

Fabrication of Laminated Solid Electrolytes with Compressive Surface Stresses for Lithium Batteries



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Declaration of Originality

I, Leonhard Tannesia, certify that the work presented in this thesis is the result of my own work and has not been submitted to the University of Oxford or any other institution for any degree, diploma or other qualification. Any collaborations on this work or work performed by others included in this thesis has been clearly referenced and acknowledged. The work for this thesis, which is approximately 23,000 words in length, has been carried out within the Department of Materials at the University of Oxford from January 2021 to August 2022 under the supervision of Prof. Richard I Todd.

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Abstract

The use of solid-state electrolyte (SSE) for all-solid-state batteries (ASSB) has long been touted to be the next big step for rechargeable lithium-ion batteries. Inorganic oxide SSE was thought to be able to mitigate the Li dendriting problem in such batteries, owing to the high Young's modulus of this class of SSE. However, this is not the case, with a recent discovery showing that dendrites can still penetrate through by propagating cracks through the brittle oxide SSE. Therefore, should it be possible that the SSE be made more resistant to crack propagation, it should also inhibit the dendriting phenomenon. One main idea by which this can be achieved is by introducing residual compressive stress to the SSE. A question then arises: Is it possible for compressively stressed SSE, induced by means of a symmetrically laminated structure, be fabricated and if it is how will it affect the conductivity and dendrite resistance of said laminated SSE? This thesis presents that such laminated SSE is possible.

Perovskite-type $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Zr}_{1/4}\text{O}_3$ (LSTZ) and differently doped garnet type $(\text{Al,Ga,Ta})_y - \text{Li}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) SSEs were synthesized using solid-state method, with an optimized calcining regime. It was found that 10% Li excess and 12.5% Li excess was needed for LSTZ and LLZO respectively, to compensate for lithium loss during calcination. After sintering, the resulting pellets show good conductivity, in the order of $10^{-4} \text{ S cm}^{-1}$. Elastic properties of the pellets were also measured and presented.

Having verified that the synthesized powders are conductive, an innovative sintering technique to co-sinter Ta-doped and Al-doped LLZO was presented. Al-LLZO – Ta-LLZO – Al-LLZO laminated pellets with surface compressive residual stresses were successfully sintered and was demonstrated to be twice as conductive compared to the constituent's monolithic pellets. CCD cycling suggests that the laminate can withstand higher current compared to similarly prepared monolithic Al-LLZO.

List of Abbreviations

°C	-	degree Celsius
μm	-	micrometer
3D	-	three dimensional
ASSB	-	all solid-state batteries
AC	-	alternating current
Al-LLZO	-	Al doped LLZO
CCD	-	critical current density
CIP	-	cold isotactic press
cm	-	centimeter
CTE	-	thermal expansion coefficient
DC	-	direct current
EBSD	-	electron back-scattered diffraction
EDX	-	energy dispersive X-ray spectroscopy
EIS	-	electron impedance spectroscopy
FESEM	-	field emission SEM
g	-	gram
Ga-LLZO	-	Ga doped LLZO
GCPL	-	galvanostatic cycling with potential limitation
GPa	-	gigapascal
GWh	-	gigawatt hours
h	-	hour
HP	-	hot press
Hz	-	hertz
IPA	-	isopropanol
K	-	kelvin
kPa	-	kilopascal
LD	-	laser diffraction
LiB	-	lithium-ion battery
LISICON	-	lithium super ionic conductor
LLTO	-	$\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$
LLZO	-	$\text{Li}_x\text{La}_3\text{Al}_y\text{Zr}_2\text{O}_{12}$
LPSCI	-	$\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$
LSTZ	-	$\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Zr}_{1/4}\text{O}_3$
LZO	-	$\text{La}_2\text{Zr}_2\text{O}_7$
M	-	mole
mA	-	milliampere
MHz	-	megahertz
min	-	minutes
ml	-	milliliter
mm	-	millimeter
MPa	-	megapascal
NASICON	-	sodium super ionic conductor
pA	-	picoampere
PVB	-	polyvinyl butyrate
S	-	siemens
s	-	seconds
SEM	-	scanning electron microscope
SHE	-	standard hydrogen electrode
SPS = FAST	-	spark plasma sintering = field-assisted sintering technique

SSE	-	solid-state electrolyte
Ta-LLZO	-	Ta doped LLZO
TGA	-	thermogravimetric analysis
V	-	volt
wt%	-	weight percent
XRD	-	X-ray diffraction

Elements

Al	-	Aluminum
C	-	Carbon
Cl	-	Chlorine
Cu	-	Copper
Ga	-	Galium
Ge	-	Germanium
Au	-	Gold
H	-	Hydrogen
La	-	Lanthanum
Li	-	Lithium
Nb	-	Niobium
N	-	Nitrogen
O	-	Oxygen
P	-	Phosphate
Si	-	Silicon
Na	-	Sodium
Sr	-	Strontium
Ta	-	Tantalum
Te	-	Tellurium
Ti	-	Tin
Ti	-	Titanium
Zn	-	Zinc
Zr	-	Zirconium

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Chapter 1 Introduction

1.1 Introduction to Rechargeable Batteries

Rechargeable batteries are devices that store energy as they are “charged” and release that energy for use while in “discharge” mode (Figure 1). To do so, rechargeable batteries in a broader sense convert electrical energy into another form of energy that can be easily stored, such as chemical or potential energy [1, 2]. In practice, most of what we refer to as batteries nowadays are electrochemical devices where reversible conversion between electrical energy and chemical potential energy happens through redox reactions [3].

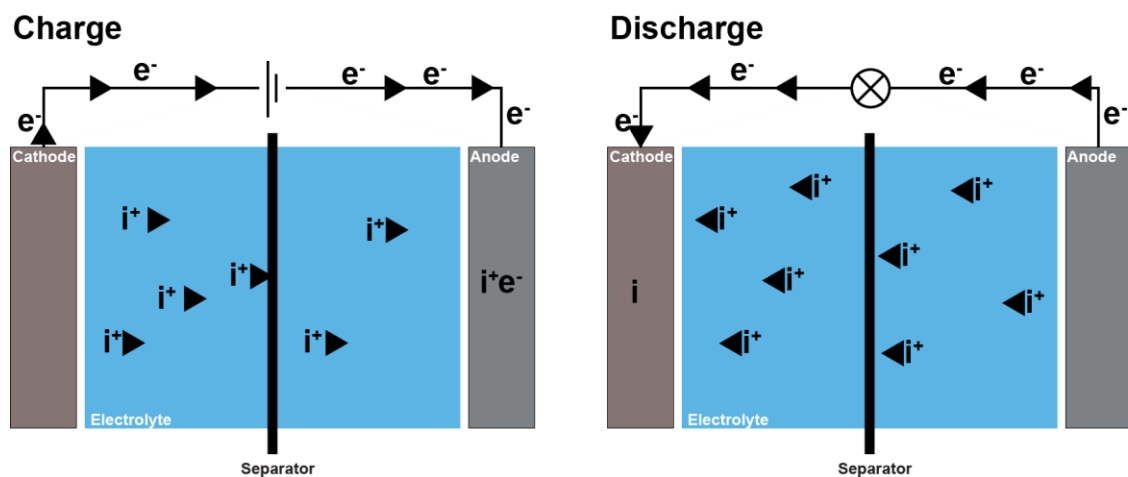


Figure 1. Schematics of ion and electron migration in battery cell on charge and discharge

These so-called electrochemical batteries are composed of cells, containing a cathode, an anode, and electrolyte usually with a separator to prevent a continuous electronic circuit through the electrolyte [4]. As external charge is applied, an oxidation reaction occurs in the cathode, which releases charge-carrier ions. These ions travel through the electrolytes into the anode, where there is a build-up of negatively charged electrons. On discharge, these electrons are released back through the external circuit into the cathode,

driven by a reversed migration of the ions back through the electrolyte. The self-contained reaction path means that rechargeable electrochemical batteries are portable and are able to power devices without connection to the power grid.

Due to their usefulness as portable energy storage, batteries have been proposed as the ultimate solution to some of the world's current problems. This viewpoint can be justified as in our mobile world today, we rely on batteries to power our increasingly essential electronics. In fact, since they were conceived in the '80s [5, 6], the demand for lithium-ion batteries (LiB) has grown to satisfy a capacity of 185 GWh by 2020 and it is forecast to grow even further [7]. This dominance of LiBs can be attributed to their higher energy density, and long cycle life amongst other reasons [8].

Current LiB applications include electric vehicles, mobile consumer appliances, as well as stationary energy storage. This being the case, the battery industry is always racing to further enhance the energy density, to produce more compact batteries with higher energy storage capacity.

1.2 Current Battery Electrolytes

To date, the majority of commercial LiBs utilize liquid electrolyte solution between their cathode and anode as the ion transfer medium. Liquid electrolyte is easier to apply, as the fluidic nature of this type of electrolyte conforms to the shape of the electrodes, maximizing and maintaining contact [9]. However, the high volatility of liquid electrolytes poses significant danger, as they can combust and explode in contact with air [10]. This might then lead to harmful explosions or batteries catching on fire.

1.3 Solid-State Batteries

One proposed idea to achieve higher energy density is to employ all-solid-state batteries (ASSB). In principle, ASSBs are defined as batteries that utilize solid electrodes, as well as solid

electrolytes in place of liquid or polymer electrolytes [11]. The use of solid electrolytes can theoretically be beneficial due to the inherent nature of solids compared to liquid, i.e. solid-state electrolytes (SSE) are less flammable compared to the volatile liquid electrolyte [10], intrinsically allows for larger operating temperature range [10], and can be commercially scaled up to be cheaper, smaller, and more energy dense [10, 12, 13]. Additionally, SSEs were thought to be able to resist dendrite growth better than liquid electrolytes [4], resulting in the ability to utilize metallic lithium electrodes that possess higher specific charge, allowing for higher energy density.

1.4 Lithium Metal Anodes

One of the primary allures for SSE is the possibility of using metallic lithium as the anode in ASSBs. Lithium metal, as an element with the lowest negative electrochemical potential (-3.04 V vs SHE) and high specific charge capacity (3860 mAh g^{-1}), makes it the ultimate material for battery anodes [14-16]. However, adoption of metallic lithium anodes is difficult due to their tendency to form lithium dendrites that penetrate through the electrolyte, causing short circuit between the electrodes, resulting in cell failure [14].

Intuitively, SSEs should be able to resist this dendritic growth better than the commercially used separator and liquid electrolyte due to their solid nature. However, attempts so far have shown that SSEs must be made stronger and more resistant to lithium dendrite penetration [16] in order to maximize their application.

1.4.1 Dendritic Growth

It was long known that Li dendrites grow in cells utilizing lithium metals due to inhomogeneous deposition and dissolution of Li metals in the electrolyte during cycling [17], resulting in the formation of “dead lithium” – lithium metal deposits that are not able to be stripped [18]. This phenomenon can usually be observed to happen above a certain current

threshold, appropriately named critical current density (CCD). Therefore, CCD has been used widely as a metric to measure how resistant an electrolyte is to the effects of dendrites.

1.4.2 SSE Resistance to Dendrite Penetration

Monroe and Newman [19] proposed that the use of high shear modulus separator material, twice that of the shear modulus of the lithium anode, mechanically suppresses interfacial roughening. However, this criterion assumes that the separator is a polymer, and that no defect or imperfection is present. Although SSEs typically have much higher shear modulus than the lithium electrode, this criterion seems to be inapplicable to ceramic SSEs so far, which have been shown to develop lithium dendrites at far lower measured critical current than predicted by this criterion, mainly in presence of grain boundaries, defects, and impurities [20].

More recent findings have shown that Li dendrite can happen in SSE in a number of different scenarios [17] :

1. Inhomogeneous contact between electrolyte and electrode as shown in Figure 2, resulting in areas with localized currents higher than the critical current density [21].
2. Grain boundary propagation; propagation of dendrite through grain boundaries with higher local resistivity [22] and shear modulus lower than the overall SSE [23].
3. Nucleation of Li metal inside the SSE, mainly in nucleation points such as defects and pores, as opposed to dendritic growth from one electrode to the other [14].
4. Interphase formation when unstable electrolytes react with lithium metal [24].

In addition, Ning et al. have used computed X-ray tomography of lithium dendrite propagation in SSE to conclude that cracks in the SSE propagates ahead of the actual lithium dendrite growth [25].

Consequently, as can be inferred from the studies on lithium dendrite growth in SSE so far, well-sintered ceramics with higher density, less porosity and less cracking, are beneficial to suppress dendritic lithium penetration. Increasing crack resistance, both to transgranular and intergranular cracking, should also benefit dendrite growth resistance of SSE.

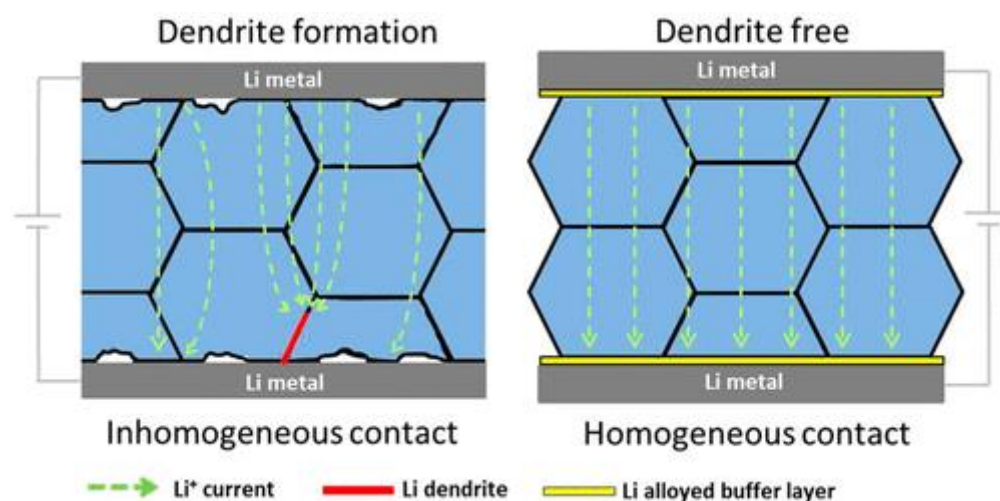


Figure 2. Illustration of inhomogeneous and homogeneous contact of SSE with Li metal electrodes. Inhomogeneous contact affects conduction path between electrodes, resulting in localized higher resistance. Reprinted with permission [21]. Copyright 2016, American Chemical Society.

1.5 Residual Stresses as a Crack Resistance Improvement Strategy

One method of improving the crack resistance of ceramics is by introducing residual stresses into the sintered body. In general, compressive residual stresses on the crack plane are known to inhibit crack growth in ceramics [26-28].

However, it is also crucial to consider the effects of stresses on the electrochemical properties of the resulting SSE structure, in addition to the mechanical effects. It should be intuitive that internal stresses in a crystalline solid might affect the overall bulk internal energy, which might then affect the structure and conduction activation energy of the solid. A recent publication used molecular dynamics simulation to predict that lithium diffusivity is indeed negatively affected by residual compression stress, nevertheless it was concluded that for SSE applications this effect is small enough that the introduction of compressive

stress into SSE, by means of ion implantation, to ameliorate dendrite formation should be attempted [29]. However, ion implantation is costly, and it is difficult to make sure that the implanted ions are in the correct locations while preserving the beneficial crystal structure of the material. A simpler method that introduces residual stresses in ceramics that this project proposes is via laminated ceramics.

1.5.1 Laminated Ceramics

Laminated ceramics have been shown to exhibit enhanced properties compared to their monolithic counterparts [30]. These laminate-structured ceramics were of interest as structural materials as they are shown to be less sensitive to surface defects and demonstrates non catastrophic failure owing to their internal residual stresses and microstructural features [30, 31]. The mechanisms by which these superior mechanical properties can be achieved in laminated ceramics are either:

1. crack deflection, along interface between layers [32-34] or through bifurcation [35];
2. by inhibition of crack propagation due to the biaxial compressive stress itself, resulting in counteracting forces preventing the widening of the crack tip (Figure 3) [36-38].

In a multi-layered laminated ceramic, crack deflection can play a significant role in preventing catastrophic failure. Weak interfaces between layers allows cracks to propagate perpendicular to the direction of the lamination, causing energy reduction by the delamination of the interface [32]. Bifurcation in the compressive stressed layers is also shown to deflect the propagation of cracks parallel to the direction of the lamination, increasing the overall toughness of the ceramic before failure [35].

A more recent study by Gee et al. observed improvement to the fracture toughness in a laminated $\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4$ - TiN system [36]. This study investigated the multiple mechanisms of toughness improvement as previously discussed but found that significant improvement to the fracture toughness of their sample was achieved by a design avoiding bifurcation and

delamination of adjacent layers. This finding was echoed by subsequent experiments with different materials system in our research group, where compressive stressed layer is shown to suppress crack without introducing delamination or bifurcation [37, 38].

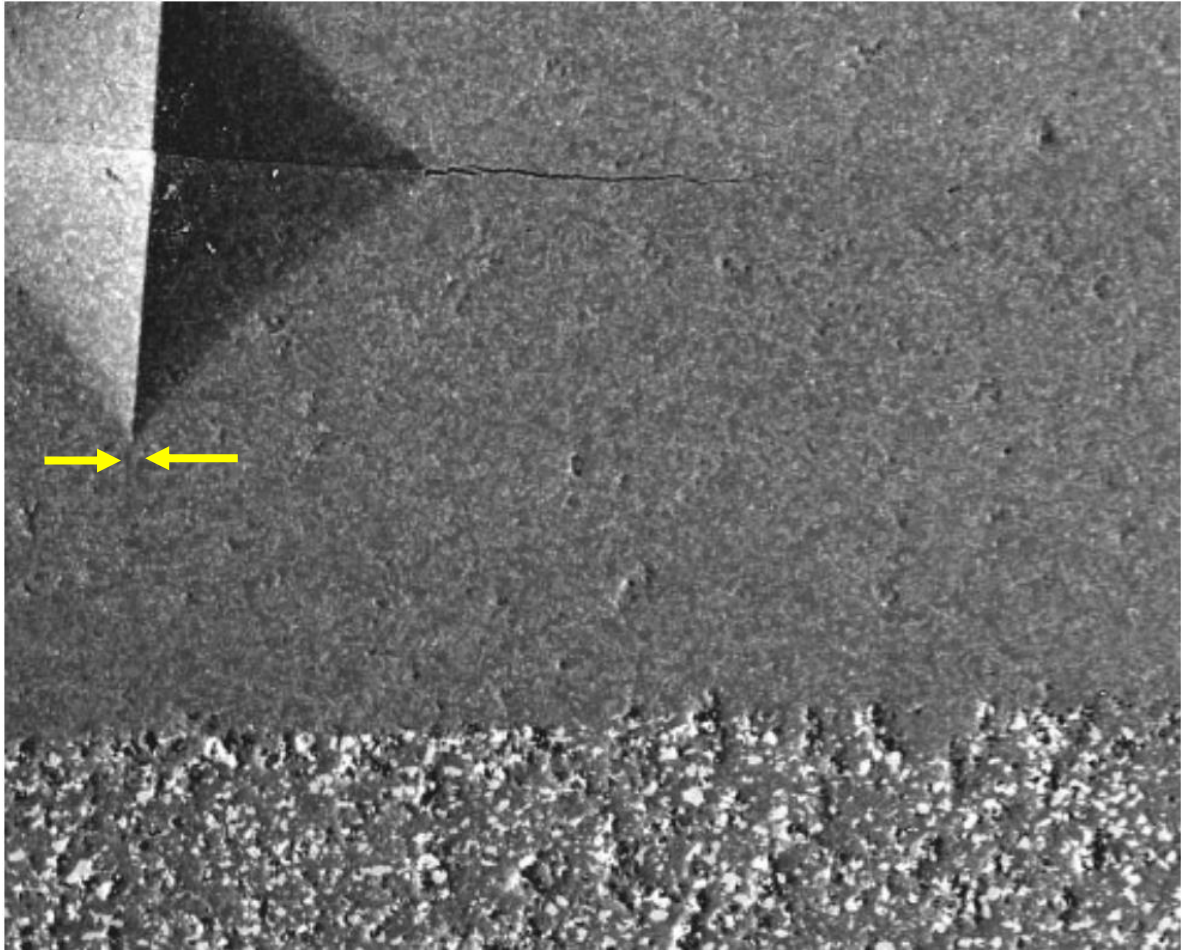


Figure 3 Vickers indentation shows anisotropic crack propagation in compressive layer. Arrows denoting residual biaxial compressive stress preventing crack propagation. Adapted from Gee et al. with permission [36].

