0.66	0.63	0.58	0.55	0.57	0.60

Table 10.1. Ionic radii of M^{II} -cations in tetrahedral geometry

10.2 Synthesis

Synthesis of $M^{\text{II}}\text{CaTa}_2\text{O}_7$ ($M = \text{Fe, Co, Ni, Cu, Zn}$) was carried out by performing cation exchange reactions starting from $\text{Li}_2\text{CaTa}_2\text{O}_7$. The synthesis of polycrystalline $\text{Li}_2\text{CaTa}_2\text{O}_7$ is described in chapter 6. $\text{Li}_2\text{CaTa}_2\text{O}_7$ was ground together with anhydrous $M\text{Cl}_2$ in a 1:5 molar ratio using an agate pestle and mortar in an argon-filled glove box. The mixtures were then placed in pyrex tubes, which were sealed using a blow torch under vacuum. The tubes were heated at temperatures between 300 °C and 400 °C for two periods of 3 days.

Phase pure samples of $\text{NiCaTa}_2\text{O}_7$ and $\text{CuCaTa}_2\text{O}_7$ were never achieved. All the trials to synthesize these phases indicate an incomplete cation exchange reaction.

Samples of $\text{FeCaTa}_2\text{O}_7$, $\text{CoCaTa}_2\text{O}_7$, $\text{ZnCaTa}_2\text{O}_7$ were prepared by heating the mixtures at 350 °C, 360 °C and 400 °C respectively. After the final heat treatment, the reaction mixtures were

washed with distilled water to remove the remaining chlorides. Reaction progress was assessed by collecting X-ray powder diffraction using a PANalytical X'Pert diffractometer.

Since ZnCl_2 has a melting point of 290 °C, the reaction tube that contains ZnCl_2 was placed vertically in a furnace.

10.3 Results

10.3.1 Characterisation of $\text{FeCaTa}_2\text{O}_7$

10.3.1.1 Synchrotron X-ray diffraction data

Synchrotron X-ray diffraction (SXRD) data collected from $\text{FeCaTa}_2\text{O}_7$ at room temperature could be indexed using a tetragonal unit cell ($a = b = 5.509 \text{ \AA}$, $c = 18.646 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Ruddlesden-Popper aristotype unit cell. Systematic absences indicate a primitive cell is required to index all the peaks in the diffraction pattern. Powder SHG measurements reveal that the sample is not SHG active; hence adopts a centrosymmetric structure. Symmetry analysis of the structural distortions of the $n = 2$ Ruddlesden-Popper framework reveals two tetragonal candidate structures described in the $P4_2/mnm$ and $P4_2/mcm$ space groups. Further extinction conditions eliminate the $P4_2/mcm$ symmetry structure. A structure model was constructed in the $P4_2/mnm$ space group and refined against the SXRD data which gives good fitting.

Fe^{2+} cations in the cation exchanged $\text{FeCaTa}_2\text{O}_7$ Ruddlesden-Popper phase occupy only half of the available pseudo-tetrahedral coordination sites in the framework, so can adopt either ordered or disordered arrangements. There are two sites for Fe ($4d$ and $4e$) in the $P4_2/mnm$ model. The Fe-site occupancies were refined within the constraint of total occupancy being one. After refinement, the occupancy of the $4d$ site moved towards one and the occupancy of the $4e$ site moved towards zero, indicating that the Fe^{2+} ions are ordered. If an ordered model with only $4e$ site is used and the occupancy is refined freely, the occupancy of this site reached a value of 0.99. The $4e$ site was fixed as fully occupied which did not change the fitting

statistics. Moreover, the ordered model results in a better fit to the data than the disordered model as shown in Figure 10.1. The observed, calculated and difference plots from the structural refinement of the ordered $P4_2/mnm$ model of $\text{FeCaTa}_2\text{O}_7$ against the SXRD data collected at room temperature are shown in Figure 10.2.

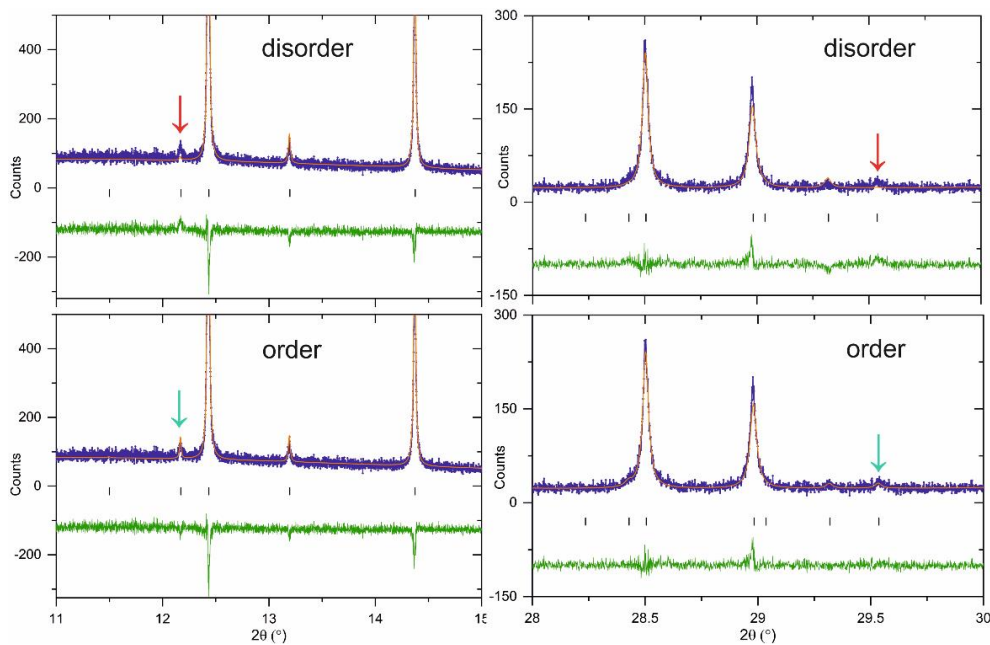


Figure 10.1. Comparison of the refinements of the disordered and ordered model of $P4_2/mnm$ symmetry structure of $\text{FeCaTa}_2\text{O}_7$. The arrows indicate the Fe-ordering peaks.