1.5.2 Thermal Expansion Coefficient

In laminated ceramics, the difference of thermal expansion coefficient (CTE) between layers is utilized to introduce tensile and compressive stresses into the ceramic body [26, 38]. The CTE mismatch of the different layers means that as the sintered pellets cool down, the layer with the lower CTE will shrink less than the layer with higher CTE. As a result, in a bonded laminated structure, the different shrinkage rates will result in tensile stress in the

higher CTE layer, and compressive stress in the lower CTE layer. By designing a process in which the outer layers of the laminated ceramics are in compressive stress, it should be possible to improve the crack resistance of SSE, and consequentially suppress dendrite growth.

Therefore, careful study of the CTE of SSE candidates is necessary. For the laminate to be sufficiently strengthened, the thermal expansion difference must be substantial enough that the residual stresses are of significant magnitude, while not enough that the materials crack under the thermal stresses [32].

1.5.3 Fabrication Techniques of Laminated Ceramics

The fabrication of laminated ceramics can be done by stacking pellets/sheets of green body on top of another. These sheets/pellets of green body can be formed by tape casting, slip casting [33], cold isotactic pressing (CIP) [37], or hot pressing [38]. This layered green body can be co-sintered if the sintering temperatures of the different layers are in the same range, or pre-sintered layers then diffusion bonded if not. In addition, laminated ceramics can also be made either to be two-layered [38], multi-layered [31] or functionally graded [37]. Functionally graded ceramics are more complex to fabricate but benefit from more controlled lesser residual stress differences between adjacent layers, as well as more chances for crack deflection to occur [28, 37]. Symmetrically stacked laminates might also be preferable in case of SSE as the coupled forces prevents distortion of the laminate [32].

1.5.4 Tensile Cracking

Tensile stressed layers might be detrimental to the overall toughness of the laminate, as they are known to promote crack propagation in the form of channel cracking (Figure 4) [36]. Therefore, a design to minimize the tensile stress at the higher CTE layer is beneficial unless crack propagation in the tensile layer is preferred. This can be achieved by manipulating the thickness of the tensile layer, with stress being inversely proportional to the layer thickness up to a certain point [35, 36].

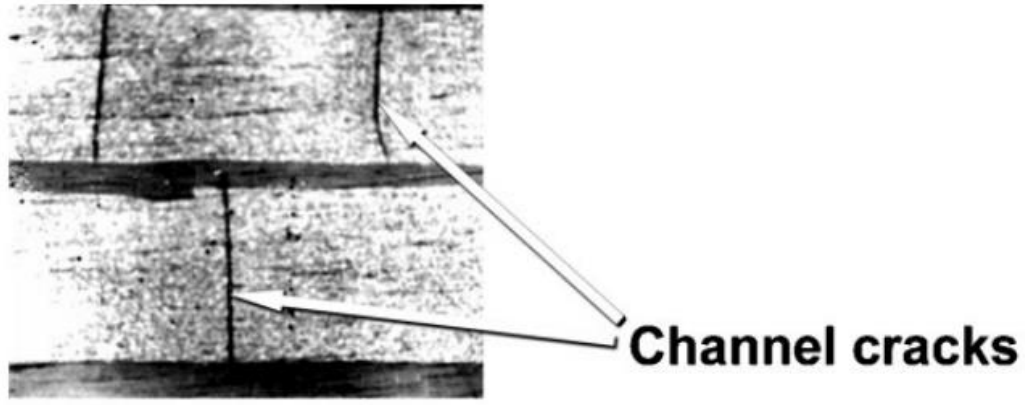


Figure 4 Channel cracks in the tensile stressed layers of a ceramic laminate. Lighter shaded layers are in tensile, while the darker shaded layers are compressive stressed. Adapted from Gee et al. [36] with permission.

1.5.5 Edge Considerations

Residual stresses present near the free surface at the edges of laminates are widely known to differ from the residual stresses in the bulk [28, 36]. Finite element analysis shows that stresses perpendicular to the layers exist near the free surface and become negligible rapidly as distance from the edge increases [36]. This antagonistic stress is known to be of opposite sign to that of the bulk in a compressive layer.

Without proper design and control of the free surface stresses, problems such as cracks and delamination can occur to the structural integrity of the laminate, both naturally and when removing the ceramic from a confining die if one is used.

1.6 Solid-State Electrolyte Classifications

SSE are solid materials that can conduct charge-carrying cations, such as Li^+ , by means of ion diffusion [39]. SSE can further be grouped into inorganic solid electrolytes, solid polymer electrolytes, and composite polymer electrolytes. For this project, we are mainly interested in inorganic lithium-ion solid electrolyte, as this class of SSE is known to have sufficiently high ionic conductivity ($> 10^{-4} \text{ S cm}^{-1}$), higher Young's modulus [40], and higher hardness compared with other classes of SSE.

Presently known inorganic solid electrolytes are either amorphous, semi-crystalline, or crystalline ceramics – which are mostly oxides, sulfides, or phosphate-based. Of these, oxides are generally easier to work with, as they are more stable in air compared to the sulfides. Oxide SSEs are generally classified based on their crystal structure:

1.6.1 Li-ion Conducting NASICON

The term NASICON (Na super ionic conductor) was coined for fast sodium-ion conducting solid electrolytes containing $\text{Na}[\text{Ge},\text{Si},\text{Ti},\text{Zr}]_2(\text{PO}_4)_3$ due to the compounds' superior sodium ion conduction [41, 42]. As an analogue to this, a Li-ion conducting counterpart with similar structure was developed and found to also have sufficiently high ionic conductivity, with some reports mentioning conductivity on the magnitude of $10^{-3} \text{ S cm}^{-1}$ at room temperature [43, 44]. In addition, Li-ion conducting NASICON such as $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) has been shown to be quite stable in air [45], and can even be stable in aqueous solution of LiCl [46]. This unique characteristic can be useful as a form of protection for other more sensitive electrolytes, as well as potentially applicable for aqueous lithium batteries [47].

Despite its promising properties, Li-ion conducting NASICON is not considered a good candidate for this project, due to the high anisotropy reported on the thermal expansion coefficient. This anisotropy was observed to have caused microcrack formation in sintered

specimens [48]. This factor is not suitable to induce residual stress in a laminated ceramic structure nor to produce a flaw-free ceramic.

1.6.2 LISICON

LISICON (Lithium Super Ionic Conductor) is a term coined in 1977 for lithium oxide-based ceramic with chemical formula $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ [49]. It is known that Li^+ ions have poor mobility in oxide-based ceramics due to the strong bond formed between Li-O. To address this, Hong et al. successfully synthesized an oxide-based ceramic in which interstitial Li ions in partially-filled-interstitial sites can diffuse more easily by bonding the network O anions with strong chemical bonding cations (Zn, Ge, and network Li), lowering the resistivity bottleneck of the entire matrix to lithium-ion mobility. The reported LISICON, was “the best Li^+ -ion conductor for the 300-400 °C range” [49], although at room temperature the reported ionic conductivity of only $10^{-6} \text{ S cm}^{-1}$ was not satisfactory [50]. Furthermore, this material is not stable against metallic lithium, restricting its usability [50].

1.6.3 Garnet

Garnet-like SSE is a class of oxide SSE generally with the formula $\text{Li}_x\text{M}_2\text{M}'_3\text{O}_{12}$, where Li substitutes the tetrahedral Si sites of the ideal garnet $\text{A}_3\text{B}_2(\text{SiO}_4)_3$. An example of such SSE is $\text{Li}_3\text{La}_3\text{Te}_2\text{O}_{12}$. Although $\text{Li}_3\text{La}_3\text{Te}_2\text{O}_{12}$ was shown to have low conductivity, it was quickly found that increasing the Li content tends to exponentially increase ionic conductivity [51].

At the moment, the most popular garnet-like SSEs are lithium-containing garnets with lithium, lanthanum, zirconium networks (LLZO). Different stoichiometric compositions of LLZOs have been successfully synthesized with varying degrees of ionic conductivity, some up to the order of $10^{-3} \text{ S cm}^{-1}$ [52]. This high ionic conductivity, in addition to the exceptional chemical and electrochemical stability, especially against metallic lithium [53], made LLZO the focus of multiple recent SSE research reports.

Since its first identification by Thangadurai et al. [54-56] many researchers have published works on garnet-type SSE. LLZO was first synthesized by Murugan et al. in 2007,

promising good stability with molten lithium and higher ionic conductivity ($3 \times 10^{-4} \text{ S cm}^{-1}$) [57] compared to previous generation compounds of the garnet-like SSE. Attempts afterwards have been focused on increasing the ionic conductivity of LLZO by different synthesis routes of powder [58, 59], tuning the stoichiometric composition [51, 52, 60-62], tweaking the sintering process [51, 63, 64] and optimizing the lattice parameter [62], relative density, and microstructure of sintered products [63, 65, 66].

Uncharacteristically for garnet-like materials, which usually favor cubic crystals, the thermodynamically favored phase of LLZO at room temperature is tetragonal garnet. This is problematic for the purpose of SSE, as the tetragonal phase of LLZO has inferior ionic conductivity compared to that of the high-temperature form cubic garnet LLZO, for which the transition temperature is reported to be in the 450K-1000K range [67]. Supervalent cation (i.e. Al^{3+} , Ga^{3+} , Ta^{5+} , etc.) dopants are found to have a stabilizing effect on cubic LLZO [61, 68], allowing the synthesis of cubic LLZO that is stable at room temperature for SSE application.

Theoretical and computational research on the mechanism of Li^+ ion conduction through bulk LLZO has also been proposed. Meier et al. calculated that coulombic mismatch forces between adjacent Li sites in the cubic phase of LLZO, which limits the available occupancy sites of Li, might have contributed to the superior ionic conductivity [69]. In addition, it was shown that the asynchronous conduction mechanism, which relies on the lithium site vacancies, in cubic LLZO requires lower activation energy [69].

1.6.3.1 Dopant effects

Geiger et al. determine that the difference in conductivity between cubic and tetragonal garnet LLZO is most likely caused by the different conduction path the 2 distinct structures provide for Li ion conduction. In their study, it was discussed that previously some different structure of similar or same composition of LLZO were reported, with significant effects to its respective conductivity. The study reports that possible inclusion of Al from alumina crucibles

used to calcine the LLZO might have resulted in the higher conductivity cubic structures [68]. The role of Al dopant in LLZO has been widely studied since then, with the consensus being that Al substitutes into the Li sites, promoting an increase in Li vacancies, which in turn is believed to promote cubic-garnet phase formation [61, 68, 70]. The stabilizing effect of Al dopant in LLZO is an effect of heterovalent substitution involving $\text{Al}^{3+} \Leftrightarrow 3\text{Li}^+$, which results in 2 lithium site vacancies. Similarly Ga^{3+} doping has also been observed to preferentially substitute the Li site in LLZO, stabilizing the cubic-garnet phase at room temperature [71].

Analogous to the stabilizing effect of Al dopant in LLZO, Ta doping also promotes an increase of Li site vacancy concentration which leads to energetic preference of the cubic phase. However, instead of substituting into the Li sites, Ta^{5+} has been observed to substitute into the Zr^{4+} site [70]. Substitution on this site is energetically preferred due to the higher oxidation charge of Ta^{5+} .

1.6.3.2 Thermal Expansion Coefficient

The thermal expansion coefficient of garnet-like LLZO has been studied by Hubaud et al. [72]. Intuitively, the composition of the SSE affects the thermal expansion coefficient of the sintered bulk, by changing the bond distance and bond strength of adjacent atoms. However, it was found that different amounts of Al dopant in LLZO have negligible effect on the thermal expansion coefficient as the Al substitution was predominantly in the Li sites, which does not affect the 3D structure. This 3D structure of garnet-like LLZO is primarily determined by the matrix of La.

A recent investigation into the CTE behavior of Al-LLZO outlines that there can be three distinct regions of displacement behavior for Al-LLZO: [30-200 °C], [200-500 °C], [500-1000 °C] during a thermal-displacement experiment, with the main difference between these 3 regions being a drop in CTE to 10^{-6} K^{-1} in the [200-500 °C] region. This was attributed to the formation of LaZr_2O_7 [48]. Regardless, the studies agree that LLZO has a linear expansion coefficient of the magnitude 10^{-5} K^{-1} , well above the range of typical garnet structures [72].

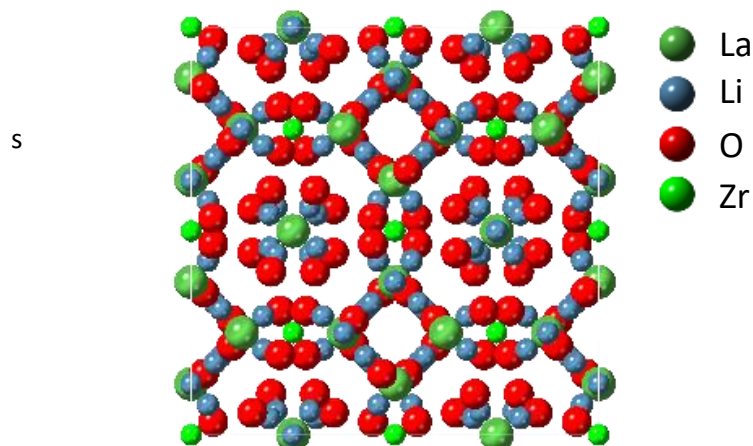


Figure 5 Cubic LLZO unit cell as seen from (100)

1.6.4 Perovskite

Perovskite type SSE is another class of potential inorganic SSE with high Li^+ ionic conductivity. A compound of this class of SSE, $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ (LLTO), has been known to achieve bulk ionic conductivity as high as $10^{-3} \text{ S cm}^{-1}$ at room temperature [73, 74]. However, the grain boundary conductivity of around $10^{-5} - 10^{-4} \text{ S cm}^{-1}$ as well as the low electrochemical stability of LLTO against metallic lithium makes its adoption as a SSE difficult [75].

Much work has been done to synthesize perovskite-type inorganic SSEs with the high bulk ionic conductivity of LLTO but with better boundary conductivity and electrochemical stability windows. One such proposed compound is in the form of $\text{LiSr}_{1.65}(\text{ })_{0.35}\text{B}_{1.3}\text{B}'_{1.7}\text{O}_9$, (where () = vacancy, $\text{B} = \text{Ti, Zr}$; $\text{B}' = \text{Nb, Ta}$), proposed in 1998 by Thangadurai et al. [76]. This composition is shown to offer better overall ionic conductivity and electrochemical stability, by optimizing the structure and lattice parameter, as well as stoichiometry control to allow for vacancy sites [76].

Another problem with LLTO that was also addressed was the low electrochemical stability due to the reduction of Ti^{4+} . $\text{LiSr}_{1.65}(\text{ })_{0.35}\text{Zr}_{1.3}\text{Ta}_{1.7}\text{O}_9$ was therefore proposed as an attractive material for use with metallic Li anode, as Zr(IV) and Ta(V) are less likely to be

reduced [76]. Following up from this proposal, Chen et al. successfully investigated the proposed lithium, tantalum doped strontium zirconate and concluded that the highest conductivity was achieved for $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Zr}_{3/4}\text{Ta}_{1/4}\text{O}_3$ (LSTZ), which was shown to have a total ionic conductivity in the magnitude of $10^{-4} \text{ S cm}^{-1}$, comparable to that of LLZO in general [75, 77]. The compositional effect of $\text{Li}_{2x-y}\text{Sr}_{1-x}\text{Ta}_y\text{Zr}_{1-y}\text{O}_3$ was further studied, with the maximum total conductivity achieved being $2.0 \times 10^{-4} \text{ S cm}^{-1}$ ($y = 0.75$) [75].

The crystal structure of perovskite type LSTZ, shown in Figure 6a, follows the simple perovskite crystal structure of ABO_3 , with Li, Sr, and vacancies on the A sites, while Ta and Zr occupy the B sites. In contrast to the tetragonal phase of LLTO, LSTZ is known to have a cubic perovskite structure, with the A-site ions and vacancies forming octahedral channels. The ion transport mechanism in perovskite type SSE is that of vacancy transport between an A-site ion to an adjacent A-site vacancy [78], with a potential bottle neck due to the presence of the oxygen ions. This bottleneck is dependent upon the lattice parameter [78].

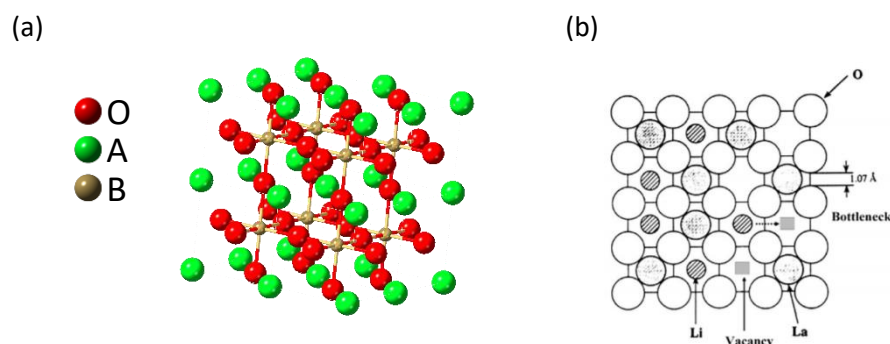


Figure 6a) Crystal structure of LSTZ; b) conduction mechanism of Li^+ ion through vacancy in LSTZ reproduced from [79]

Although many more variations of inorganic SSEs have been proposed, this project is interested in the electrolytes discussed, mainly due to their good stability against metallic lithium, ease of processing outside of glovebox, as well as promising high conductivity at room temperature.

1.7 Advances on Multilayered Solid Electrolytes

Recently, a report of multilayered solid electrolytes suggests that layering different SSEs can help dendrite suppression in the electrochemical cell [80]. In the aforementioned study, sulfide type $\text{Li}_{10}\text{Ge}_1\text{P}_2\text{S}_{12}$ (LGPS) was sandwiched between $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ (LPSCI) before being packed into a half-cell with electrode and anode, or a symmetric cell with 2 anodes. LPSCI was chosen as the outer layer, due to it having better stability against the lithium metal anode. The study concludes that the multilayered design provides better stability and prolongs the life cycle of the symmetric cell by suppressing dendrite penetration. It was proposed that the less electrochemically stable LGPS inner layer actually plays a role in suppressing dendrite penetration as it reacts with deposited lithium in the unstable layer [80].

It is worth noting that in their study, Ye et al. do not sinter/bond the different layers of SSE. Instead, the different layers of powders are compacted together via cold pressing. Significant pressure is therefore needed during the testing period of the multilayer design [80]. Regardless, seeing the success that the study has achieved, it serves as more proof that laminated ceramic SSE might have merit towards dendrite resistant SSE without introducing significant complication due to the extra interface between the layers.

1.8 Sintering

Sintering is a process where solid is compacted and densified without liquefaction [81]. This is most traditionally achieved by applying heat, in a process called “firing” for ceramics, to materials with high melting temperature. Sintering can also be accomplished by pressure, or a combination of heat and pressure in order to achieve the desired result.

Modern theories on the mechanism of sintering explains that sintering occurs due to diffusion caused by chemical potential gradient, driven by the removal of surface free energy from pores [81]. With this explanation, there are 2 different competing processes that can lead to equilibrium: densification and coarsening mechanisms such as grain growth. With densification, atoms diffuse from the grain boundary into the pores. On the other hand, in grain growth atoms are diffused from one grain into another bigger grain. Frequently, due to the growing size of the grain, pores get detached from their original location in the grain boundaries, and get embedded into the grain, making it harder for the diffusion necessary for densification to occur. As a result, ceramists generally dislike grain growth in sintering, as it inhibits sintered products from being fully densified [81].

1.8.1 Considerations for good densification

As densification is competitive with grain growth in sintering, it is crucial for the control of some factors, so that densification is kinetically preferred over grain growth. In solid-state sintering, as the green body is composed of powders, particle size and shape play an important role in controlling the density of sintered ceramics. A high concentration of elongated particles can result in irregularly shaped pores, which are significantly harder to remove during sintering. Finer particles are usually preferred, as they usually sinter more rapidly, due to the increased contact surface area between particles relative to volume and the small pores produced during compaction [81].

In addition to particle geometry control, sintering aids in the form of liquid-phase sintering and reactive liquid sintering can help densification dominate over grain growth. Good wetting from the viscous liquid allows rearrangement of particles, as well as serving as a good pathway for increased-rate material transfer [81]. These sintering mechanisms are commonly found in silicates but can be reproduced in other ceramics by the addition of sintering aids.

Another consideration to achieve high density ceramics is that of the heating rate of specimens. It was theorized that faster heating rate promotes mass transfer preferring densification over coarsening, and that there is an inverse behavior between grain size of sintered ceramics and their heating rate [82]. In addition, Ji et al. proposed that, even in some of the novel innovative sintering techniques as discussed below, the common factor in rapid sintering phenomena is the ultra-fast heating rate of the specimens [83]. This conclusion demonstrated different sintering techniques show similar acceleration of sintering rate as the heating rate was increased to an ultra-rapid rate, even without other external assistance. However, the authors of that study also rightly noted that accurate measurement of the specimen temperature is difficult, as temperatures of a solid body might be affected by conduction rate, and there might be thermal gradients throughout the bulk of the specimen itself [83]. Regardless, this paper does not discuss the mechanism of the rapid sintering behavior, and only investigated the effect that ultra-fast heating rate has on the sintering rate of ceramics.

1.8.2 Other Sintering Techniques

To encourage densification without promoting grain growth, many novel sintering techniques have been designed to favor one phenomenon over the other. Usually, the general wisdom is that by heating the green body fast enough, there is not enough time for grain growth by surface diffusion at lower temperature to occur before the sample has been fully densified [82]. Accordingly, two-step sintering techniques, in which samples were

treated at two distinct temperatures with a rapid constant-rate cooling, have been developed to successfully obtain fully dense ceramics [84-86]. Additionally, some innovative techniques also employ external forces, to achieve densification at temperatures lower than the grain growth temperature, such that grain growth cannot occur.

1.8.2.1 Reaction Sintering

As the name suggests, the mass transfer in reaction sintering is done by chemical reactions between the green body particles with an externally introduced component. A major advantage of reaction sintering is that reaction sintered ceramics do not undergo major shrinkage during densification [81]. This is mainly due to the densification occurring by means of introduction of new atoms into the sintered body, instead of mass transfer of existing atoms from bulk into pore.

Li et al. have reported a 90% dense cubic LLZO sintered with the assistance of 1 wt% CuO by solid state reactive sintering [87]. The study proposed that CuO assists the sintering process of cubic LLZO by decomposing LiOH, forming intermediary $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ phase [87]. In doing so, the 90% dense specimens can be achieved at a lower sintering temperature of 1100 °C, compared with the more widely used 1200 °C sintering temperature, allowing less lithium loss to occur due to sintering.

Avila et al. have also reported reactive sintering of LLZO from oxide precursors by flash sintering them together. The resulting specimen was only 86% dense with ionic conductivity no better than previously reported in the literature, but simplifies the synthesis steps by removing the need for calcination [88].

1.8.2.2 Hot Pressing

Hot Pressing (HP) is a sintering technique in which both heat and external pressure are applied simultaneously in order to promote solidification and densification of a green body. This applied pressure accelerates densification by supplementing mass diffusion forces and further improving the packing of particles, increasing the contact between particles [81]. At

the same time, the external pressure does not promote the kinetics of grain growth, due to the pressure being applied to the grain boundary serving as a much bigger driving force compared to that of grain boundary curvature [89]. For simple ceramics, hot pressing is usually done by putting a green body or powder inside a mold, to which uniaxial pressure is then applied.

An important consideration for a HP setup is the selection of material used for the die set. For higher sintering temperature above 1200 °C or even 2000 °C, graphites are usually the material of choice due to its ability to withstand the high temperature [90].

HP is reported to be able to achieve near 100% density LLZO, with reduced need for sintering aids [61, 81]. This might be beneficial for application in solid state electrolyte production, as the absence of sintering aids, even those that should be decomposed after sintering, meant that there is less risk for impurities that can alter the electrochemical property of the ceramics. The presence of external pressure allowing the reduction of sintering temperature might also benefits SSE sintering by reducing Li loss.

Luo et al. successfully sintered a 96.7% dense LSTZ pellet by hot pressing it in an argon atmosphere. The tested electrolyte was reported to achieve Li^+ total ionic conductivity of $4.1 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C, with small overpotential and high coulombic efficiency for 100 cycles [91].

1.8.2.3 Spark Plasma Sintering

Spark Plasma Sintering (SPS), interchangeably termed as Field-Assisted Sintering Technique (FAST), is a sintering technique similar to hot pressing, in which pressure is applied to the specimen during densification. What differentiates SPS is in the way that heat is applied, using low voltage DC current to promote Joule heating in conductive materials, or in conductive parts of the press [92]. Similar to that in HP, pressure applied in SPS helps break agglomerates and rearranges particles at low temperature, allowing for increased packing

and smaller pore sizes [92]. In addition, SPS benefits from the higher heating rate allowed by the Joule heating from the applied electric current.

However, a commonly cited problem in SPS is the uneven thermal gradient, where volumes in the plungers and die closer to the electrodes heat up faster than the rest of the bulk, which might introduce thermal stress and cracks in the specimen [92]. The interaction of the sample with the electric current is another phenomenon that might occur in SPS. As current flows through the specimen for conductive materials, fluctuating hot spots with high local current densities might form in the network, resulting in microstructure formation unique to SPS [92].

Despite its challenges, SPS has been used to sinter different types of SSE with varying degrees of success [93]. The main point of interest in using this method for SSE production is in its short processing time and lower furnace temperature, which is supposed to prevent lithium loss [63]. Zhang et al. successfully densified Al-doped garnet-type LLZO via SPS at 1150 °C [94]. The resulting pellets are measured to be 99.8% dense, denser than reported for conventionally sintered LLZO. Although XRD spectra of the resulting pellets after SPS shows the presence of $\text{La}_2\text{Zr}_2\text{O}_7$ and characteristic peaks belonging to tetragonal LLZO, the author also observed that a high ionic conductivity on the order of $\sim 3 \times 10^{-4} \text{ S cm}^{-1}$ is achieved, comparable to reports on the best phase pure cubic LLZO at the time, arguing that these impurities does not affect the ionic conductivity as much in SPS sintered samples compared to that prepared by conventional sintering [94]. Baek et al. also show that SPS sintering of Ta-doped LLZO yields highly dense pellets, which is difficult to achieve by conventional sintering of Ta-LLZO [52]. The resulting pellets, when assembled into ASSBs demonstrate superior ionic conductivity reaching $1.3 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, one of the highest reported.

SPS sintering of other types of SSE has been reported, with most of them reporting higher density and consequentially higher ionic conductivity compared to its conventionally sintered counterparts [52, 93-95].

1.8.2.4 Flash Sintering

Although a few similarly named techniques have been reported previously, the term Flash Sintering as currently used was coined by Cologna et al. [96], working with Professor Rishi Raj, as 'A method of sintering a material comprising simultaneously exposing the material to an electric field and to heat' [97].

At first, Cologna et al. proposed that the reason for the near instantaneous sintering is due to Joule heating at grain boundaries, whereby the higher resistance in the grain boundary gives rise to more power dissipation in the grain boundary, which in turn lowers the grain boundary resistance. However, it was also acknowledged that this explanation leaves two crucial unanswered questions, namely: 1. that Joule heating in the bulk of the grain might also give rise to similar instability, and 2. that the effect is only seen at higher fields [98].

Further investigation by Todd et al. [99] argued that the condition for Joule heating is achieved before the flash point. As such, there must be another factor that causes the flash event in flash sintering. It was proposed that although Joule heating plays a significant role in electricity-assisted sintering, the cause for the flash event is due to the exponential reduction of sample resistivity as specimen temperature increases [99]. This was proven by the almost coincidental occurrence of a peak in the electrical response readings with the flash event.

Recently, Clemenceau et al., published an attempt to flash sinter LLZO ceramic [100]. In this attempt, commercial Al-doped LLZO powder was pressed into a dog bone shaped green body with 2 holes on opposing sides for electrodes. The resulting specimen was then flash sintered at 850 °C furnace temperature. It was reported that the resulting specimen was $96.5\% \pm 1\%$ dense, relative to a theoretical density of 5.107 g cm^{-3} . In addition, the total

conductivity was measured to be $5 \times 10^{-4} \text{ S cm}^{-1}$ [100]. These values are well within the average reported for Al doped LLZO, signifying that this attempt does not really improve on the properties of Al LLZO so much as to provide a quicker sintering alternative to the typical 12 -50 h methods previously reported for high density specimens.

1.9 Summary and Aims of the Project

Solid-state electrolytes for all solid-state batteries are believed to be the way forward in the development of lithium-ion batteries with higher charge density and improved safety. The higher energy density is allowed by the ability of inorganic SSEs to resist dendrite growth as well as overall electrochemical stability when used with metallic lithium anodes. Further resistance to dendrite formation, by means of residual stress strengthening and defect minimization by sintering optimization will benefit the applicability and longer life cycle of ASSBs utilizing inorganic SSEs.

Novel sintering techniques, such as reactive sintering, hot pressing, spark plasma sintering, and flash sintering have been shown to improve sintered body density, resulting in higher conductivity and theoretically better resistance to lithium dendrite formation. Computational modelling proves to be foundational to the possibility of laminated ceramic SSEs, as it was calculated that the residual stresses needed to strengthen the laminated ceramic do not significantly degrade the ionic conductivity and might be beneficial to the dendrite resistance of SSE. A recent publication on unsintered multi-layered sulfide SSE has shown that interfaces between the different layers of SSE can be stable and do not necessarily detract from the overall ionic conductivity of the electrolyte and might also offer higher resistance to dendrite penetration due to the different electrochemical stability of constituent layers' material with lithium dendrite.

Therefore, this thesis aims to prove that laminated ceramics, a well-studied ceramists' technique that strengthens inorganic ceramics, might lead to improvement in inorganic SSE

processing. It is hypothesized that the compressive surface stresses caused by CTE differences in the layers of the laminates will result in increased resistance to Li dendrite propagation through the SSE. To do so, it must be proven that laminates of SSEs can be sintered without delamination and cracking, and that the laminates can still maintain a sufficiently high ionic conductivity. If successful, this proof of concept might allow future opportunities to study the mechanical behavior of SSEs.

1.10 References

1. Liu, H. and J. Jiang, *Flywheel energy storage—An upswing technology for energy sustainability*. Energy and Buildings, 2007. **39**(5): p. 599-604.
2. Chaturvedi, D.K., S. Yadav, . . . T. Kumari. *Electricity storage system: A Gravity Battery*. in *2020 Fourth World Conference on Smart Trends in Systems, Security and Sustainability (WorldS4)*. 2020.
3. Schmidt-Rohr, K., *How Batteries Store and Release Energy: Explaining Basic Electrochemistry*. Journal of Chemical Education, 2018. **95**(10): p. 1801-1810.
4. Goodenough, J.B., *Rechargeable batteries: challenges old and new*. Journal of Solid State Electrochemistry, 2012. **16**(6): p. 2019-2029.
5. Yoshino, A., K. Sanekika, and T. Nakajima, *Secondary Battery*, U.S. Patent, Editor. 1987.
6. Mizushima, K., P.C. Jones, . . . J.B. Goodenough, *LixCoO₂ (0<x<-1): A new cathode material for batteries of high energy density*. Materials Research Bulletin, 1980. **15**(6): p. 783-789.
7. Placek, M., *Projected battery demand worldwide by application 2020-2030*. 2021: Statista.
8. Nishi, Y., *Lithium ion secondary batteries; past 10 years and the future*. Journal of Power Sources, 2001. **100**(1): p. 101-106.
9. Busche, M.R., M. Weiss, . . . J. Janek, *The Formation of the Solid/Liquid Electrolyte Interphase (SLEI) on NASICON-Type Glass Ceramics and LiPON*. Advanced Materials Interfaces, 2020. **7**(19): p. 2000380.
10. Sun, Y.-K., *Promising All-Solid-State Batteries for Future Electric Vehicles*. ACS Energy Letters, 2020. **5**(10): p. 3221-3223.
11. Vandervell, A. *What is a solid-state battery? The benefits explained*. 2017 [cited 2021 5 May]; Available from: <https://www.wired.co.uk/article/what-is-solid-state-battery-toyota-dyson>.
12. Power, S. *Solid Power's High Energy, Automotive-Scale All Solid-State Batteries Surpass Commercial Lithium-Ion Energy Densities*. 2021 [cited 2021 5 May]; Available from: <https://www.prnewswire.com/news-releases/solid-powers-high-energy-automotive-scale-all-solid-state-batteries-surpass-commercial-lithium-ion-energy-densities-301190450.html>.
13. Fletcher, S. *Secretive Company Claims Battery Breakthrough*. 2014 [cited 2021 05 May 2021]; Available from: <https://www.scientificamerican.com/article/secretive-company-claims-battery-breakthrough/>.
14. Aguesse, F., W. Manalastas, . . . J. Kilner, *Investigating the Dendritic Growth during Full Cell Cycling of Garnet Electrolyte in Direct Contact with Li Metal*. ACS Applied Materials & Interfaces, 2017. **9**(4): p. 3808-3816.
15. Liu, T., J. Zheng, . . . X. Tao, *In-situ construction of a Mg-modified interface to guide uniform lithium deposition for stable all-solid-state batteries*. Journal of Energy Chemistry, 2021. **55**: p. 272-278.
16. Sun, M., T. Liu, . . . J. Lu, *Visualizing Lithium Dendrite Formation within Solid-State Electrolytes*. ACS Energy Letters, 2021. **6**(2): p. 451-458.
17. Cao, D., X. Sun, . . . H. Zhu, *Lithium Dendrite in All-Solid-State Batteries: Growth Mechanisms, Suppression Strategies, and Characterizations*. Matter, 2020. **3**(1): p. 57-94.
18. Kazyak, E., R. Garcia-Mendez, . . . N.P. Dasgupta, *Li Penetration in Ceramic Solid Electrolytes: Operando Microscopy Analysis of Morphology, Propagation, and Reversibility*. Matter, 2020. **2**(4): p. 1025-1048.