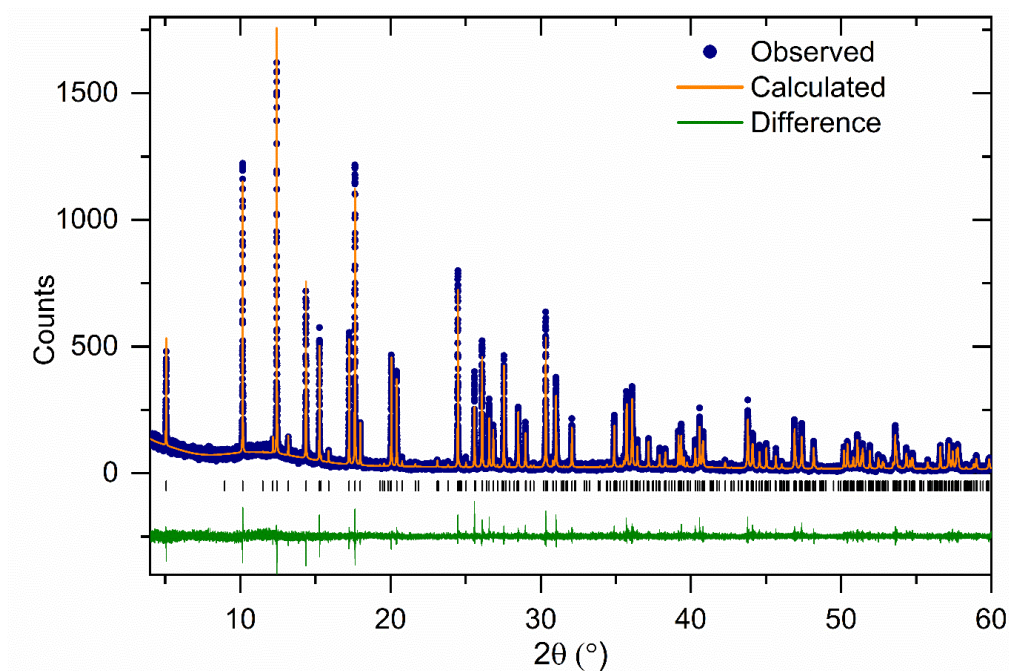


Figure 10.2. Observed, calculated and difference plots from the structure refinement of the ordered $P4_2/mnm$ model of $\text{FeCaTa}_2\text{O}_7$ against the SXRD data collected at room temperature.

10.3.1.2 SQUID magnetometry

Magnetisation data were collected from a sample of $\text{FeCaTa}_2\text{O}_7$ in an applied field of 100 Oe in the temperature range of $5 \text{ K} \leq T(\text{K}) \leq 300 \text{ K}$. The ZFC and FC data are shown in Figure 10.3. The H/M data can be fitted at high temperatures (150 K to 300 K) to the Curie-Weiss law, which yields a value of $C = 4.594(9) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -123.62(76) \text{ K}$. The negative value of θ indicates that the spins are interacting antiferromagnetically. The μ_{eff}^2 from the Curie-Weiss fit is $36.75(7)$, which is significantly larger than the μ_s^2 expected (24) from the spin only moment of high-spin $S = 2 \text{ Fe}^{2+}$ centre in tetrahedral ligand field. Since the ground state of tetrahedral Fe^{2+} is an E -term, not much spin-orbit coupling is expected. The anomaly in μ^2 could be because of the presence of a small amount of magnetic impurity or because of intralayer 2-dimensional ordering between the Fe^{2+} spins. The ZFC-FC data diverge below 38 K, suggesting a transition to a magnetically ordered state. The magnetisation-field isotherm collected at 300 K is linear. Both 300 K and 5 K data pass through the origin as shown in Figure 10.4.

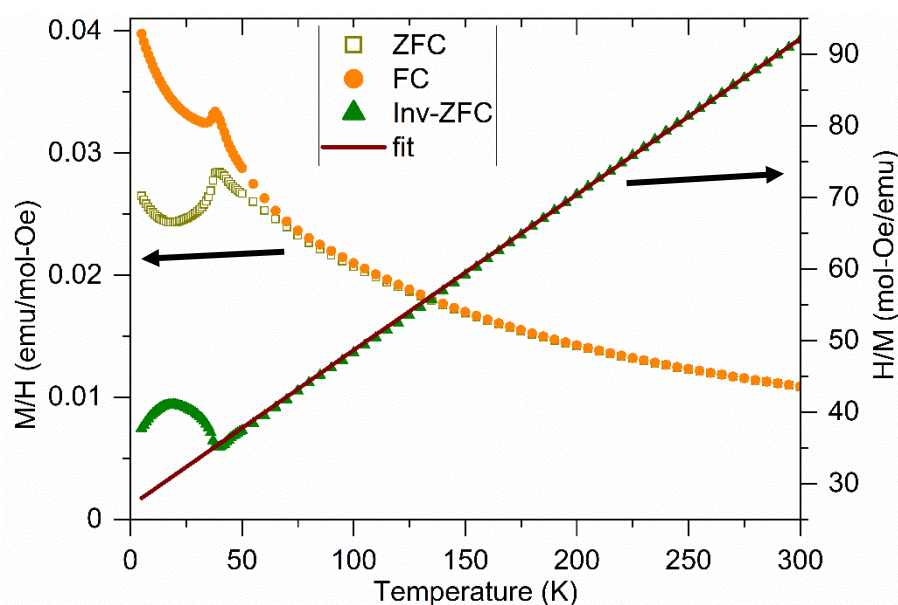


Figure 10.3. Zero field cooled and field cooled magnetization data collected from $\text{FeCaTa}_2\text{O}_7$. A fit to the Curie-Weiss law is shown which yields $C = 4.594(9) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -123.62(76) \text{ K}$

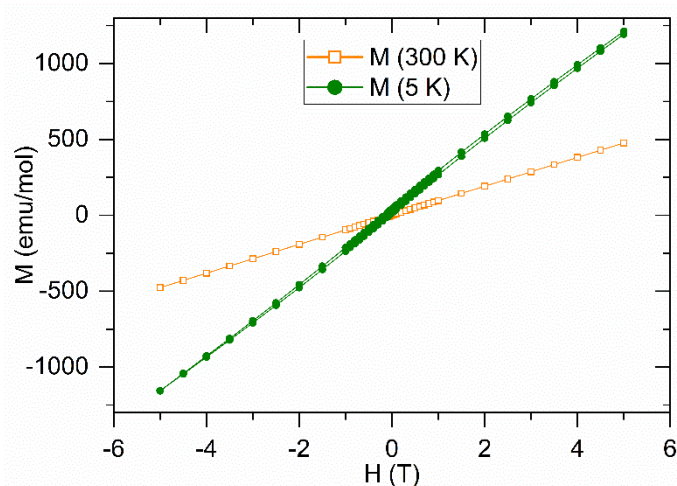
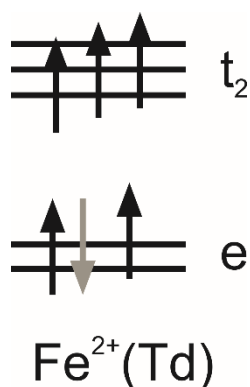


Figure 10.4. (Left) splitting of d -orbitals of Fe^{2+} in a tetrahedral ligand field. (Right) Magnetisation-field isotherms collected from $\text{FeCaTa}_2\text{O}_7$ at 300 K and 5 K.

10.3.2 Structural characterisation of $\text{CoCaTa}_2\text{O}_7$

10.3.2.1 Synchrotron X-ray diffraction data

Synchrotron X-ray diffraction (SXRD) data collected from $\text{CoCaTa}_2\text{O}_7$ at room temperature could be indexed using a tetragonal unit cell ($a = b = 5.507 \text{ \AA}$, $c = 18.593 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Ruddlesden-Popper aristotype unit cell. Systematic absences indicate a primitive cell is required to index all the peaks in the diffraction pattern. Powder SHG measurement reveals that the sample is not SHG active; hence adopts a centrosymmetric structure. Symmetry analysis of the structural distortions of the $n = 2$ Ruddlesden-Popper framework reveals two tetragonal candidate structures described in $P4_2/mnm$ and $P4_2/mcm$ space groups. Further extinction conditions eliminate the $P4_2/mcm$ symmetry structure. A structure model was constructed in the $P4_2/mnm$ space group and refined against the SXRD data which resulted in a good fitting.