19. Monroe, C. and J. Newman, *The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces*. Journal of The Electrochemical Society, 2005. **152**: p. A396-A404.
20. Liu, H., X.-B. Cheng, . . . Q. Zhang, *Controlling Dendrite Growth in Solid-State Electrolytes*. ACS Energy Letters, 2020. **5**(3): p. 833-843.
21. Tsai, C.-L., V. Roddatis, . . . O. Guillon, *Li₇La₃Zr₂O₁₂ Interface Modification for Li Dendrite Prevention*. ACS Applied Materials & Interfaces, 2016. **8**(16): p. 10617-10626.
22. Yu, S. and D.J. Siegel, *Grain Boundary Contributions to Li-Ion Transport in the Solid Electrolyte Li₇La₃Zr₂O₁₂ (LLZO)*. Chemistry of Materials, 2017. **29**(22): p. 9639-9647.
23. Yu, S. and D.J. Siegel, *Grain Boundary Softening: A Potential Mechanism for Lithium Metal Penetration through Stiff Solid Electrolytes*. ACS Applied Materials & Interfaces, 2018. **10**(44): p. 38151-38158.
24. Wang, S., H. Xu, . . . A. Manthiram, *Interfacial Chemistry in Solid-State Batteries: Formation of Interphase and Its Consequences*. Journal of the American Chemical Society, 2018. **140**(1): p. 250-257.
25. Ning, Z., D.S. Jolly, . . . P.G. Bruce, *Visualizing plating-induced cracking in lithium-anode solid-electrolyte cells*. Nature Materials, 2021. **20**(8): p. 1121-1129.
26. Kuo, D.-H. and W.M. Kriven, *A Strong and Damage-Tolerant Oxide Laminate*. Journal of the American Ceramic Society, 1997. **80**(9): p. 2421-2424.
27. Zhang, X., P. Zhou, . . . W. Han, *Toughening of laminated ZrB₂-SiC ceramics with residual surface compression*. Journal of the European Ceramic Society, 2011. **31**(13): p. 2415-2423.
28. Dancer, C.E.J., M. Achintha, . . . R.I. Todd, *Residual stress distribution in a functionally graded alumina-silicon carbide material*. Scripta Materialia, 2012. **67**(3): p. 281-284.
29. Qi, Y., C. Ban, and S.J. Harris, *A New General Paradigm for Understanding and Preventing Li Metal Penetration through Solid Electrolytes*. Joule, 2020. **4**(12): p. 2599-2608.
30. Bermejo, R., R. Daniel, . . . C. Mitterer, *Hierarchical architectures to enhance structural and functional properties of brittle materials*. Advanced Engineering Materials, 2017. **19**(4): p. 1600683.
31. Bermejo, R., J. Pascual, . . . R. Danzer, *Optimal strength and toughness of Al₂O₃-ZrO₂ laminates designed with external or internal compressive layers*. Journal of the European Ceramic Society, 2008. **28**(8): p. 1575-1583.
32. Kuo, D.-H. and W.M. Kriven, *A Strong and Damage-Tolerant Oxide Laminate*. Journal of the American Ceramic Society, 2005. **80**: p. 2421-2424.
33. Clegg, W.J., K. Kendall, . . . J.D. Birchall, *A simple way to make tough ceramics*. Nature, 1990. **347**(6292): p. 455-457.
34. Bermejo, R., *"Toward seashells under stress": Bioinspired concepts to design tough layered ceramic composites*. Journal of the European Ceramic Society, 2017. **37**(13): p. 3823-3839.
35. Gogotsi, G.A., N.I. Lugovoi, and V.N. Slyunyaev, *Bifurcation of Cracks in Laminated Ceramic Composites with Rigid Interlaminar Bonds*. Strength of Materials, 2003. **35**(3): p. 248-259.
36. Gee, I.A., R.S. Dohedoe, . . . J. Kuebler, *Enhanced fracture toughness by ceramic laminate design*. Advances in Applied Ceramics, 2005. **104**(3): p. 103-109.
37. Xu, C. and R.I. Todd, *Functionally graded ceramics by a new in situ processing route: Residual stress and wear resistance*. Journal of the European Ceramic Society, 2015. **35**(9): p. 2693-2698.

38. Dancer, C.E.J., N.A. Yahya, . . . G. de Portu, *Effect of residual compressive surface stress on severe wear of alumina–silicon carbide two-layered composites*. Tribology International, 2014. **74**: p. 87-92.
39. Bachman, J.C., S. Muy, . . . Y. Shao-Horn, *Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction*. Chemical Reviews, 2016. **116**(1): p. 140-162.
40. Zhao, Q., S. Stalin, . . . L.A. Archer, *Designing solid-state electrolytes for safe, energy-dense batteries*. Nature Reviews Materials, 2020. **5**(3): p. 229-252.
41. Hong, H.Y.P., *Crystal structures and crystal chemistry in the system $\text{Na}_{1+x}\text{Zr}_2\text{SixP}_{3-x}\text{O}_{12}$* . Materials Research Bulletin, 1976. **11**(2): p. 173-182.
42. Kimpa, M., M. Mayzan, . . . M. Agam. *Review on material synthesis and characterization of sodium (Na) super-ionic conductor (NASICON)*. in *IOP Conference Series: Earth and Environmental Science*. 2018. IOP Publishing.
43. Aono, H., E. Sugimoto, . . . G.y. Adachi, *Ionic conductivity of solid electrolytes based on lithium titanium phosphate*. Journal of the electrochemical society, 1990. **137**(4): p. 1023.
44. Waetzig, K., A. Rost, . . . J. Schilm, *Synthesis and sintering of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) electrolyte for ceramics with improved Li^+ conductivity*. Journal of Alloys and Compounds, 2020. **818**: p. 153237.
45. Xuefu, S., H. Nemori, . . . N. Imanishi, *High Lithium-Ion-Conducting NASICON-Type $\text{Li}_{1+x}\text{Al}_x\text{Ge}_y\text{Ti}_{2-x-y}(\text{PO}_4)_3$ Solid Electrolyte*. Frontiers in Energy Research, 2016. **4**.
46. Shimonishi, Y., T. Zhang, . . . N. Sammes, *A study on lithium/air secondary batteries—Stability of the NASICON-type lithium ion conducting solid electrolyte in alkaline aqueous solutions*. Journal of Power Sources, 2011. **196**(11): p. 5128-5132.
47. Zhang, T., N. Imanishi, . . . N. Sammes, *A novel high energy density rechargeable lithium/air battery*. Chemical Communications, 2010. **46**(10): p. 1661-1663.
48. Bertrand, M., S. Rousselot, . . . M. Dollé, *Compatibility assessment of solid ceramic electrolytes and active materials based on thermal dilatation for the development of solid-state batteries*. Materials Advances, 2021. **2**(9): p. 2989-2999.
49. Hong, H.Y.P., *Crystal structure and ionic conductivity of $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ and other new Li^+ superionic conductors*. Materials Research Bulletin, 1978. **13**(2): p. 117-124.
50. Alpen, U.v., M.F. Bell, . . . G.J. Dudley, *Ionic conductivity of $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (Lisicon)*. Electrochimica Acta, 1978. **23**(12): p. 1395-1397.
51. Wang, C., K. Fu, . . . L. Hu, *Garnet-Type Solid-State Electrolytes: Materials, Interfaces, and Batteries*. Chemical Reviews, 2020. **120**(10): p. 4257-4300.
52. Baek, S.-W., J.-M. Lee, . . . Y. Park, *Garnet related lithium ion conductor processed by spark plasma sintering for all solid state batteries*. Journal of Power Sources, 2014. **249**: p. 197-206.
53. Zhao, N., W. Khokhar, . . . C.-W. Nan, *Solid Garnet Batteries*. Joule, 2019. **3**(5): p. 1190-1199.
54. Thangadurai, V., H. Kaack, and W.J.F. Weppner, *Novel Fast Lithium Ion Conduction in Garnet-Type $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$)*. Journal of the American Ceramic Society, 2003. **86**(3): p. 437-440.
55. Thangadurai, V. and W. Weppner, *$\text{Li}_6\text{Ala}_2\text{Ta}_2\text{O}_{12}$ ($\text{A} = \text{Sr}, \text{Ba}$): Novel Garnet-Like Oxides for Fast Lithium Ion Conduction*. Advanced Functional Materials, 2005. **15**(1): p. 107-112.
56. Thangadurai, V. and W. Weppner, *$\text{Li}_6\text{Ala}_2\text{Nb}_2\text{O}_{12}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$): A New Class of Fast Lithium Ion Conductors with Garnet-Like Structure*. Journal of the American Ceramic Society, 2005. **88**(2): p. 411-418.
57. Murugan, R., V. Thangadurai, and W. Weppner, *Fast Lithium Ion Conduction in Garnet-Type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$* . Angewandte Chemie International Edition, 2007. **46**(41): p. 7778-7781.

58. Zheng, D., J. Zhang, . . . J. Yang, *Synthesis and characterization of Li₇La₃Zr₂O₁₂ via a novel solid-liquid route*. Solid State Ionics, 2020. **345**: p. 115179.
59. Janani, N., S. Ramakumar, . . . R. Murugan, *Synthesis of cubic Li₇La₃Zr₂O₁₂ by modified sol–gel process*. Ionics, 2011. **17**(7): p. 575.
60. Thangadurai, V., S. Narayanan, and D. Pinzaru, *Garnet-type solid-state fast Li ion conductors for Li batteries: critical review*. Chemical Society Reviews, 2014. **43**(13): p. 4714-4727.
61. Han, G., B. Kinzer, . . . J. Sakamoto, *Correlating the effect of dopant type (Al, Ga, Ta) on the mechanical and electrical properties of hot-pressed Li-garnet electrolyte*. Journal of the European Ceramic Society, 2020. **40**(5): p. 1999-2006.
62. Mishra, M., C.-W. Hsu, . . . J.-K. Chang, *Ga-doped lithium lanthanum zirconium oxide electrolyte for solid-state Li batteries*. Electrochimica Acta, 2020. **353**: p. 136536.
63. Xue, J., K. Zhang, . . . B. Luo, *Spark plasma sintering plus heat-treatment of Ta-doped Li₇La₃Zr₂O₁₂ solid electrolyte and its ionic conductivity*. Materials Research Express, 2020. **7**(2): p. 025518.
64. Yang, L., Q. Dai, . . . X. Wang, *Rapid sintering method for highly conductive Li₇La₃Zr₂O₁₂ ceramic electrolyte*. Ceramics International, 2020. **46**(8, Part A): p. 10917-10924.
65. Uddin, M.-J. and S.-J. Cho, *Reassessing the bulk ionic conductivity of solid-state electrolytes*. Sustainable Energy & Fuels, 2018. **2**(7): p. 1458-1462.
66. Sharafi, A., C.G. Haslam, . . . J. Sakamoto, *Controlling and correlating the effect of grain size with the mechanical and electrochemical properties of Li₇La₃Zr₂O₁₂ solid-state electrolyte*. Journal of Materials Chemistry A, 2017. **5**(40): p. 21491-21504.
67. Raju, M.M., F. Altayran, . . . Q. Zhang, *Crystal Structure and Preparation of Li₇La₃Zr₂O₁₂ (LLZO) Solid-State Electrolyte and Doping Impacts on the Conductivity: An Overview*. Electrochem, 2021. **2**(3): p. 390-414.
68. Geiger, C.A., E. Alekseev, . . . W. Weppner, *Crystal Chemistry and Stability of “Li₇La₃Zr₂O₁₂” Garnet: A Fast Lithium-Ion Conductor*. Inorganic Chemistry, 2011. **50**(3): p. 1089-1097.
69. Meier, K., T. Laino, and A. Curioni, *Solid-State Electrolytes: Revealing the Mechanisms of Li-Ion Conduction in Tetragonal and Cubic LLZO by First-Principles Calculations*. The Journal of Physical Chemistry C, 2014. **118**(13): p. 6668-6679.
70. Shin, D.O., K. Oh, . . . K. Kang, *Synergistic multi-doping effects on the Li₇La₃Zr₂O₁₂ solid electrolyte for fast lithium ion conduction*. Scientific Reports, 2015. **5**(1): p. 18053.
71. Rettenwander, D., J. Langer, . . . G. Amthauer, *Site Occupation of Ga and Al in Stabilized Cubic Li_{7-3(x+y)}Ga_xAl_yLa₃Zr₂O₁₂ Garnets As Deduced from ²⁷Al and ⁷¹Ga MAS NMR at Ultrahigh Magnetic Fields*. Chemistry of Materials, 2015. **27**(8): p. 3135-3142.
72. Hubaud, A.A., D.J. Schroeder, . . . J.T. Vaughey, *Thermal expansion in the garnet-type solid electrolyte (Li_{7-x}Al_x/3)La₃Zr₂O₁₂ as a function of Al content*. Journal of Alloys and Compounds, 2015. **644**: p. 804-807.
73. Inaguma, Y., C. Liqun, . . . M. Wakihara, *High ionic conductivity in lithium lanthanum titanate*. Solid State Communications, 1993. **86**(10): p. 689-693.
74. Inaguma, Y. and M. Nakashima, *A rechargeable lithium–air battery using a lithium ion-conducting lanthanum lithium titanate ceramics as an electrolyte separator*. Journal of Power Sources, 2013. **228**: p. 250-255.
75. Inada, R., K. Kimura, . . . Y. Sakurai, *Synthesis and lithium-ion conductivity for perovskite-type Li_{3/8}Sr_{7/16}Ta_{3/4}Zr_{1/4}O₃ solid electrolyte by powder-bed sintering*. Solid State Ionics, 2014. **261**: p. 95-99.

76. Thangadurai, V., A.K. Shukla, and J. Gopalakrishnan, *LiSr_{1.650.35}B_{1.3B 1.709} (B = Ti, Zr; B = Nb, Ta): New Lithium Ion Conductors Based on the Perovskite Structur....* Chemistry of Materials, 1999. **11**: p. 835-839.
77. Chen, C.H., S. Xie, . . . K. Amine, *Stable lithium-ion conducting perovskite lithium–strontium–tantalum–zirconium–oxide system*. Solid State Ionics, 2004. **167**(3): p. 263-272.
78. Lu, J. and Y. Li, *Perovskite-type Li-ion solid electrolytes: a review*. Journal of Materials Science: Materials in Electronics, 2021. **32**(8): p. 9736-9754.
79. Stramare, S., V. Thangadurai, and W. Weppner, *Lithium Lanthanum Titanates: A Review*. Chemistry of Materials, 2003. **15**(21): p. 3974-3990.
80. Ye, L. and X. Li, *A dynamic stability design strategy for lithium metal solid state batteries*. Nature, 2021. **593**(7858): p. 218-222.
81. Richerson, D.W., *Modern ceramic engineering : properties, processing, and use in design*. Manufacturing engineering and materials processing ; 8. 1982, New York: Dekker.
82. Stanciu, L.A., V.Y. Kodash, and J.R. Groza, *Effects of heating rate on densification and grain growth during field-assisted sintering of α -Al₂O₃ and MoSi₂ powders*. Metallurgical and Materials Transactions A, 2001. **32**(10): p. 2633-2638.
83. Ji, W., B. Parker, . . . R.I. Todd, *Ultra-fast firing: Effect of heating rate on sintering of 3YSZ, with and without an electric field*. Journal of the European Ceramic Society, 2017. **37**(6): p. 2547-2551.
84. Lóh, N.J., L. Simão, . . . O.R.K. Montedo, *A review of two-step sintering for ceramics*. Ceramics International, 2016. **42**(11): p. 12556-12572.
85. Chu, M.-Y., L.C. De Jonghe, . . . F.J.T. Lin, *Precoarsening to Improve Microstructure and Sintering of Powder Compacts*. Journal of the American Ceramic Society, 1991. **74**(11): p. 2902-2911.
86. Chen, I.W. and X.H. Wang, *Sintering dense nanocrystalline ceramics without final-stage grain growth*. Nature, 2000. **404**(6774): p. 168-171.
87. Li, C., A. Ishii, . . . K. Brinkman, *Solid-state reactive sintering of dense and highly conductive Ta-doped Li₇La₃Zr₂O₁₂ using CuO as a sintering aid*. Journal of Materials Science, 2020. **55**(35): p. 16470-16481.
88. Avila, V. and R. Raj, *Reactive flash sintering of powders of four constituents into a single phase of a complex oxide in a few seconds below 700°C*. Journal of the American Ceramic Society, 2019. **102**(11): p. 6443-6448.
89. Chiang, Y.-M., D.P. Birnie, and W.D. Kingery, *Physical ceramics : principles for ceramics science and engineering*. 1997, New York; Chichester: Wiley.
90. Kingery, W.D., H.K. Bowen, and D.R. Uhlmann, *Introduction to ceramics*. 1976, New York: Wiley.
91. Luo, J., S. Zhong, . . . C.-A. Wang, *High Li⁺-conductive perovskite Li₃/8Sr_{7/16}Ta₃/4Zr_{1/4}O₃ electrolyte prepared by hot-pressing for all-solid-state Li-ion batteries*. Solid State Ionics, 2019. **338**: p. 1-4.
92. Guillon, O., J. Gonzalez-Julian, . . . M. Herrmann, *Field-Assisted Sintering Technology/Spark Plasma Sintering: Mechanisms, Materials, and Technology Developments*. Advanced Engineering Materials, 2014. **16**(7): p. 830-849.
93. Zhu, H. and J. Liu, *Emerging applications of spark plasma sintering in all solid-state lithium-ion batteries and beyond*. Journal of Power Sources, 2018. **391**: p. 10-25.
94. Zhang, Y., F. Chen, . . . L. Zhang, *Field assisted sintering of dense Al-substituted cubic phase Li₇La₃Zr₂O₁₂ solid electrolytes*. Journal of Power Sources, 2014. **268**: p. 960-964.
95. Duluard, S., A. Paillassa, . . . F. Ansart, *Lithium conducting solid electrolyte Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ obtained via solution chemistry*. Journal of the European Ceramic Society, 2013. **33**(6): p. 1145-1153.

96. Yu, M., S. Grasso, . . . M.J. Reece, *Review of flash sintering: materials, mechanisms and modelling*. Advances in Applied Ceramics, 2017. **116**(1): p. 24-60.
97. Rishi Raj, M.C., Andre Luiz Geromel Prette, Vincenzo M. Sglavo, John Francis, *Methods of flash sintering*. 2012: United State.
98. Cologna, M., B. Rashkova, and R. Raj, *Flash Sintering of Nanograin Zirconia in <5 s at 850°C*. Journal of the American Ceramic Society, 2010. **93**(11): p. 3556-3559.
99. Todd, R.I., E. Zapata-Solvas, . . . P.R. Wilshaw, *Electrical characteristics of flash sintering: thermal runaway of Joule heating*. Journal of the European Ceramic Society, 2015. **35**(6): p. 1865-1877.
100. Clemenceau, T., N. Andriamady, . . . R. Raj, *Flash sintering of Li-ion conducting ceramic in a few seconds at 850 °C*. Scripta Materialia, 2019. **172**: p. 1-5.

Chapter 2 Powder Synthesis

2.1 Objective

Powder sintering is a common method of oxide pellet manufacturing. To ensure optimal densification, it is essential to obtain the best possible powders to ensure good quality pellets.

Owing to the interest in LLZO as a potential solid-state electrolyte, in recent years commercially made LLZO powders have become available to purchase. However, this project seeks to also synthesize the LLZO powders from their precursors to ensure greater control composition-wise.

On the other hand, LSTZ commercial powder is not available, therefore understanding the synthesis steps of LSTZ powder is a crucial part of this research.

The goal of the powder synthesis was to achieve phase pure, fine-sized powders that will result in good densification to produce ionically conductive pellets.

2.2 Experimental methods

2.2.1 Synthesis of $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Zr}_{1/4}\text{O}_3$ Powders.

A solid-state synthesis method for LSTZ was followed [1]. Stoichiometric amounts of precursor powders: lithium carbonate ($\geq 99.0\%$, Sigma-Aldrich), strontium carbonate ($\geq 99.9\%$, Aldrich), tantalum (V) oxide (99.85% , Alfa-Aesar), and zirconium (IV) oxide (99% , Aldrich); were put together in a zirconia lined attrition mill vessel (Szegvari 01HD attrition mill). An additional 10% excess by weight of lithium carbonate was then added to account for potential lithium loss throughout the process. A set amount of 3 mm diameter yttria-stabilized zirconia balls was added to approximately 50% of the height of the vessel, and appropriate amount of isopropanol (IPA) to around the ball line. 20 g per batch of precursor

powders were attrition milled for 6 h and then dried in a rotary evaporator. The dried powder was sieved through a 150 μm sieve, and then calcined in a lidded alumina crucible at 1200 $^{\circ}\text{C}$ for 6 h with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ under air atmosphere. A 250mm polypropylene bottle was then filled with the calcined powder, 5 mm diameter yttria-stabilized zirconia balls, and around 100 ml of IPA. The bottle was purged with argon gas to replace the oxygen before being ball milled for 24 h. The resulting slurry was dried again in a rotary evaporator, after which the resulting powder was passed through the 150 μm sieve.