Co^{2+} cations in the cation exchanged $\text{CoCaTa}_2\text{O}_7$ Ruddlesden-Popper phase occupy only half of the available pseudo-tetrahedral coordination sites in the framework, so can adopt either ordered or disordered arrangements. There are two sites for Co ($4d$ and $4e$) in the $P4_2/mnm$ model. The Co-site occupancies were refined within the constraint of total occupancy being one. After refinement, the occupancy of the $4d$ site reached 0.97 and the occupancy of the $4e$

site reached 0.03, indicating that the Co^{2+} ions are ordered. The 4e site was fixed as fully occupied which did not change the fitting statistics. Moreover, the ordered model results in a better fit than the disordered model as shown in Figure 10.5. The observed, calculated and difference plots from the structural refinement of the ordered $P4_2/mnm$ model of $\text{CoCaTa}_2\text{O}_7$ against the SXRD data collected at room temperature are shown in Figure 10.6.

Alternate orthorhombic models were tried as candidate space groups, refinement of which results in lattice parameters that demonstrate the crystal structure is metrically tetragonal.

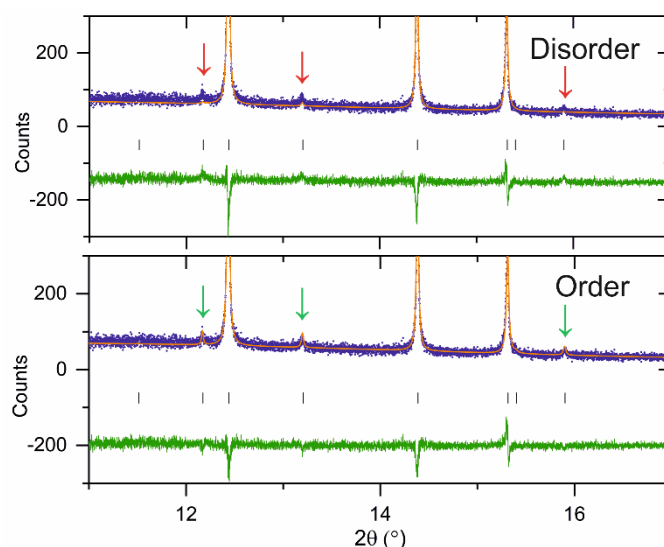


Figure 10.5. Comparison of the refinements of the disordered and ordered model of $P4_2/mnm$ symmetry structure of $\text{CoCaTa}_2\text{O}_7$. The arrows indicate the Co-ordering peaks.

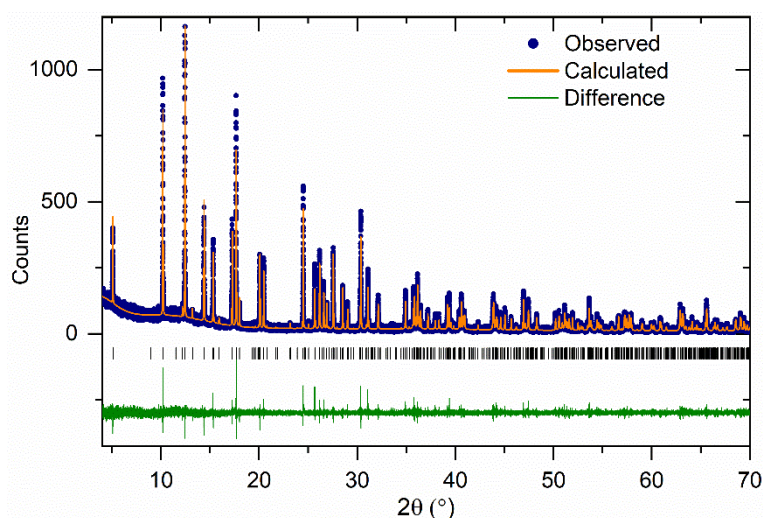


Figure 10.6. Observed, calculated and difference plots from the structure refinement of the ordered $P4_2/mnm$ model of $\text{CoCaTa}_2\text{O}_7$ against the SXRD data collected at room temperature.

10.3.2.2 SQUID magnetometry

Magnetisation data were collected from a sample of $\text{CoCaTa}_2\text{O}_7$ in an applied field of 100 Oe in the temperature range of $5 \text{ K} \leq T(\text{K}) \leq 300 \text{ K}$. The ZFC and FC data are shown in Figure 10.7, which diverge below 10 K, suggesting a transition to a magnetically ordered state. The M/H against temperature plot could be fitted using a modified Curie-Weiss law as shown in Figure 10.8 which yields a value of $\chi_0 = 0.00440(2) \text{ emu/mol-Oe}$, $C = 2.56(1) \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -70.91(46) \text{ K}$. The μ_{eff}^2 from the fit is $20.48(8)$; which is reasonably close to the expected $\mu_s^2 = 15$ for high-spin $S = 3/2$, Co^{2+} centre in tetrahedral ligand field. The negative value of θ indicates that the spins are interacting antiferromagnetically.

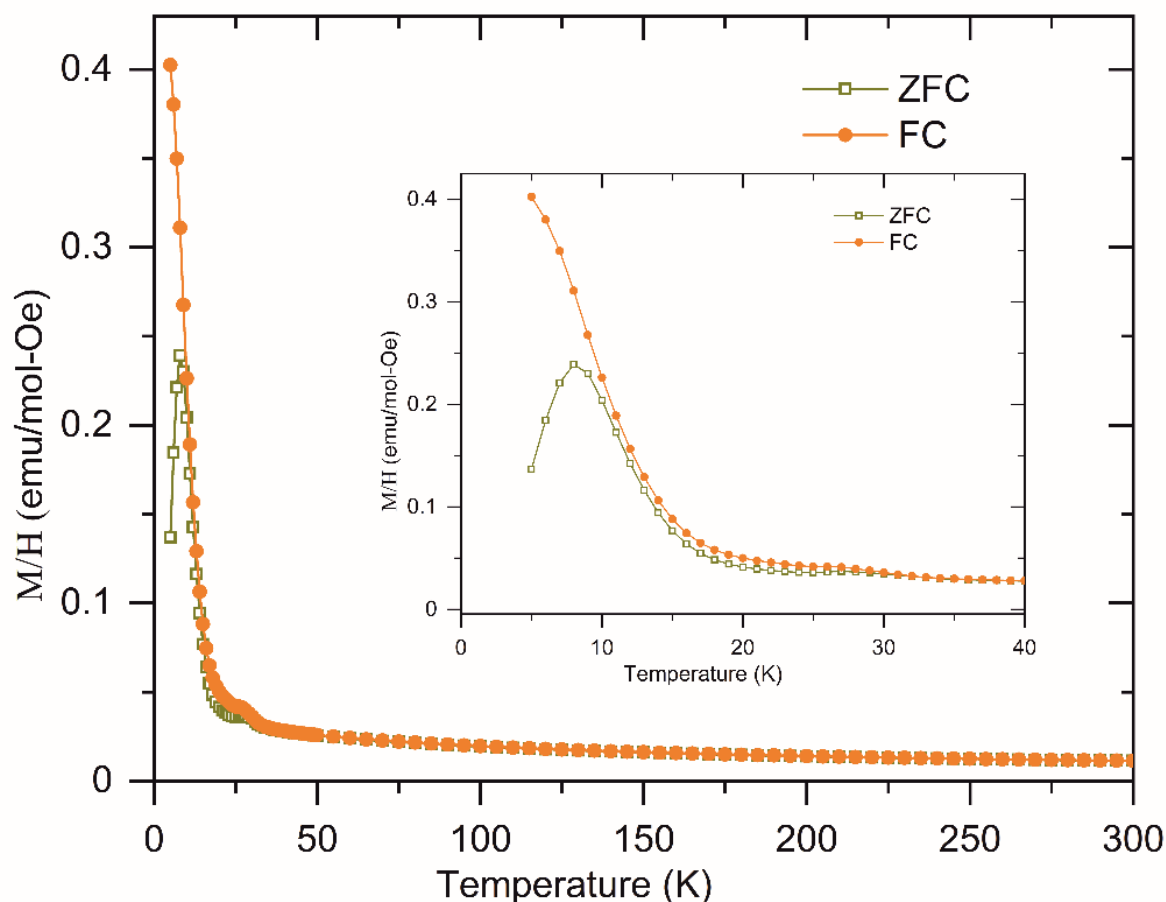


Figure 10.7. Zero field cooled and field cooled magnetization data collected from $\text{CoCaTa}_2\text{O}_7$.

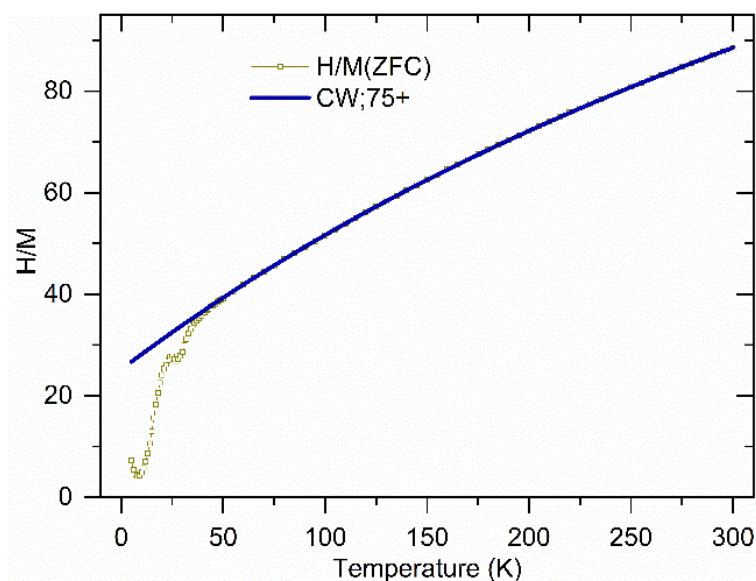


Figure 10.8. A fit to the modified Curie-Weiss law which yields $\chi_0 = 0.00440(2)$ emu/mol-Oe, $C = 2.56(1)$ cm³ K mol⁻¹, $\theta = -70.91(46)$ K.

The magnetisation field isotherm collected at 300 K is a straight line that passes through the origin. But the 5 K and 10 K data show a small hysteresis as shown in Figure 10.9; which indicates canting in the antiferromagnetic ordering of Co²⁺ spins.

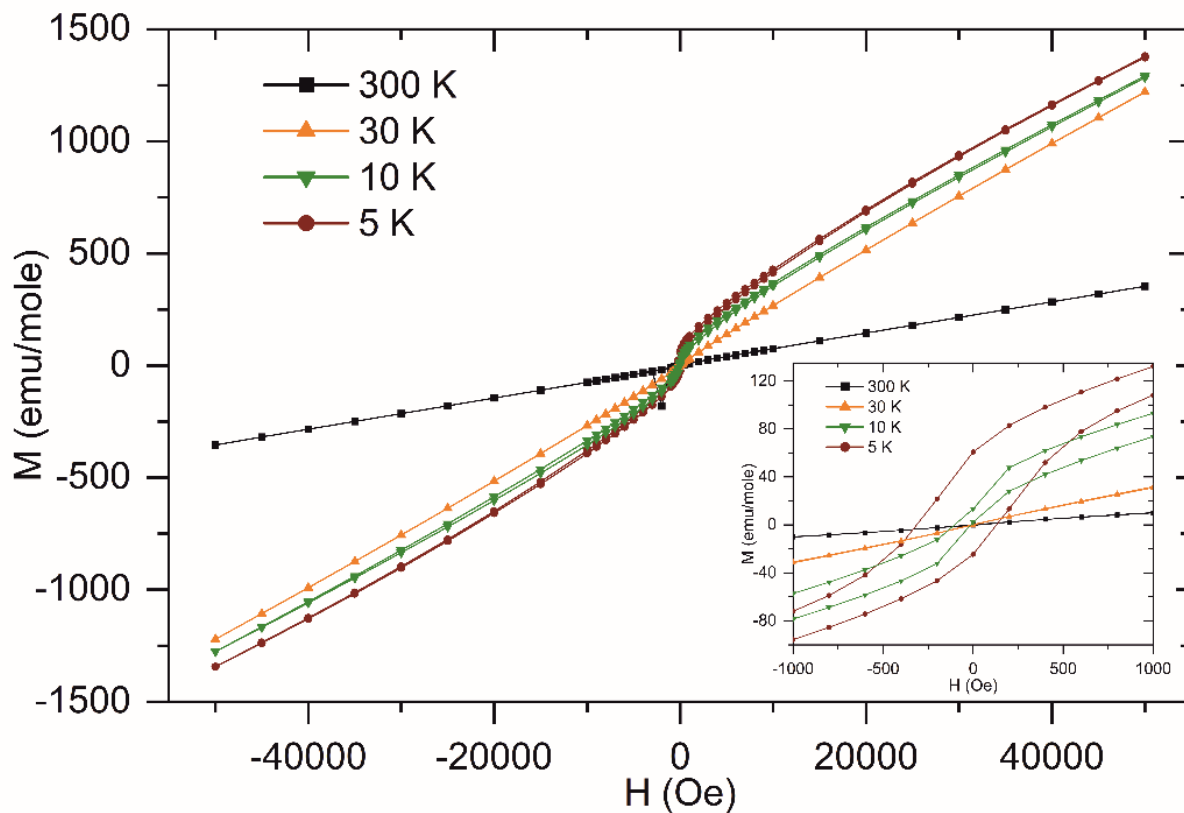


Figure 10.9. Magnetisation-field isotherms collected from CoCaTa₂O₇ at 300 K, 30 K, 10 K and 5 K.