2.2.2 Synthesis of Garnet Type Powder

Picking up from a previous work by William Connolly, a Part II student in the group [2], a solid state synthesis route for aluminum or tantalum doped LLZO [3] with the compositions $\text{Li}_{6.25}\text{La}_3\text{Al}_{0.25}\text{Zr}_2\text{O}_{12}$ (Al-LLZO) and $\text{Li}_{6.50}\text{La}_3\text{Ta}_{0.50}\text{Zr}_{1.5}\text{O}_{12}$ (Ta-LLZO) respectively, was followed due to the reported high conductivity of sintered pellets and ease of processing. Lanthanum (III) oxide (99.9%, Alfa-Aesar), lithium carbonate ($\geq 99.0\%$, Sigma-Aldrich), zirconium (IV) oxide (99%, Aldrich), tantalum (V) oxide (99.85%, Alfa-Aesar), aluminum oxide (99%, Sigma-Aldrich) were used as precursor powders. Additionally, 10%, 12.5%, or 15% by mass of excess lithium carbonate was added to investigate the optimal Li excess necessary to counteract lithium loss.

Similar solid-state processes to that of the LSTZ powder synthesis were followed, with the only difference being the calcining regime of 1000 $^{\circ}\text{C}$ for 4 h with a heating rate of 5 $^{\circ}\text{C}/\text{min}$ instead of the higher temperature longer calcination for LSTZ.

2.2.3 Characterizations

Gas evolution during calcination of LSTZ were monitored by TGA measurement throughout the calcination temperature range. This measurement was necessary to determine the optimal calcination, and eventually sintering temperature range, by means of compound stability. Dried, ball-milled powder of mixed precursors was placed inside an alumina crucible. Measurements were done in a TGA chamber on an alumina stage with

argon atmosphere, using a heating rate of 10 °C/min. TGA measurement of the more widely studied LLZO has been conducted previously by the part II student in our lab [2] using the same methodology, so to avoid redundancy this study continued based on the part II's result.

X-ray diffraction (XRD; Rigaku Miniflex) with Cu K α radiation in an argon glovebox was used to determine the crystalline phases in the as-calcined powders, scanning over the 10 - 80° 2 θ range to identify characteristic peaks of crystalline phases. XRD analysis software (Highscore+, Malvern Panalytical) was used in conjunction with an appropriate diffraction peak database to process the resulting spectra and identify phases by peak fitting. A measurement of the blank sample holder with identical measurement conditions was also taken to account for holder peaks.

To ensure optimal densification, particle size is of importance. Laser diffraction (LD) particle size analysis (LA960, Horiba) measurement was performed to observe the statistical particle size distribution of respective calcined powders. Measurements were done in ethanol solvent, with powders pre-dispersed in ethanol and ultrasonicated for 1 min to break agglomerates. An estimated refractive index value of 1.4 was used, following prior publication [4].

Electron micrographs of the powders were taken using FESEM (field emission scanning electron microscope, Merlin, Zeiss). Powders were dispersed in IPA, ultrasonicated, then dropped using a pipette onto carbon felts on 9mm SEM stubs. The stubs were then left to dry for at least 24 hours. The powders were then carbon coated (ACE600, LEICA) up to a thickness of 5 nm before being mounted onto the SEM stage. Low emission voltage (5 kV) with relatively small current (100 pA) were employed to achieve a good resolution while avoiding charging on the powder.

2.3 Results and Discussion

2.3.1 Calcination

2.3.1.1 Perovskite type LSTZ

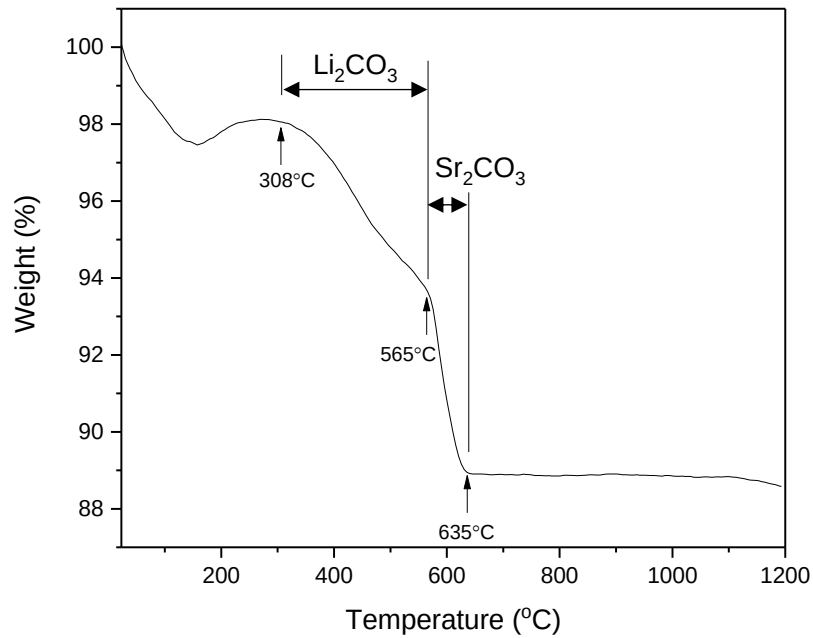
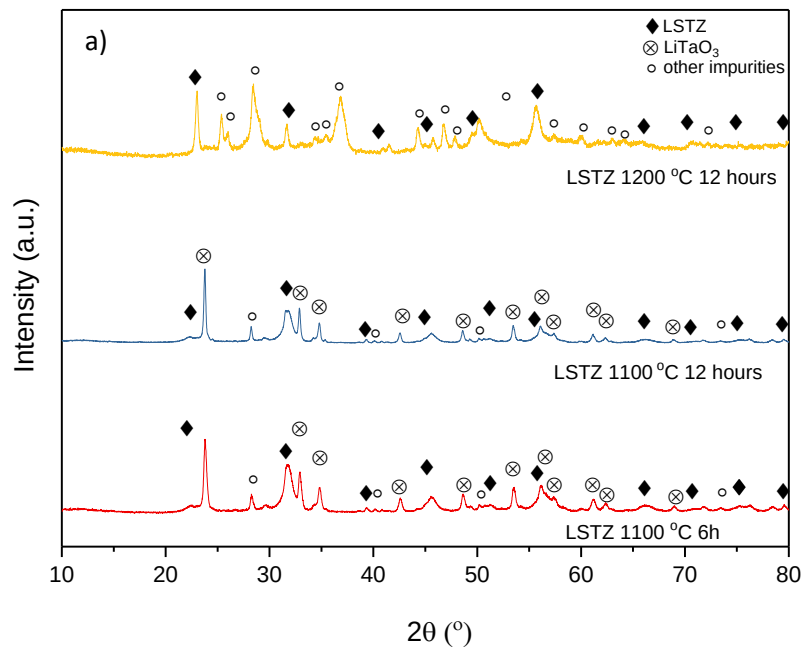


Figure 7 TGA measurement results of LSTZ mixture



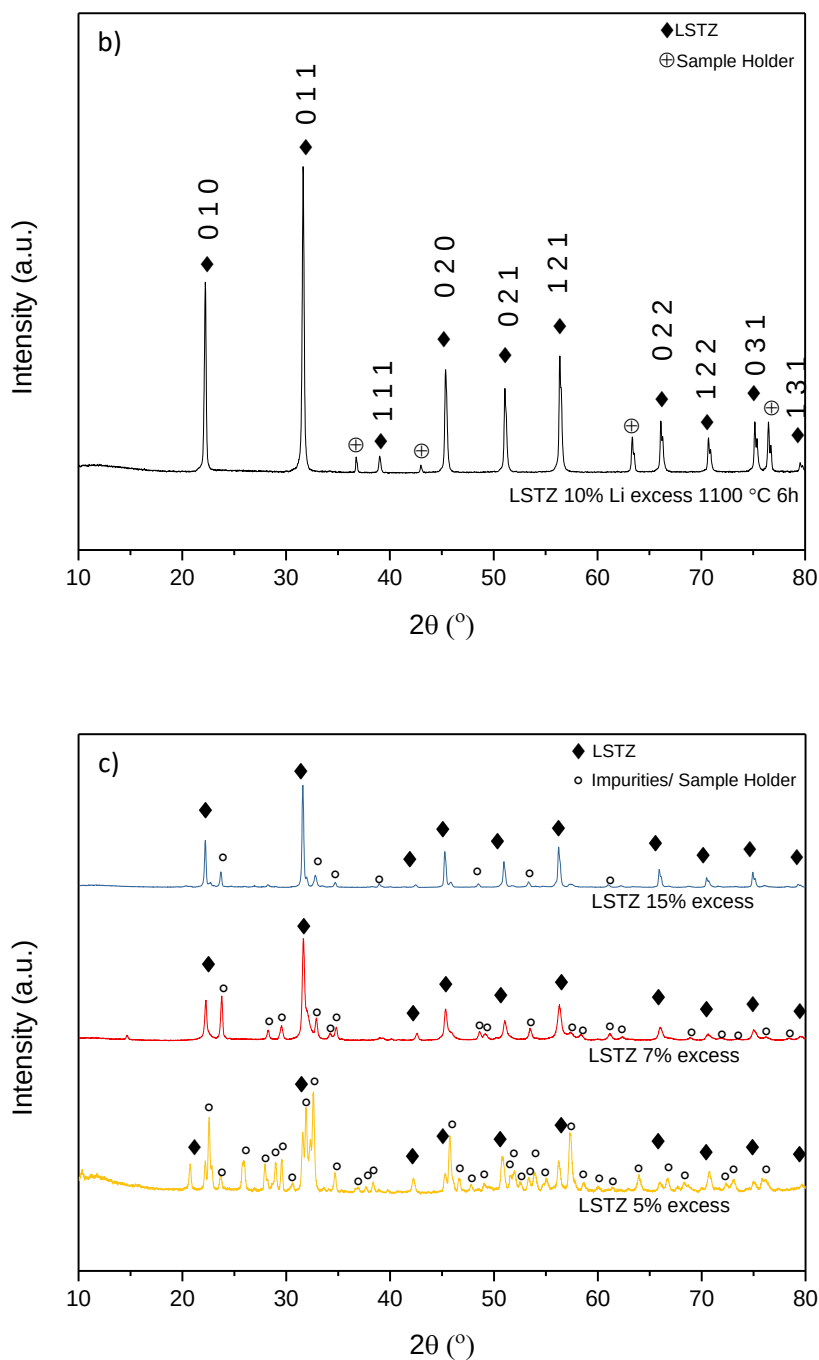


Figure 8 XRD spectra of a) LSTZ powders calcined at different temperatures and durations b) 10% Li excess LSTZ powder calcined at 1200 °C for 6 h c) LSTZ powder with different amount of Li excess calcined at 1200 °C for 6 h

Disregarding the initial dip around 100 °C which can be attributed to the instrument, TGA measurement of LSTZ (Figure 7) showed two distinct regions of weight loss, consistent to that reported by a previous study [5]. These two regions are caused by the decomposition of Li_2CO_3 and SrCO_3 . However, it should also be acknowledged that these mass loss regions start 100 °C lower compared to the previous study [4]. This difference in mass loss

temperature might be due to different atmosphere used for the TGA experiment, difference in number of surrounding elements, and/or the different heating rate employed. Regardless, the pattern and percentage of mass loss is similar, suggesting the same gaseous evolution occurred.

The first weight loss region starts at 308 °C and advances almost linearly until 565 °C. In this region, approximately 4.4% weight loss can be observed. This approximates to the theoretical weight loss of C and O coinciding with the decomposition of Li_2CO_3 , calculated to be 4% by weight. A steeper second weight loss region can be observed, starting from 565 °C up to 640 °C, resulting in 6% weight loss. The sum of weight loss after the two regions equals 10.4%, which fits well with the theoretical calculated 10% weight loss due to evolution of CO_2 gas from the formation of LSTZ. At temperatures higher than 600 °C, the compound stabilizes and does not experience substantial weight loss up to at least 1200 °C. Furthermore, the difference in weight loss shown in Figure 7 compared to the calculated value of 10% can be attributed to the loss of volatile Li. Therefore, this TGA result convincingly validates that the remaining molecular species in the sample is conducive to the formation of LSTZ throughout this latter temperature range.

XRD spectra of LSTZ calcined for 6 and 12 h at 1100 °C (Figure 8a) show the dominant impurity peaks are mostly those of LiTaO_3 , suggesting incomplete reaction at this temperature and sintering duration. At 1200 °C, phase pure LSTZ was formed after 6 h calcination (Figure 8b). Increasing the calcination length to 12 h led to more significant loss of lithium, resulting in other impurity phases (Figure 8a). This sweet spot for calcination of LSTZ is a balancing act of calcination regime and managing lithium loss, as (Figure 8c) shows that decreasing the lithium excess affects the phase purity of calcined powders with identical calcination regimes. Increasing the Li excess to 15 wt% also introduce a different set of impurity peaks (Figure 8c).

2.3.1.2 Al- and Ta-doped garnet type LLZO

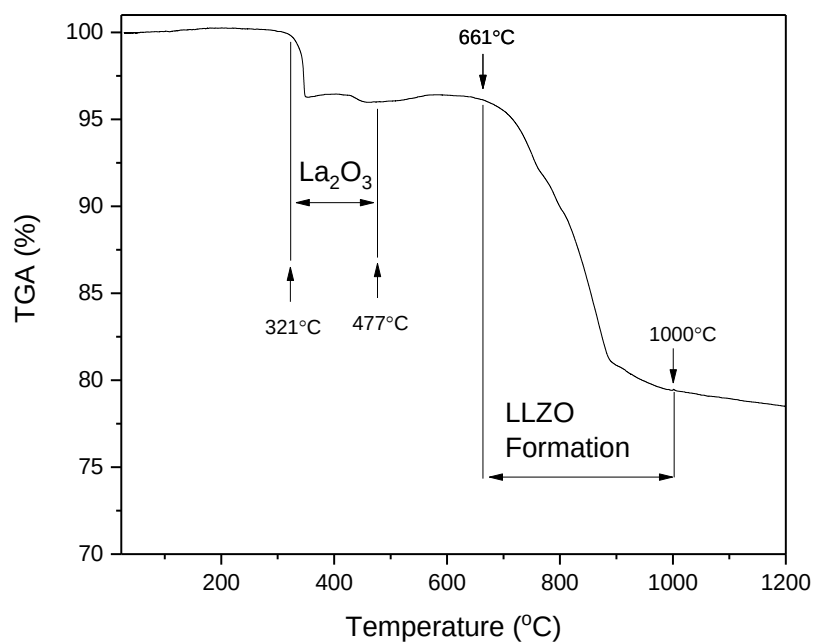


Figure 9 TGA measurement result of LLZO precursor mixture

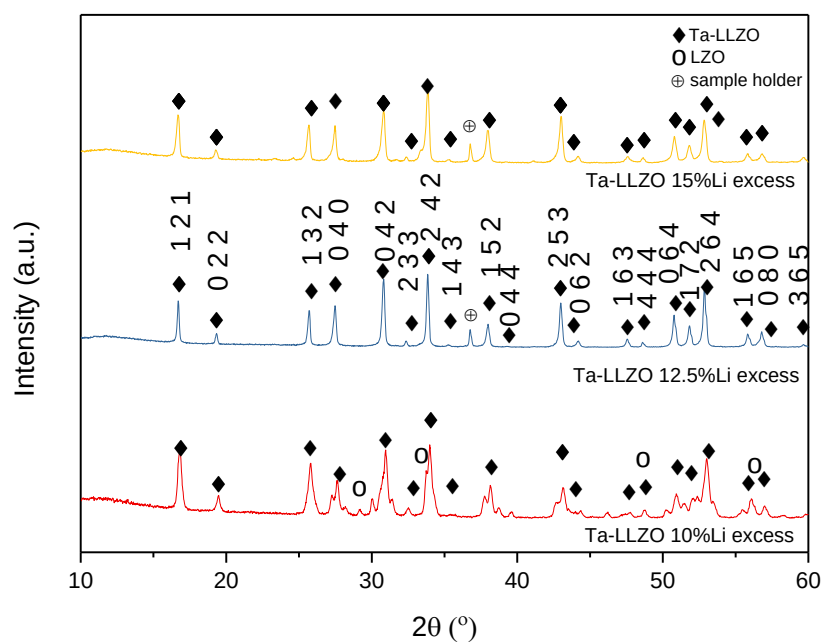


Figure 10 XRD spectra of Ta-LLZO powders calcined at 1000 °C for 4 h with different amounts of Li excess

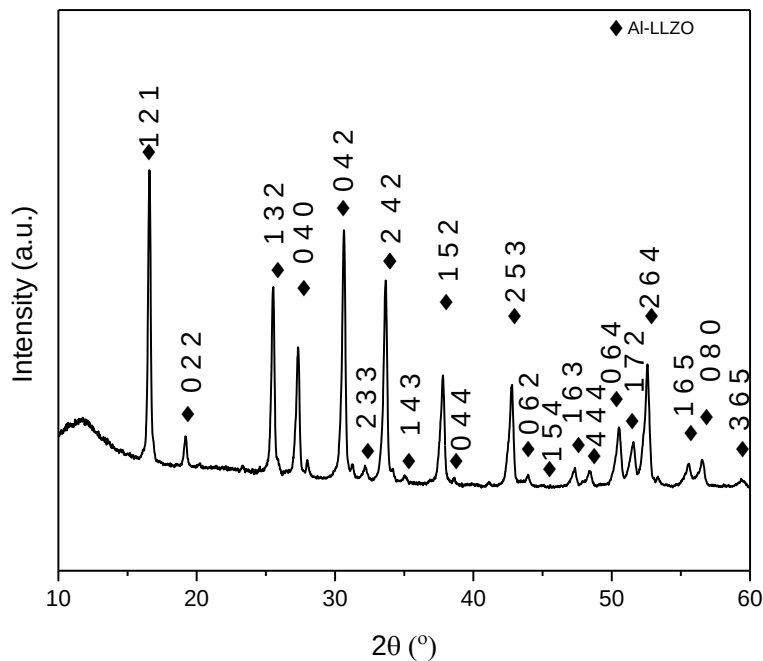


Figure 11 XRD spectrum of Al-LLZO powder calcined at 1000 °C for 4 h

The TGA result in Figure 9 shows mass loss pattern consistent with a previous study on the formation mechanism of LLZO, with the mass losses between around 320 °C to 480 °C attributed to the complex reaction undergone by La_2O_3 [5]. Another big mass loss at around 660 °C until 1000 °C can be attributed to the formation of LLZO or $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO) for cases where not enough Li is present to substitute into the La sites [5]. The total weight loss at the end of the calcination regime in the TGA was observed to be around 20%, which fits well with the weight loss due to C and excess O molecules evolution, calculated from the weight of the precursors compared with the stoichiometric weight of the product.