10.3.3 Characterisation of ZnCaTa₂O₇

10.3.3.1 Synchrotron X-ray diffraction data

Synchrotron X-ray diffraction (SXR) data collected from ZnCaTa₂O₇ at room temperature could be indexed using an orthorhombic unit cell ($a = 5.533 \text{ \AA}$, $b = 5.379 \text{ \AA}$, $c = 19.757 \text{ \AA}$) consistent with an $a' \approx \sqrt{2} \times a$, $b' \approx \sqrt{2} \times b$, $c' \approx c$ geometric expansion of the undistorted $n = 2$ Ruddlesden-Popper aristotype unit cell. Systematic absences in the diffraction pattern indicate that the diffraction peaks could be indexed using a B -centred unit cell. Symmetry analysis of the structural distortions of the $n = 2$ Ruddlesden-Popper frameworks revealed six orthorhombic candidate structures described in $Bbcm$, $Bbcb$, $Bbmm$, $Bmcm$, $Bb2_1m$ and $B2cm$ space groups. Further extinction conditions eliminate $Bbcm$, $Bbcb$, $Bbmm$ and $Bb2_1m$ symmetry structures leaving only $Bmcm$ and $B2cm$ as the candidate structure. Powder SHG measurement reveals that ZnCaTa₂O₇ is not SHG active, hence adopts a centrosymmetric structure. On this basis, $B2cm$ symmetry structure was eliminated leaving only the $Bmcm$ symmetry structure. A structure model in $Bmcm$ space group was constructed and refined against the SXR data collected at room temperature which resulted in a good fitting.

Zn²⁺ cations in the cation exchanged ZnCaTa₂O₇ Ruddlesden-Popper phase occupy only half of the available pseudo-tetrahedral coordination sites in the framework, so can adopt either ordered or disordered arrangements. There are two sites for Zn ($4a$ and $4b$) in the $Bmcm$ structure model. The Zn-site occupancies were refined within the constraint of total occupancy being one. After refinement, the occupancy of the $4a$ site reached 0.90 and the occupancy of the $4b$ site reached 0.10, indicating that the Zn²⁺ ions are ordered. The $4a$ site was fixed as fully occupied which did not change the fitting statistics. Moreover, the ordered model results in a better fit than the disordered model as shown in Figure 10.10. The observed, calculated and difference plots from the structural refinement of the ordered $Bmcm$ model of ZnCaTa₂O₇ against the SXR data collected at room temperature are shown in Figure 10.11.

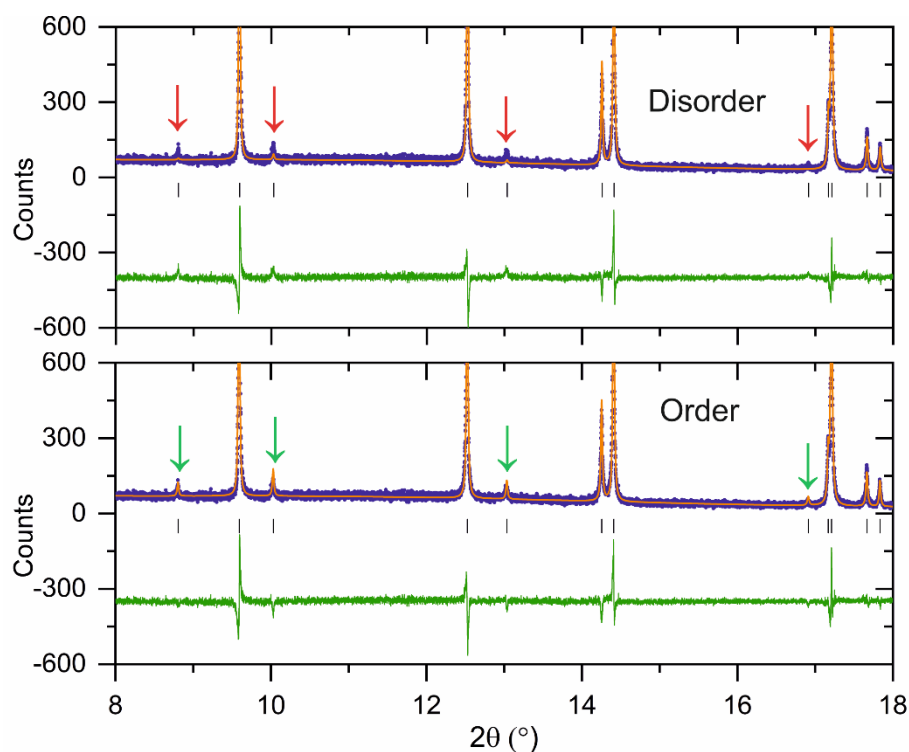


Figure 10.10. Comparison of the refinements of the disordered and ordered model of *Bmcm* symmetry structure of $\text{ZnCaTa}_2\text{O}_7$. The arrows indicate the Zn-ordering peaks.

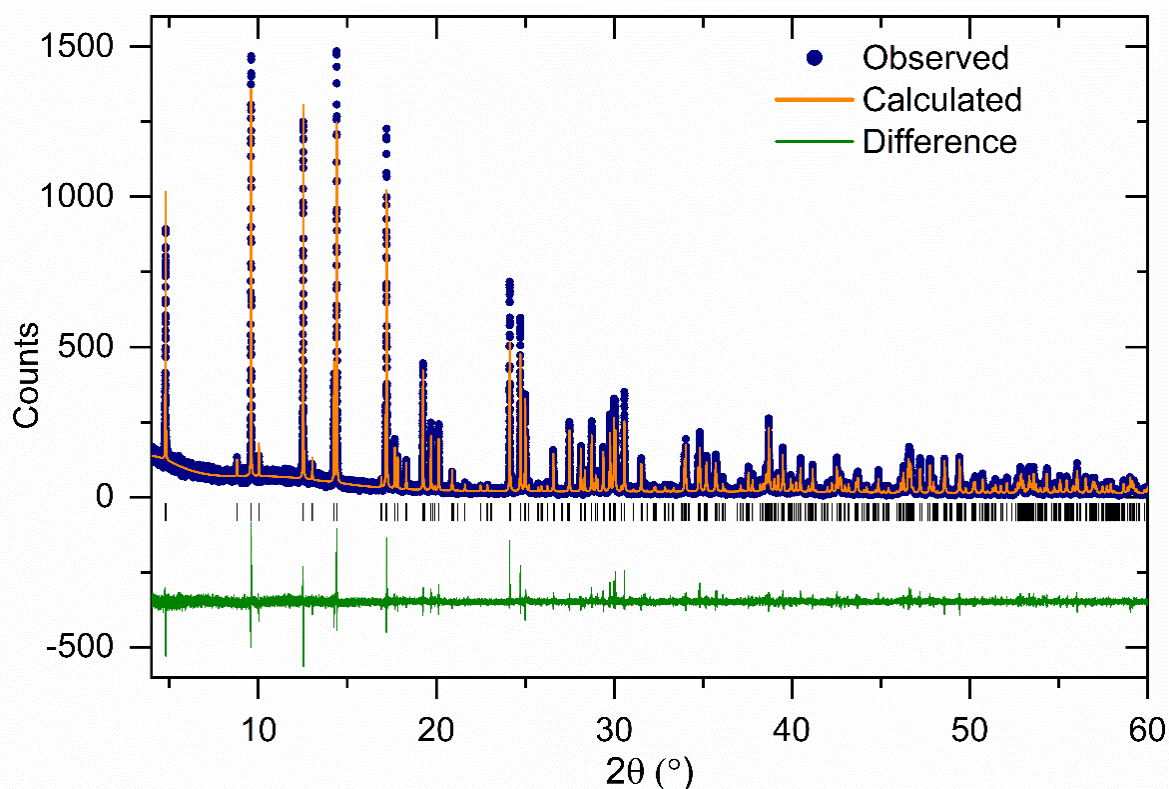


Figure 10.11. Observed, calculated and difference plots from the structure refinement of the ordered *Bmcm* model of $\text{ZnCaTa}_2\text{O}_7$ against the SXRD data collected at room temperature.

10.4 Discussion

The successful synthesis of $\text{MnCaTa}_2\text{O}_7$ (chapter 8), $\text{FeCaTa}_2\text{O}_7$, $\text{CoCaTa}_2\text{O}_7$ and $\text{ZnCaTa}_2\text{O}_7$ from $\text{Li}_2\text{CaTa}_2\text{O}_7$ indicates that it is usually possible to exchange Li^+ cations by divalent 3d transition metal cations; which have similar ionic radii to Li^+ . The synthesis of the Ni-phase was not achieved, probably because Ni^{2+} ($3d^8$ electronic configuration) disfavors tetrahedral coordination site. Similarly, Cu^{2+} , being a Jahn-Teller active cation, does not prefer a tetrahedral coordination environment. As a monovalent cation is substituted by a divalent cation, the number of available sites in the exchanged phase is twice than the number of transition metal cations available. Hence the metal cations in the interlayer sites can either be ordered or disordered.

The unit cell parameters and the possible structure models of $\text{FeCaTa}_2\text{O}_7$, $\text{CoCaTa}_2\text{O}_7$ and $\text{ZnCaTa}_2\text{O}_7$ were constructed based on high-resolution synchrotron X-ray diffraction data. But for complete structure characterisation, the accurate determination of the position of the light oxide ions is necessary, which is not possible using X-ray especially in the presence of heavier Ta-atoms. Hence, the atomic positions are not reported here, but important structural information, for example, the centering of unit cell, space group symmetry and ordering scheme of A'-transition metals, can be determined to a certain accuracy.

The $P4_2/mnm$ structure of $\text{FeCaTa}_2\text{O}_7$ and $\text{CoCaTa}_2\text{O}_7$ can be constructed by applying the X_3^- distortion mode with the undistorted aristotype $I4/mmm$ structure. The X_3^- distortion mode in the $P4_2/mnm$ structure describes the $a^-b^0c^0/b^0a^-c^0$ tilting distortion of TaO_6 octahedra as shown in Figure 10.12. In the $\text{Li}_2\text{CaTa}_2\text{O}_7$ phase, the Li^+ cations occupy a pseudo tetrahedral coordination environment. However, the Fe^{2+} and Co^{2+} cations are located in five coordinate sites (Figure 10.12). The $\text{Fe}^{2+}/\text{Co}^{2+}$ cations are ordered in a checkerboard pattern within the interlayer 5-coordinate sites as shown in Figure 10.13.

The *Bmcm* structure of $\text{ZnCaTa}_2\text{O}_7$ can be constructed by applying X_4^- distortion mode with the undistorted aristotype *I4/mmm* structure. The X_4^- distortion mode in the *Bmcm* structure describes the $a^-a^-c^0/-(a^-a^-)c^0$ tilting distortion of TaO_6 octahedra as shown in Figure 10.12. The Zn^{2+} cations in the $\text{ZnCaTa}_2\text{O}_7$ phase are ordered in stripes as shown in Figure 10.13. Similar competition between different ordering schemes is also observed in related Ruddlesden-Popper phases, $A'\text{ANb}_2\text{O}_7$ ($A' = \text{Li, Na}$; $A = \text{Nd, Bi}$);^{42,110} where it is observed that the relatively smaller Li^+ cations adopt stripes ordering but the relatively larger Na^+ cations are ordered in a chequerboard pattern. The differing ordering pattern adopted by the Li^+ and Na^+ cations in these phases have been attributed to a competition between minimizing the repulsion between the A' -cations and optimization of bonding of the A -cation, with stripe and chequerboard order being the optimum solution of the Li^+ and Na^+ cations respectively. A similar argument can be made for the ordering of $\text{Fe}^{2+}/\text{Co}^{2+}$ in the $\text{FeCaTa}_2\text{O}_7/\text{CoCaTa}_2\text{O}_7$ phase and Zn^{2+} in the $\text{ZnCaTa}_2\text{O}_7$ phase. The size of the $3d$ transition metal cations decreases consecutively while moving to the right of the periodic table. Hence the size of the Zn^{2+} in tetrahedral coordination ($0.60 \text{ \AA}$) is smaller than the size of Fe^{2+} ($0.63 \text{ \AA}$). Fe^{2+} cations being larger, prefer to have a chequerboard ordering as this pattern minimizes the interionic Coulombic repulsion. In contrast, the smaller Zn^{2+} cations prefer to order in the bonding optimized stripes scheme.

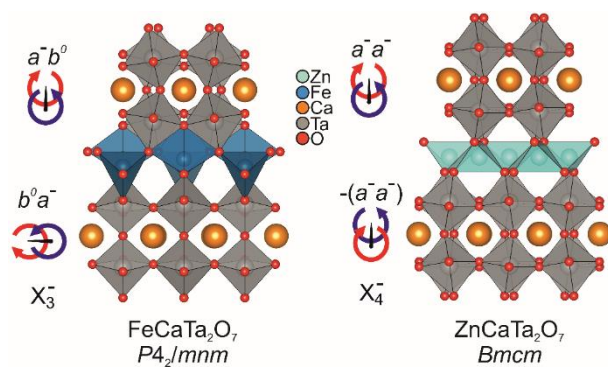


Figure 10.12. Structure and tilting patterns of $\text{FeCaTa}_2\text{O}_7$ and $\text{ZnCaTa}_2\text{O}_7$ as obtained from the refinement of $P4_2/mnm$ and *Bmcm* model respectively against the SXRD data collected at room temperature.