A previous work by the Part II student shows that cubic Ta-LLZO can be formed by calcination above 900 °C [2]. However, when a similar calcination was attempted in this work, some secondary LZO phase peaks could be identified in the XRD spectra (Figure 10). This is due to lithium loss, resulting in insufficient lithium to stabilize the LLZO phase. Addition of 12.5% excess lithium to the precursor powders was found to have mitigated this lithium loss, resulting in consistently phase pure cubic Ta-LLZO after calcination at 1000 °C for 4 h (Figure

10). This addition of 12.5% Li excess was found to also yield phase pure powders consistently for Al doped LLZO with an identical calcination regime (Figure 11).

2.3.2 Particle Size

2.3.2.1 Laser Diffraction

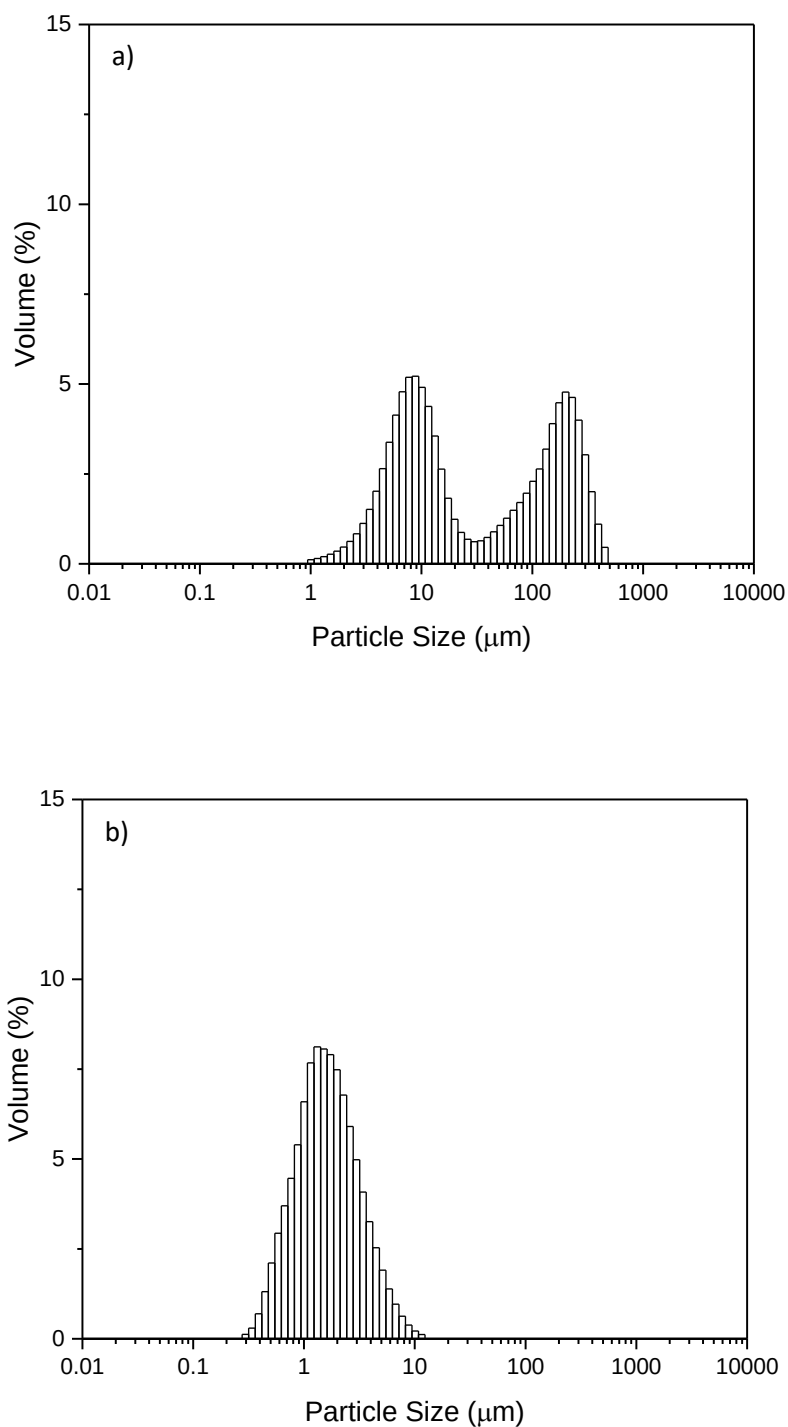


Figure 12. Average particle size histogram of calcined LSTZ powder a) before b) after 24h ball milling

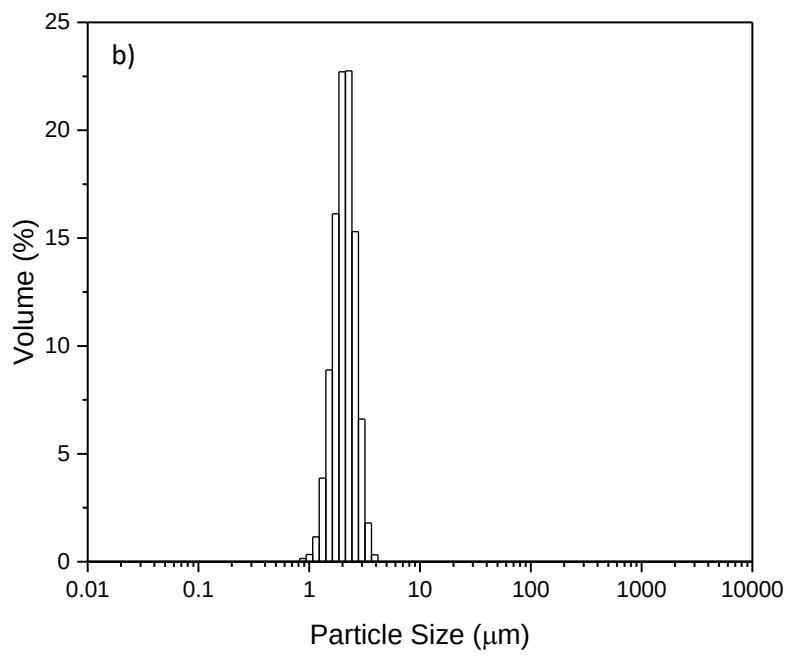
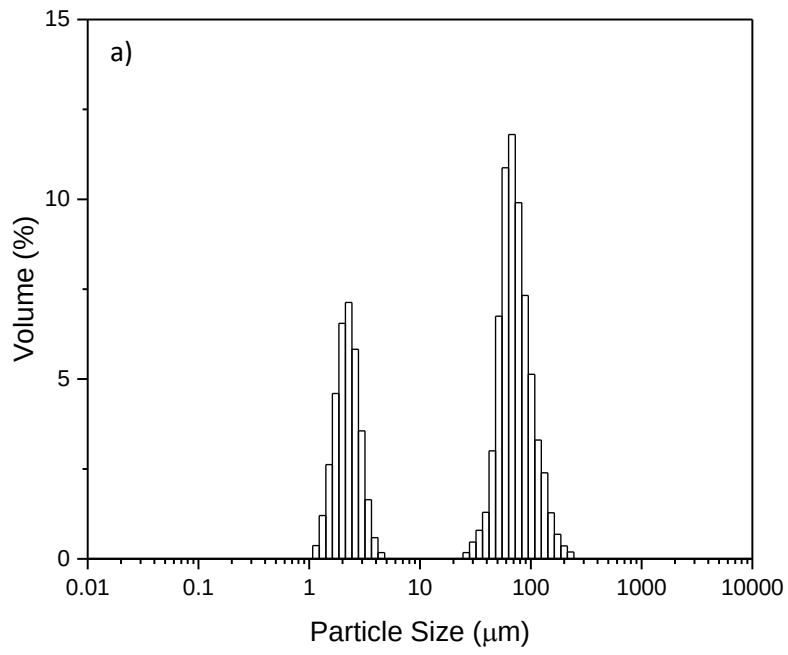


Figure 13. Average particle size histogram of calcined Ta-LLZO powder (a) before ball milling (b) after ball milling for 24 h

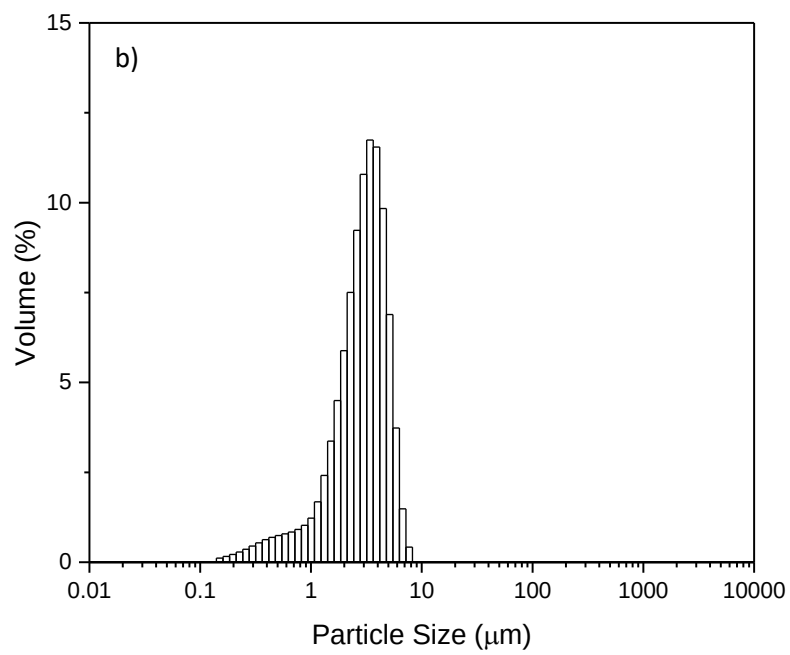
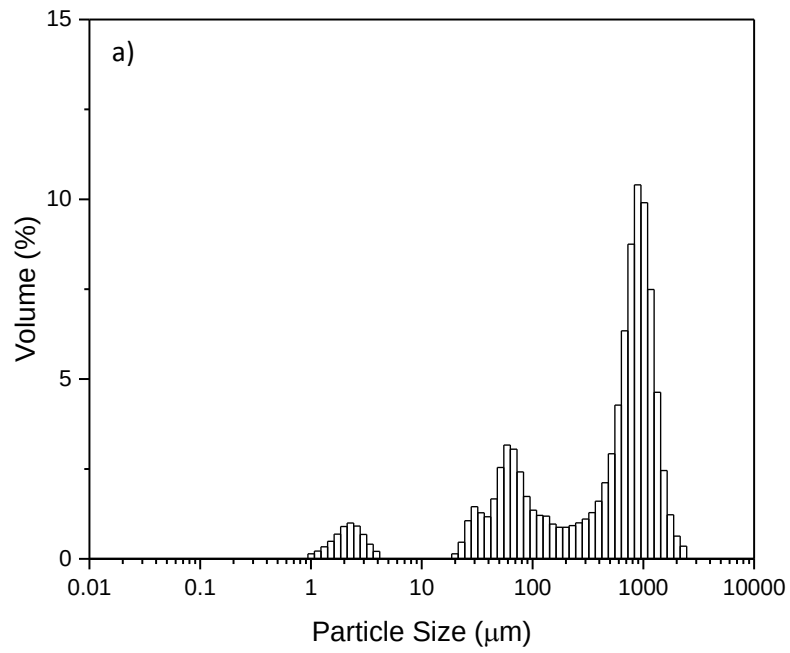


Figure 14 Average particle size histogram of calcined Al-LLZO powder (a) before ball milling (b) after ball milling for 24 h

Due to the uncertainty in the refractive index, comparisons of particle size across the different powder compositions are not definitive. However, clear particle size reduction can reliably be observed between powders of the same composition before and after ball milling. Figure 12 shows that ball milling the LSTZ powder for 24 h reduces its particle size average. The $10^2 \mu\text{m}$ peak in the histogram is absent in Figure 12b, signifying that most of the bigger particles have been broken up into particles in the order of $1 - 10 \mu\text{m}$.

Figure 13 and Figure 14 respectively show an even more significant reduction of particle size average in Ta-LLZO and Al-LLZO after 24 h ball milling. Figure 14a shows that before being ball milled, some Al-LLZO particles were in the order of $10^3 \mu\text{m}$, even though the precursor powder had been passed through a $150 \mu\text{m}$ sieve right before calcination. This suggests significant agglomeration of Al-LLZO particles during the thermal processes in the calcination step.