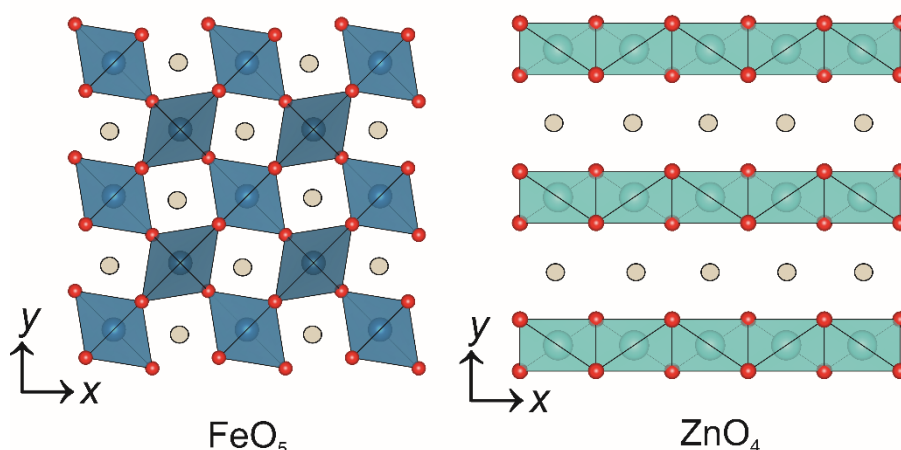


Figure 10.13. Chequerboard and stripe ordering scheme of Fe^{2+} and Zn^{2+} cations in the $P4_2/mnm$ and $Bmcm$ structure of $\text{FeCaTa}_2\text{O}_7$ and $\text{ZnCaTa}_2\text{O}_7$ respectively. Grey spheres indicate empty sites.

The size mismatch between the A -site cation and B -site cation of ABO_3 perovskites and related layered perovskite phases can be expressed by the tolerance factor.³ A smaller cation in the A -site lowers the tolerance factor which increases the tilting of BO_6 octahedra. In layered perovskites, because of the presence of interlayer A' -cations, the bonding optimization between the A' -cation site and the A -cation site plays an important role which determines the tilt patterns as well as the structures adopted by these layered perovskites. On moving from Mn^{2+} to Fe^{2+} to Co^{2+} to Zn^{2+} in the $M^{\text{II}}\text{CaTa}_2\text{O}_7$ structures; the ionic size decreases. Hence it is expected that there will be an increase in tilting pattern i.e. more distorted structure on moving right in the $3d$ transition metal series. This is somewhat true since $\text{FeCaTa}_2\text{O}_7$ and $\text{CoCaTa}_2\text{O}_7$ have only one tilt pattern in their structure, while $\text{ZnCaTa}_2\text{O}_7$ has two tilt patterns. In contrast, as discussed in the previous chapter, $\text{MnCaTa}_2\text{O}_7$ has tilting in all three directions. This supports the hypothesis that there is a competition between the bonding optimization of the A' - and A -cation sites.

The Fe^{2+} and Co^{2+} cations are ordered antiferromagnetically as discussed in the results section. In the case of $\text{FeCaTa}_2\text{O}_7$, the ZFC and FC plots start to deviate from each other even before the magnetic transition temperature as shown in Figure 10.3. This feature is observed in the related compound e. g. $\text{MnSrTa}_2\text{O}_7$ ⁹⁰ that can be attributed to the intralayer 2D ordering of

Fe^{2+} spins before they are ordered in 3-dimension. The ZFC-FC plot of $\text{CoCaTa}_2\text{O}_7$ can be fitted well to get a reasonable value of μ_{eff}^2 using a modified Curie-Weiss law. Although the ground state of Co^{2+} is an A-term; the excited state could create degeneracy in the t_2 level (Figure 10.14), which can increase magnetic moment via a second-order spin orbit coupling. A small splitting of d -orbitals is required for the second order spin orbit coupling to take place, which is the case in a tetrahedral coordination environment.

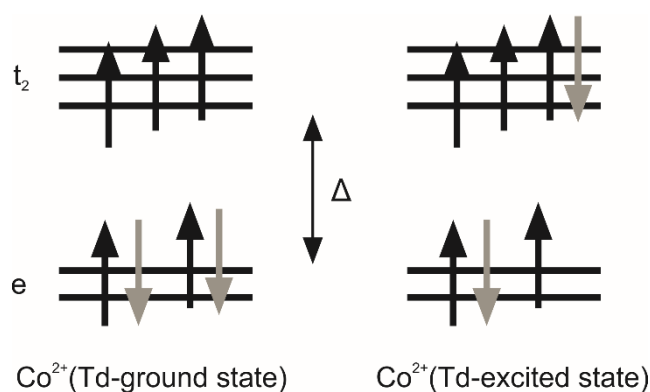


Figure 10.14. Ground state and excited state electronic configuration of tetrahedral Co^{2+} .

10.5 Conclusion

Single phase $\text{FeCaTa}_2\text{O}_7$, $\text{CoCaTa}_2\text{O}_7$ and $\text{ZnCaTa}_2\text{O}_7$ were synthesized from $\text{Li}_2\text{CaTa}_2\text{O}_7$ by cation exchange reactions. Preliminary structure analysis using SXRD data indicate that the Fe and Co phases adopt a tetragonal $P4_2/mnm$ structure, while the $\text{ZnCaTa}_2\text{O}_7$ phase adopts an orthorhombic $Bmcm$ structure. For complete structural characterisation, neutron diffraction data will be required. SQUID data indicate that $\text{FeCaTa}_2\text{O}_7$ and $\text{CoCaTa}_2\text{O}_7$ are antiferromagnetically ordered at low temperatures. Again, to determine the magnetic structures, neutron diffraction data will be required.

Chapter 11 – Conclusion

This thesis focuses on the synthesis and characterisation of a wide range of $n = 2$ layered perovskite oxides. The objective is to prepare new ferroelectric and multiferroic materials as well as to understand the chemical and structural motivations of these layered perovskites to adopt polar structures. It is demonstrated that the size of the interlayer cation species in between the double perovskite blocks plays an important role to determine the bulk crystal structure. This observation motivates to perform cation exchange chemistry on a series of layered perovskites to synthesize new phases which have different structures than the precursor phase. It is shown that the cation exchange reactions are an alternate pathway to prepare new ferroelectric and multiferroic materials. In addition, the competition between two stabilisation mechanisms: the “improper” and the “proper” is discussed for $n = 2$ layered perovskite oxides. Structural characterisation of layered perovskites with distorted structures is challenging. Usually a combination of different characterisation techniques, for example, synchrotron X-ray diffraction, neutron diffraction, second harmonic generation, electron diffraction and DFT calculation, is required to determine the structure of these phases unambiguously. Neutron diffraction is essential to study the hybrid improper ferroelectrics since the noncentrosymmetric structures of these phases arise from subtle displacements of light oxide ions. The positions of the oxide ions cannot be determined unambiguously using X-ray diffraction, especially in presence of heavier cations e.g. Nb, Ta, Nd, Bi. A useful tool to ease the complicated crystallography for characterisation of layered perovskites is the symmetry analysis starting from the aristotype structure. Usually, the low symmetry models are constructed by considering the rotation and tilting distortions of the BO_6 octahedra. This symmetry analysis is far from perfect and it is often required to consider further distortions. For example, in chapter 4, the noncentrosymmetric $P2_12_12_1$ structure of $\text{NaBiNb}_2\text{O}_7$ can be obtained by considering further Γ -point distortion from the $Pnam$ structure with $a^-a^-c^+/a^-a^-(-c^+)$ tilting distortion.

Chapter 3, 4 and 5 demonstrate the effect of interlayer cation size on the stacking of double perovskite blocks as well as the tilting distortions and the crystal structures adopted by these phases. Specifically, KNdM_2O_7 ($M = \text{Nb, Ta}$) and $A'\text{BiNb}_2\text{O}_7$ ($A' = \text{Rb, Li, Na, K}$) were synthesized and their structural distortions were characterised. The Li, Na and the K-phases cannot be prepared by high temperature solid state routes. These phases are kinetically stable and synthesized by a series of topochemical cation exchange reactions starting from the corresponding thermodynamically stable Rb-phase. The topochemically prepared $\text{LiBiNb}_2\text{O}_7$, $\text{NaBiNb}_2\text{O}_7$, KBiNb_2O_7 and KNdM_2O_7 ($M = \text{Nb, Ta}$) -phases adopt noncentrosymmetric crystal structures, among them, the Li and the K-phases are polar. Successful low-temperature synthesis of these polar phases demonstrates that the cation exchange reactions can act as a viable route to prepare new ferroelectric materials. Close inspection of their crystal structures reveals that the tilting distortion of the perovskite layers depends on both the size mismatch between the *A*-site and *B*-site cations (tolerance factor) and the size of the interlayer cation. In addition to that, a competition between the bonding optimisation of the *A*-site cation and the *A'*-site cation is evident as demonstrated by the bond valence sum analysis. The $\text{RbBiNb}_2\text{O}_7$ and $\text{LiBiNb}_2\text{O}_7$ phases adopt the same polar structure to their Nd-analogues. Symmetry analysis of their distorted structures with respect to the aristotype structure indicates that although the polar structures appear from a hybrid improper mechanism, the presence of Bi^{3+} cation enhances the polar displacements. The $6s^2$ electronic configuration of Bi^{3+} cation favours an asymmetric coordination environment which often leads to further distortion stabilized by a “proper” mechanism. The presence of the Bi^{3+} cation on the *A*-site instead of a spherical cation lowers the activation energy barrier for non-topochemical processes.

In chapter 6, the structure and the low-temperature phase transition behaviour of the solid solutions with composition $\text{Li}_2\text{Sr}_{1-x}\text{Ca}_x\text{Ta}_2\text{O}_7$ are investigated. Two end members of this solid solution, $\text{Li}_2\text{SrTa}_2\text{O}_7$ and $\text{Li}_2\text{CaTa}_2\text{O}_7$ adopt “hybrid improper” and “proper” polar structures

respectively at room temperature and at low temperatures. Therefore, the phase transition from a hybrid improper structure at room temperature to a proper polar structure at low temperature is explored for a series of intermediate compositions of this solid solution. $\text{Li}_2\text{SrNb}_2\text{O}_7$ undergoes a phase transition from a room temperature hybrid improper polar structure to low temperature proper polar structure. Substitution of $4d\text{-Nb}^{5+}$ by $5d\text{-Ta}^{5+}$ declines the transition temperature because of a lower degree of hybridisation between the Ta-5d and O-2p orbitals than Nb-4d and O-2p orbitals. Therefore, a clear competition between the hybrid improper and proper mechanism of polarity in layered perovskite structures is displayed. The presence of d^0 transition-metal ions in trilinear coupled hybrid improper polar phases raises the prospect of this competition between trilinear-coupled hybrid-improper stabilization and SOJT stabilization of polar distorted phases. In chapter 7, two polar $n = 2$ Ruddlesden-Popper phases, $\text{Li}_2\text{La}(\text{TaTi})\text{O}_7$ and $\text{Na}_2\text{La}(\text{TaTi})\text{O}_7$, the former stabilized by the trilinear-coupled hybrid-improper mechanism, the latter by an SOJT distortion are described, and the role of the Li^+ and Na^+ cations in mediating the competition between these two classes of polar distortion are discussed.

In chapter 8, the synthesis and characterisation of $\text{MnCaTa}_2\text{O}_7$, which is prepared by topochemical cation exchange reaction from $\text{Li}_2\text{CaTa}_2\text{O}_7$, is discussed. $\text{MnCaTa}_2\text{O}_7$ adopts a polar structure and orders antiferromagnetically below 56 K. Successful synthesis of polar and magnetically ordered $\text{MnCaTa}_2\text{O}_7$ demonstrates that it is possible to intercalate paramagnetic 3d transition metal cations in the interlayer of layered perovskites by low-temperature cation exchange reactions. This hypothesis was further confirmed in the next chapter. Topochemical cation exchange reactions of $\text{Li}_2\text{La}(\text{TiB})\text{O}_7$ resulted in $\text{MnLa}(\text{TiB})\text{O}_7$ ($B = \text{Ta}, \text{Nb}$) which also have polar structures and order at low temperatures. Since the ionic radius of Li^+ cation is similar to the M^{2+} cations in a tetrahedral coordination environment, in chapter 10, further cation exchange reactions were explored which were performed on $\text{Li}_2\text{CaTa}_2\text{O}_7$ to synthesize

$MCaTa_2O_7$ ($M = Fe, Co, Zn$). The successful synthesis of these phases works as a proof of concept that topochemically prepared kinetic phases are a promising avenue to prepare new ferroelectric and magnetoelectric multiferroic materials.

Overall the work presented in this thesis shows that the $n = 2$ Dion-Jacobson and Ruddlesden-Popper phases have a rich cation exchange chemistry which allows the synthesis of a series of kinetically stable noncentrosymmetric materials. The properties of these compounds are intimately linked to their structures. Therefore, detailed structural characterisation with the help of complementary characterisation techniques is mandatory to understand the integral link between the structure of a compound and the properties it exhibits, as discussed in chapter 1. This thesis demonstrates an alternative way to design the synthesis of new ferroelectric and multiferroic materials.

Several directions can build based on this work. First of all, the family of $A'AB_2O_7$ Dion-Jacobson family can be expanded to include alkaline earth metal cations in the A -site, by trading one positive charge to the B -site, therefore using the $A = Sr^{2+}, Ca^{2+}$ $B = Nb^{5+}/W^{6+}$ or Ta^{5+}/W^{6+} combinations. Now moving on to the Pseudo-Ruddlesden-Popper phases with $Li_2A^{3+}(B^{4+}B'^{5+})O_7$ composition, combinations of $A = Ln^{3+}$ and $B = Zr^{4+}, Sn^{4+}$; $B' = Nb^{5+}, Ta^{5+}$ could be explored. Moreover, $Li_2SrNb_2O_7$ has a polar structure as discussed in chapter 6. Therefore, cation exchange chemistry of this phase to incorporate paramagnetic transition metal cations (M^{2+} , $M = Mn, Fe, Co, Ni, Cu$) in between the double perovskite blocks would be possible. A further option to expand the family of polar layered perovskites is to examine layered perovskite frameworks with $n > 2$. Several complex distortion modes in principle can couple to generate polar structures. Again, the soft chemistry of these phases can lead to a number of new phases. As mentioned above, there are several degrees of freedom to manipulate in layered perovskite frameworks and therefore a lot of chemistry to explore.

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