2.3.2.2 Scanning Electron Microscopy

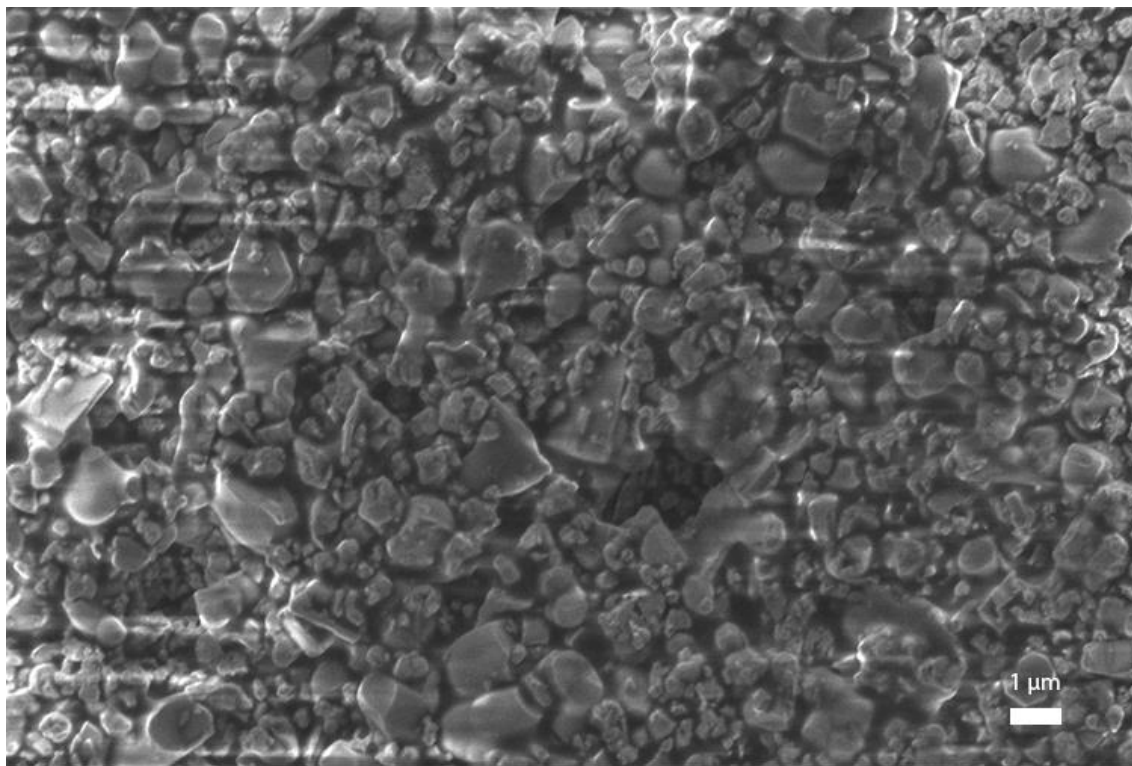


Figure 15 FESEM of calcined LSTZ powder after 24 h ball milling

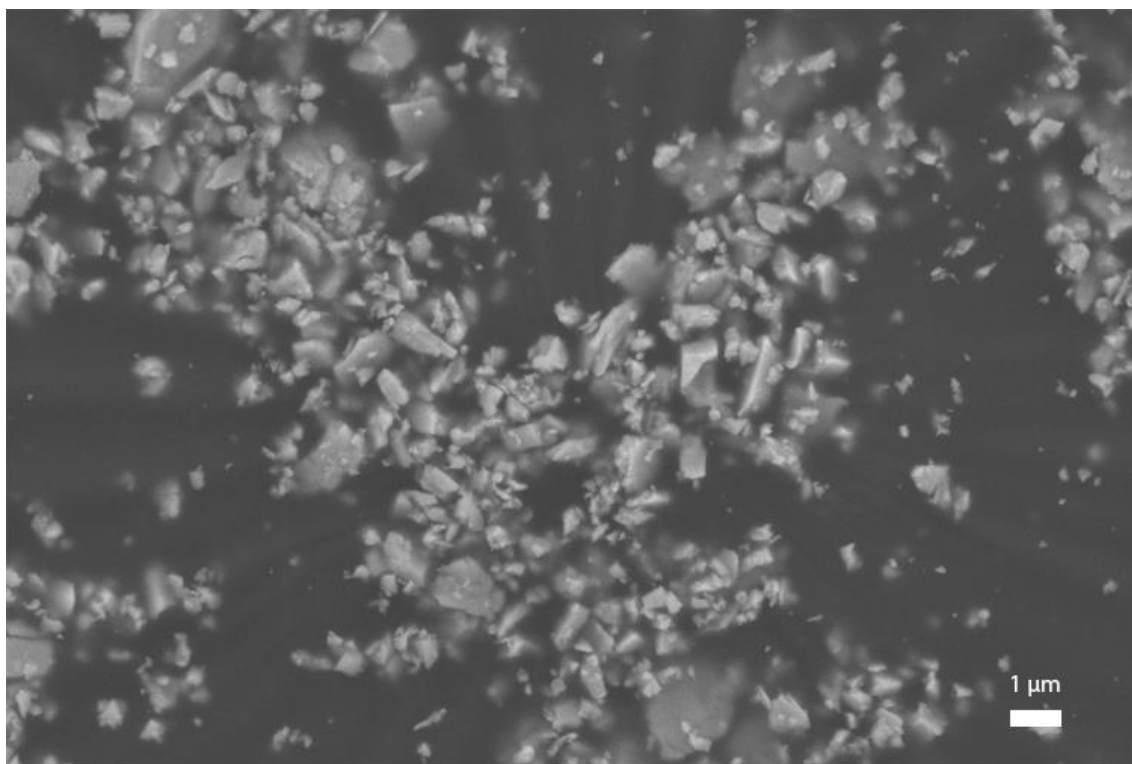


Figure 16 FESEM Image of calcined Ta-LLZO powder after 24 h ball milling

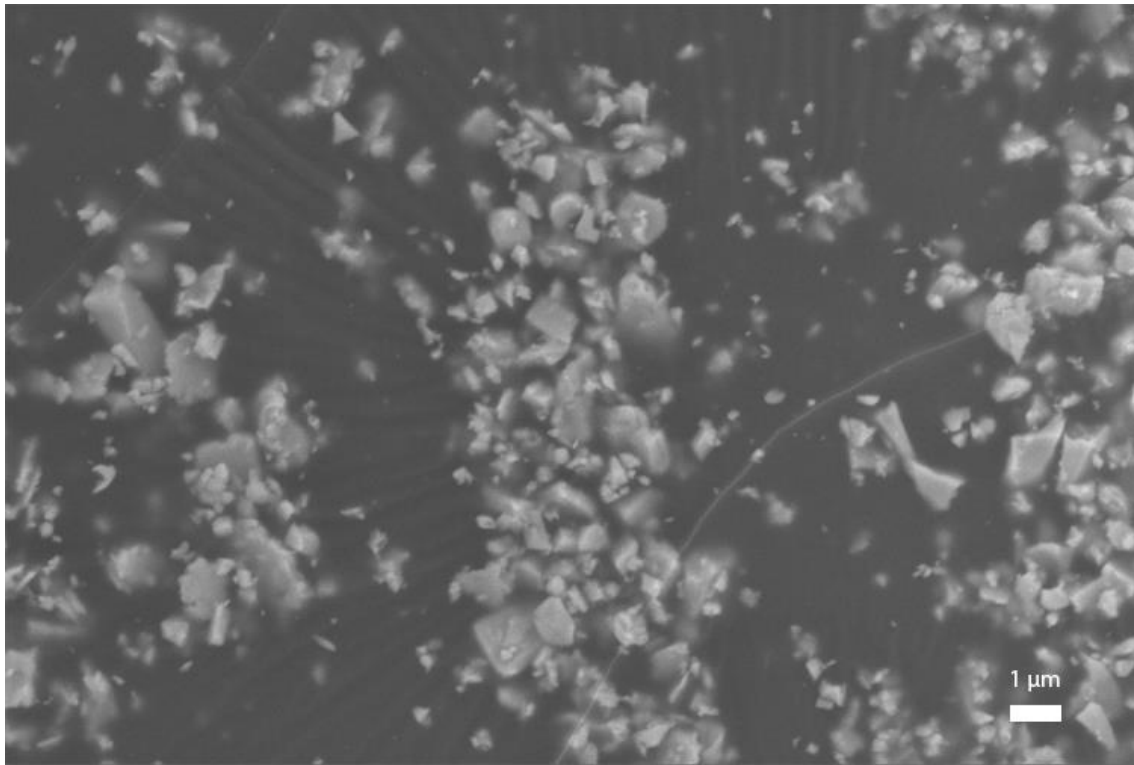


Figure 17 FESEM Image of calcined Al-LLZO powder after 24 h ball milling

Figure 15, Figure 16, and Figure 17 show micrographs of calcined LSTZ, calcined Ta-LLZO, and calcined Al-LLZO powders after 24 h ball milling respectively. All 3 images show particle sizes in the same order of magnitude, if just slightly smaller, compared to the LD measurement, suggesting that the estimated refractive index of 1.4 is valid. This slight difference in particle size between the micrograph and the LD measurement is to be expected, as LD assumes that the particles are all perfectly spherical and measures particle size by volume, while the micrographs show the particles are irregular.

Even though similar treatments were performed to each respective powder, it can clearly be seen that the LSTZ powder is significantly smoother and particulate-like, compared to the more angular, fragment-like shape of both LLZO powders particles.

2.4 Additional Notes

Synthesis of $\text{Li}_{6.25}\text{La}_3\text{Ga}_{0.25}\text{Zr}_2\text{O}_{12}$ (Ga-LLZO) was also successfully attempted, resulting in phase pure powder. However, it was found that the synthesis method for Ga-LLZO yields monophasic results less consistently. In addition, as the main purpose of the project was to utilize the difference in CTE between 2 different compositions, further characterization and synthesis attempt of Ga-LLZO was not considered due to Ga-LLZO having an intermediate CTE between the other 2 garnet type compositions (Al-LLZO and Ta-LLZO).

2.5 Conclusion

Solid state synthesis of LSTZ and LLZO with different dopants was found to be effective to consistently synthesize phase pure powders for sintering. Different calcination temperatures and times guided by the literature and TGA results were attempted, and it was found that 1200 °C for 6 h and 1000 °C for 4 h are optimal for LSTZ and doped LLZOs respectively. Addition of 10% and 12.5% Li excess for LSTZ and LLZO respectively was also found to enhance the phase purity by counteracting lithium loss during the thermal processes. Further 24 h ball milling of calcined powders in argon filled bottles were found to result in relatively uniformly sized powder particles in the μm range for LSTZ and LLZO. These resulting powders were used to sinter the respective solid state electrolyte pellets in later stages of the project.

2.6 References

1. Inada, R., K. Kimura, . . . Y. Sakurai, *Synthesis and lithium-ion conductivity for perovskite-type $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Zr}_{1/4}\text{O}_3$ solid electrolyte by powder-bed sintering*. Solid State Ionics, 2014. **261**: p. 95-99.
2. Connolly, W., *Part II thesis*. 2021, University of Oxford.
3. Han, G., B. Kinzer, . . . J. Sakamoto, *Correlating the effect of dopant type (Al, Ga, Ta) on the mechanical and electrical properties of hot-pressed Li-garnet electrolyte*. Journal of the European Ceramic Society, 2020. **40**(5): p. 1999-2006.
4. Ji, Y., C. Zhou, . . . Z. Chen, *Submicron-Sized Nb-Doped Lithium Garnet for High Ionic Conductivity Solid Electrolyte and Performance of Quasi-Solid-State Lithium Battery*. Materials, 2020. **13**(3): p. 560.
5. Feng, Z. (2018). Preparation and Application of Perovskite-Type Solid Electrolytes for All Solid State Lithium Ion Batteries. (National University of Singapore, Singapore). Retrieved from <https://scholarbank.nus.edu.sg/handle/10635/142401>

Chapter 3 Pellet Forming and Densification

3.1 Objective

Sintering is a step in ceramic manufacturing where green bodies, formed out of compacted powders, undergo densification usually by means of thermal processes. A dense ceramic, particularly for SSE, is important as the higher density means less porosity in the solid body. With less porosity, the continuous bulk solid formed in a fully dense ceramic means higher toughness and conductivity, which should offer less opportunity for lithium dendrite deposition and penetration. Therefore, it is important for this project to explore the method that can result in high density pellet. So far, multiple papers have been published attempting to create dense LLZO and LSTZ pellets while maintaining phase purity by means of different sintering techniques [1-4].

A previous study on the elastic properties of Ta and Al doped LLZO of high relative density (>98%) [1] has been published, proposing values of Young's modulus relevant to these types of oxide ceramics. In contrast, to the author's knowledge, no prior study investigating the Young's modulus of LSTZ has been published. It was therefore important to conduct nano indentation measurements to establish the Young's modulus of highly dense LSTZ.

3.2 Experimental Methods

3.2.1 Conventional Furnace sintering

2 g lots of sample powder were each formed into 10 mm diameter pellets by hydraulic uniaxial pressing in a steel die. This uniaxial pressing step is meant to give shape to the pellets, for which a low pressure of 120 MPa on the pellet's cross section is enough. The resulting green bodies were transferred into vinyl sleeves, which were then sealed inside vacuum pouches. The vacuum pouches were put into a cold-isostatic press (CIP) and subjected to 300

MPa pressure for 5 min. The CIP step improves the quality of green bodies due to the homogeneous isotactic pressure, resulting in better compacted pellets with less risk of anisotropic stresses in the green body.

CIP-ed green bodies were measured for their dimension and weight, then put fully enclosed with excess amount of mother powder containing the same composition of the pellets in a lidded alumina crucible. This addition of mother powder has been shown to counteract the lithium loss during the sintering process [2], resulting in phase pure pellets.

The lidded alumina crucibles containing mother powder and green bodies were then inserted into the middle of a tube furnace (VTF7, Vecstar Ltd). LSTZ 10% Li excess was found to sinter at 1300 °C for 15 h with heating rate of 5 °C/min, while Ta-LLZO 12.5% Li excess and Al-LLZO 12.5% Li excess at 1200 °C for 6 h with a heating rate of 5 °C/min. A commercially bought Ta-LLZO powder with no added binder (Ampcera™) was also made into a green body and sintered using this regime as a control.

3.2.2 Binder

Varying amounts of polyvinyl butylate (PVB) binder were dissolved in IPA and then added to the slurries of powder in between the calcination and second ball milling step (section 2.2.2). A de-binding step, 1 h dwell at 600 °C before ramping up to sintering temperature, was added to the sintering regime in the furnace.

3.2.3 SPS/FAST

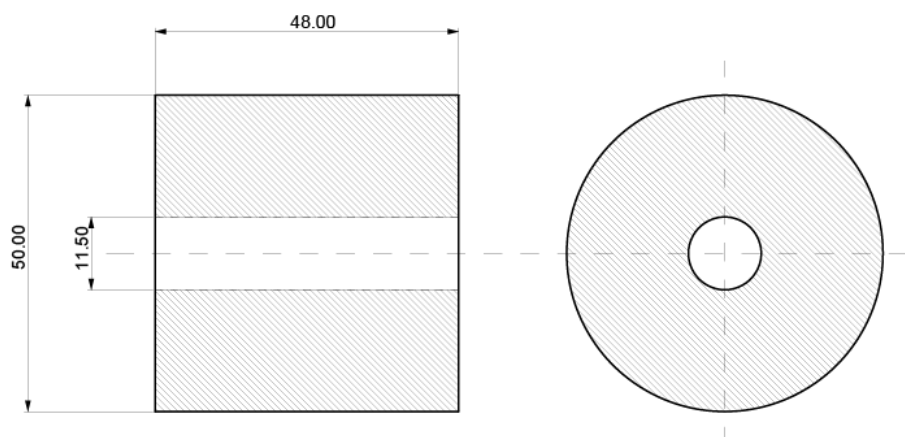


Figure 18 Schematic of SPS die

Graphite dies as shown in Figure 18 were custom made and purchased from LG Graphite. Graphite foil of 0.35 mm thickness was cut to dimension and rolled to be inserted into the die cavity, so that two layers of graphite foil lined the die wall. Same graphite foils were cut into 10 mm diameter circles, to act as barriers between the plunger of the graphite die and the powder. These graphite foil layers protect the die and allow easy removal of sintered pellets from the die.

Weighed amounts of Ta-LLZO 12.5% Li excess, Al-LLZO 12.5% Li excess, or LSTZ 10% Li excess powders, synthesized in section 2.3.1 were put into the assembled die and uniaxially pressed at 40 MPa to pack the powder. Graphite felt insulation was wrapped around the die, incorporating a small window to allow for clean line of sight for a laser pyrometer connected to the SPS. The packed and assembled die set was then put into the SPS (DSP 507, Dr. Fritsch) using graphite cones to keep the plungers upright and allow more contact area with the electrodes. A SPS regime was set to be done under vacuum with heating rate of 100 °C/min at 20 MPa pressure ramped up to 1000 °C, before a ramp up to 1100 °C with a slower heating

rate of 50 °C/min and a constant 40 MPa pressure. This was followed by a dwell for 10 min. The pressure was then relieved, allowing the die set to cool down naturally.

3.2.4 Polishing

Due to the air-and-water sensitivity of lithium, bespoke polishing techniques must be adapted to achieve the best surface for analysis. Grinding is necessary to ensure parallel surfaces of the pellets and removal of LiCO_3 which is known to form on the surface of sintered LLZOs [3]. This is crucial for some measurements such as dilatometer testing and indentation, and is preferable for electrochemical tests.

Sintered pellets were first mounted to a custom-built sample holder using low melting point wax (Crystalbond, Buehler). SiC pads of increasing grades (400, 800, 1600, 2400, 4000) with IPA as lubricant were used to grind the mounted pellets. For measurements that did not need very fine polishing, diamond lapping films of increasingly finer grit (Ultraprep 15, 9, 6, 3 and 1 μm , Agar Scientific) were used to achieve a shiny polished surface. For measurements where a better surface was needed (i.e. SEM, nanoindentation, Vickers Indent), the samples were polished using oil-based diamond suspension of decreasing diamond particle size (OP-3, OM-1, OM-1/4, Kemet) using the appropriate lapping pads.

3.2.5 Characterization Methods

3.2.5.1 SEM

In order to observe the microstructure of the pellets, samples were fractured to expose their cross section. Unfractured sample surfaces were also prepared for SEM. These samples were mounted on SEM stubs using electrodag. Mounted samples were then coated with 5 nm of carbon in a carbon sputterer (ACE600, Leica) before being mounted and observed using an SEM (EVO, Zeiss). 10 kV accelerating voltage with 100 pA beam current was used.

3.2.5.2 Phase Analysis

X-ray Diffraction (Miniflex, Rigaku) with similar parameter to that in section 2.2.3 was used to observe the phases present in the sintered pellets. In the case of SPS sintered pellets, pellets were ground to remove the outer layer that was the graphite foil. Removal of said layer can be empirically observed due to the color and softer texture of the graphite.

3.2.5.3 Mechanical Analysis

3.2.5.3.1 Relative Density

Relative densities of sintered pellets were measured by Archimedes' principle using ethanol or isopropanol as medium. The buoyancy force of a submerged body of solid is directly proportional to the volume of medium displaced, such that:

Equation 1

$$\rho_{sample} = \left(\frac{m_{sample}}{m_{medium}} \right) * \rho_{medium}$$

For measurement of sintered ceramics, the presence of open porosity in the sample can affect the calculated density, hence it is customary to weigh the pellets 3 times, once dry (m_{dry}), then submerged ($m_{submerged}$), then again saturated ($m_{saturated}$). m_{medium} can be substituted by $m_{saturated} - m_{submerged}$ such that:

Equation 2

$$\rho_{sample} = \left(\frac{m_{dry}}{m_{saturated} - m_{submerged}} \right) * \rho_{medium}$$

3.2.5.3.2 Dilatometer

As the project seeks to utilize CTE differences between the different compositions of solid-state electrolyte, measurement of CTE is crucial. Measurements were done in air atmosphere using a vertical dilatometer (L75/1550, Linseis).

After calibration to offset the CTE of the instrument and alumina discs had been done according to the manufacturer's suggestion, polished pellets were put on the alumina disc on the dilatometer stage, before positioning the furnace. The measurement chamber was

then heated to an isotherm at 50 °C and held for 10 min to ensure consistent results. Measurements were taken automatically throughout the full heating range, with a heating rate of 5 °C/min until a maximum temperature of 1000 °C and held at the maximum temperature for 2 h to achieve isotherm again before being allowed to cool down at a controlled rate of 5 °C/min. The recorded displacement of the dilatometer stage was divided by the initial thickness of the sample (dL/L_0) and then plotted against temperature change (ΔT). The resulting plots were then fitted to obtain the gradient, which translates to the CTE of measured pellets (Equation 3).

Equation 3

$$CTE = \frac{dL}{L_0 \Delta T}$$

3.2.5.3.3 Nanoindentation

Polished samples were mounted onto SEM stubs using Crystalbond, taking care not to get any wax in between the sample and the stub surface. Stubs with samples were then mounted on specially machined holders, before being put on top of the specimen holder for the nanoindenter (MTS XP). The following experiments were conducted by Rob Scales, a trained user of the nanoindenter, as the nanoindenter requires expertise to achieve highly reliable results.

Calibration indents were made according to manufacturer's suggestion. Sufficiently flat and pristine portions of the samples were then selected as the indenting location utilizing the motorized stage and internal SEM of the nanoindenter. An array of statistically significant indents was then made with a tip approach speed of 10 nm/s, making sure there was enough space between each indent so as to not cause crack interactions. The load and displacement of the indenter tip for each indent as well as SEM images of the indents were recorded and analyzed by the proprietary software to get the hardness and Young's modulus values.

3.2.5.4 Electrochemical Testing

Polished samples were coated with gold on both sides, making sure no channel was formed on the pellet's side connecting the two gold electrodes. The samples were mounted onto an EIS-specific sample holder with through-plane electrode configuration (CESH, Biologic), which were then connected using BNC/SMB cables to the appropriate ports on the impedance analyzer (MTZ-35, Biologic).

Electron impedance spectroscopy (EIS) measurement sweeps from 35 MHz to 5 Hz with 10 points per decade were conducted at 30 °C. The resulting responses were recorded and plotted on Nyquist plots in EC-Lab (Biologic). Curve fitting of appropriate equivalent circuit representing the samples was then attempted to extract the resistance of the pellets from the graphs.

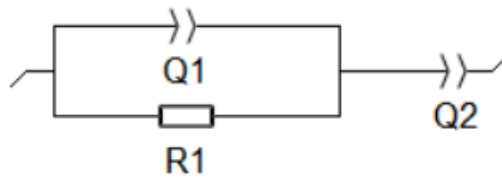


Figure 19 Equivalent circuit diagram representing the sample for EIS [4]. Q1 and Q2 represent constant phase elements, and R1 represents a resistor.

By fitting the equivalent circuit (Figure 19) to the Nyquist plot, the resistance of the electrochemical cell with the pellets as electrolyte can be calculated. The resulting value from this fitting gives the resistance. In order to calculate conductivity, the inverse of resistance multiplied by contact area over thickness was taken, such that:

Equation 4

$$\text{conductivity} = \frac{\text{thickness}}{\text{resistance} \times \text{contact area}}$$

3.3 Results and Discussion

3.3.1 Densification by Conventional Sintering

Table 1 Relative density of pellets conventionally sintered with mother powder.

Sample	Relative Density of Pellets (%)	Theoretical Density (g/cm ³)
Commercial Ta-LLZO	87	5.31
Al-LLZO 12.5% Li excess without PVB	86	5.27
Al-LLZO 12.5% Li excess 2wt% PVB	88	5.27
Ta-LLZO 12.5% Li excess without PVB	88	5.31
Ta-LLZO 12.5% Li excess 2wt% PVB	90	5.31
LSTZ 10% Li excess without PVB	95	6.48

Table 1 summarizes the relative density of some pellets sintered in a commercial furnace with mother powder with relevance to the discussion. It was observed that the addition of 2 wt% PVB was able to raise the relative density of pellets by around 2%, while LSTZ 10% achieved 95% relative density without any binder addition. Each of these results will be further discussed in the following section.

3.3.1.1 Ta-LLZO

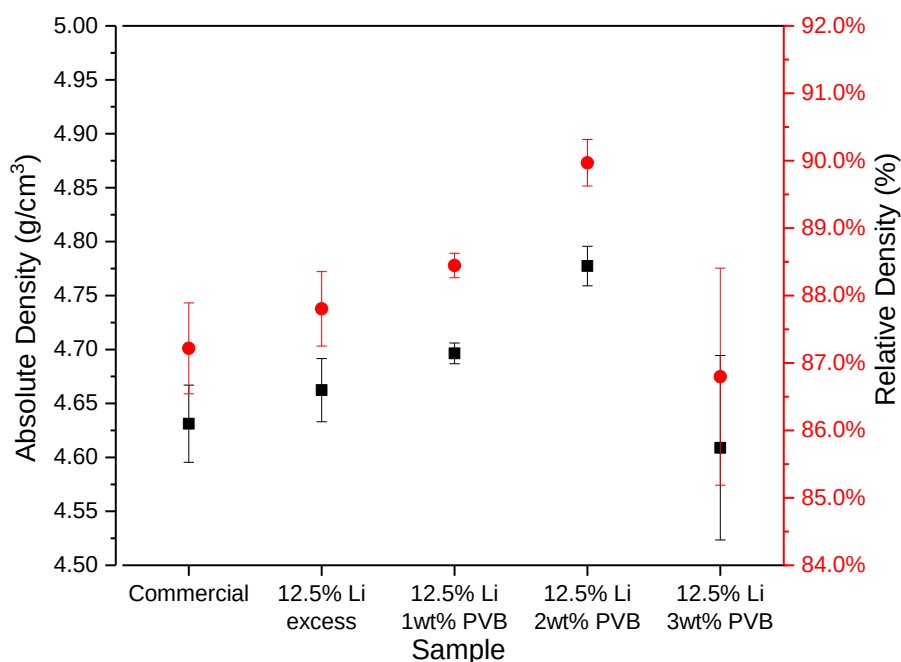


Figure 20 Absolute and relative density of conventionally sintered samples with commercial Ta-LLZO powder and 12.5% Li excess Ta-LLZO powder containing different amount of PVB binder

Figure 20 shows a plot of the resulting absolute and relative density of the Ta-LLZO pellets, sintered with mother powder at 1200 °C/min for 6 h with heating rate of 5 °C/min, against the amount of PVB binder added to the calcined powders as well as pellets made using commercially bought Ta-LLZO powder. It can be clearly seen that the synthesized Ta-LLZO powder with 12.5% Li excess even without binder achieves higher relative density compared to the commercially purchased powder, justifying the benefits of powder synthesis optimization in section 2.3.1.2.

The sintering temperature of 1200 °C/min was chosen due to it being impossible to increase the sintering temperature. An attempt to do so melted part of the pellet, fusing it with the alumina crucible used. Increasing the dwell time at the sintering temperature was also risky, as it has been shown that lithium volatility can affect the resulting phase purity of

sintered samples [2]. However, longer sintering dwell time with a controlled atmosphere such that Li loss can be avoided might have resulted in higher density of the pellets [5].

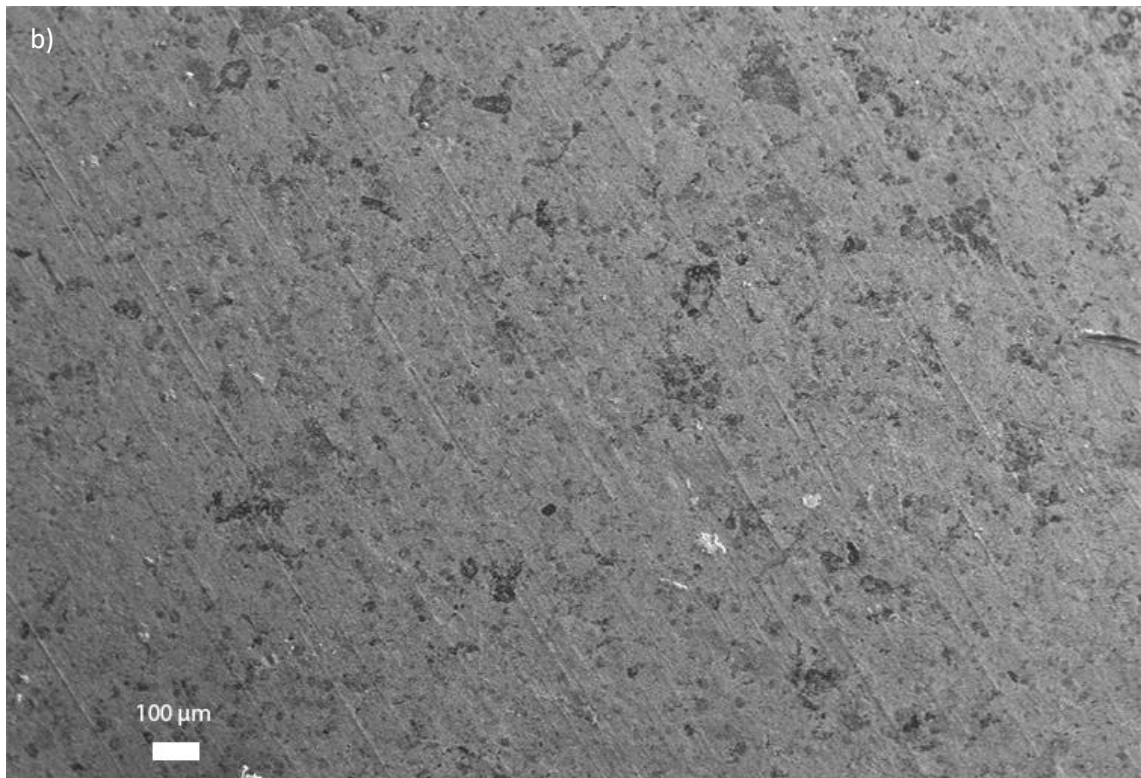
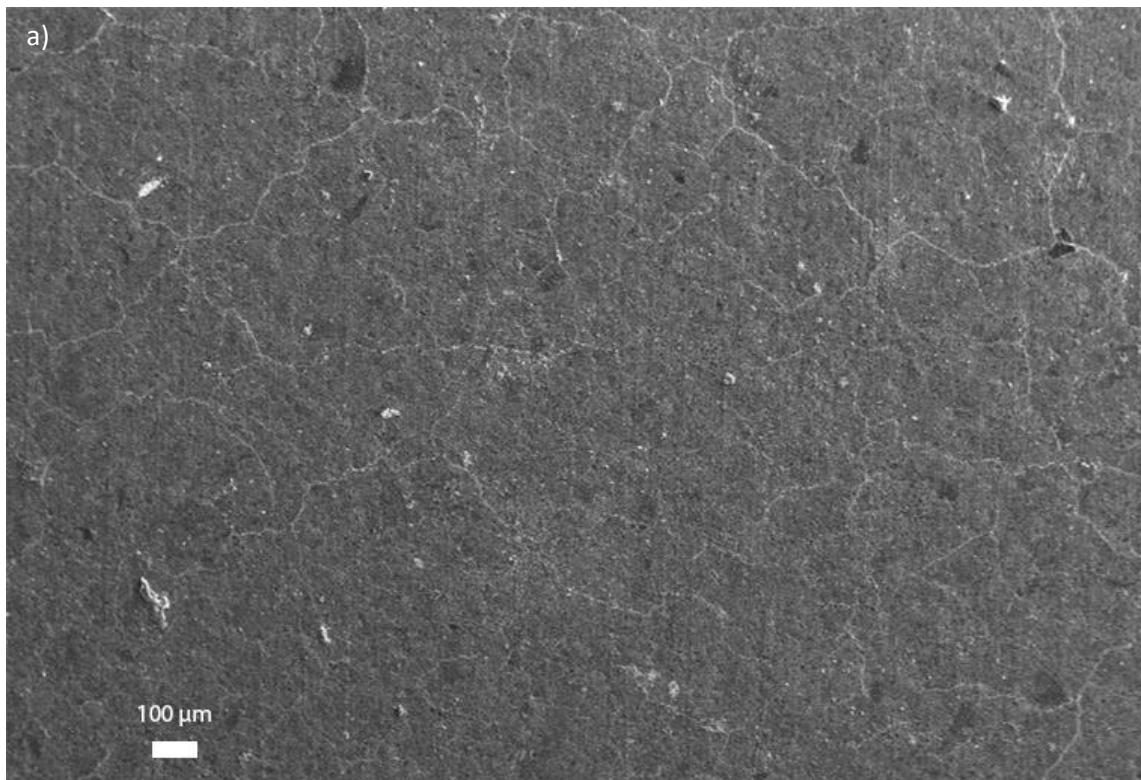


Figure 21 Secondary electron SEM images of green body surface from a) CIP-ed Ta-LLZO 12.5% Li excess no added PVB binder and b) CIP-ed Ta-LLZO 12.5% Li excess 2wt% PVB

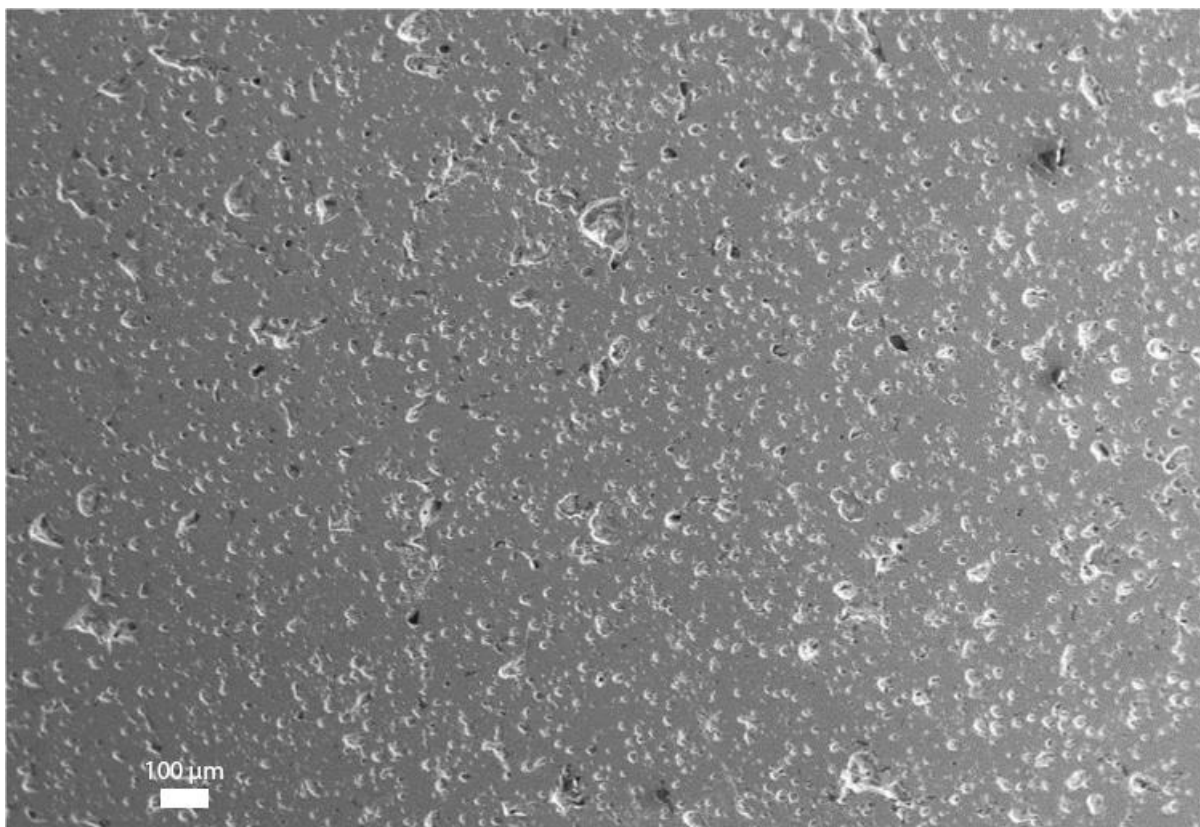


Figure 22 Secondary electron SEM image of sintered Ta-LLZO 12.5% Li excess 2 wt% PVB binder pellets polished surface

Observation of green body surfaces of Ta-LLZO 12.5% Li excess (Figure 21a) shows that cracks were present, sectioning the green body into islands of large agglomerates. These observed cracks are evidence of bad compaction of the green body, and might lead to cracks and poor densification in the sintered body.

The effect of binder addition in Ta-LLZO 12.5% Li excess 2 wt% PVB green body can be clearly seen in Figure 21b when comparing it with the image in Figure 21a. By adding 2% by weight of PVB, these cracks disappear giving a more homogeneous green body surface. Nevertheless, some black spots can still be observed, potentially due to looser packing in these regions.

Figure 22 shows that some pores are still present after sintering, which can be attributed to still suboptimal packing of particles in the green body and potentially gas evolution during sintering. Further addition of PVB binder to 3 wt% does not result in an increase in relative density of the sintered pellets. In fact, the more PVB binder leads to more

gas expulsion during the thermal process, which might causes some of the gas being trapped in pockets during sintering with the current debinding step, resulting in the lower density of the sintered pellet (Figure 20).

3.3.1.2 Al-LLZO

Due to the similarity of Al-LLZO to Ta-LLZO, identical sintering regime and addition of 2 wt% PVB binder was followed for Al-LLZO 12.5% Li excess. As shown in Table 1, Al-LLZO 12.5% Li excess 2 wt% PVB pellets were able to achieve 88% relative density, such that further optimization for Al-LLZO sintering in conventional furnace was not attempted in view of time restriction.

3.3.1.3 LSTZ

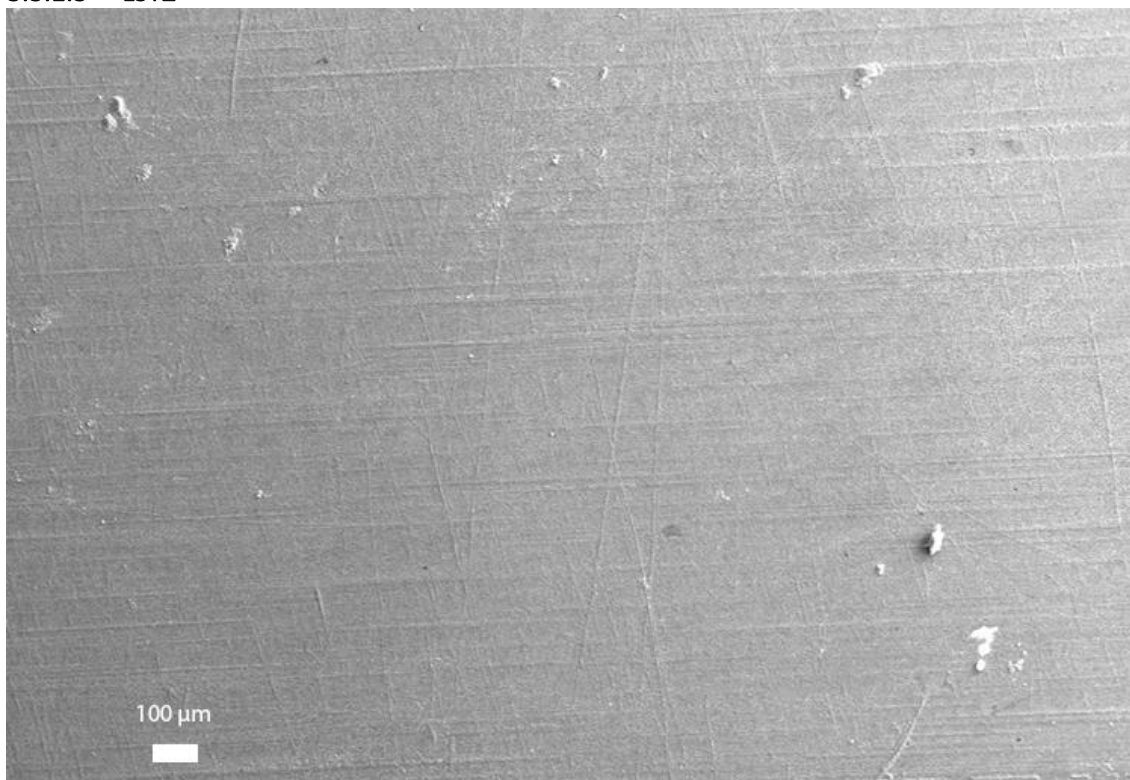


Figure 23 SEM image of LSTZ green body

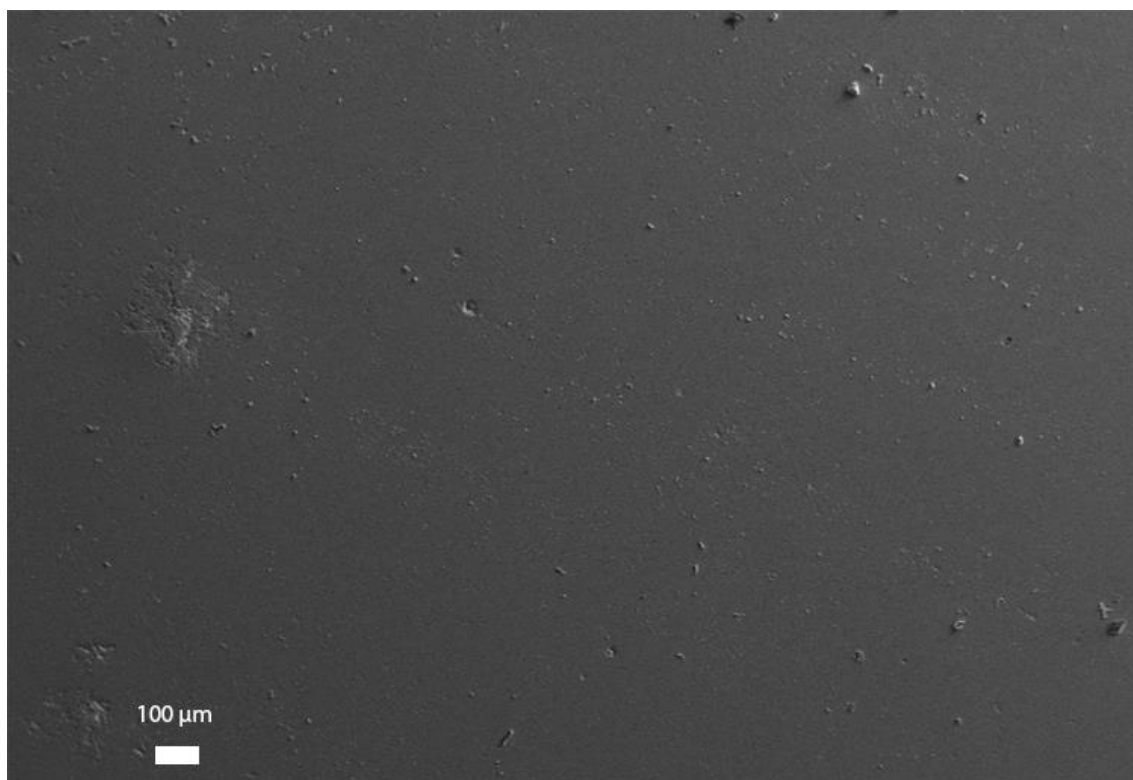


Figure 24 SEM image of sintered LSTZ pellet surface

Figure 23 shows that green body of LSTZ 10% Li excess, even without binder, were able to be compacted nicely by CIP. As a result, the resulting pellet after sintering at 1300 °C for 15 h with mother powder in a conventional tube furnace also shows homogeneous surface, with minimal closed pores. Density measurement by Archimedes principle using ethanol as medium also shows respectable relative density of around 94% dense. Therefore, addition of PVB binder was deemed unnecessary for LSTZ.

3.3.2 Phase Identification by XRD

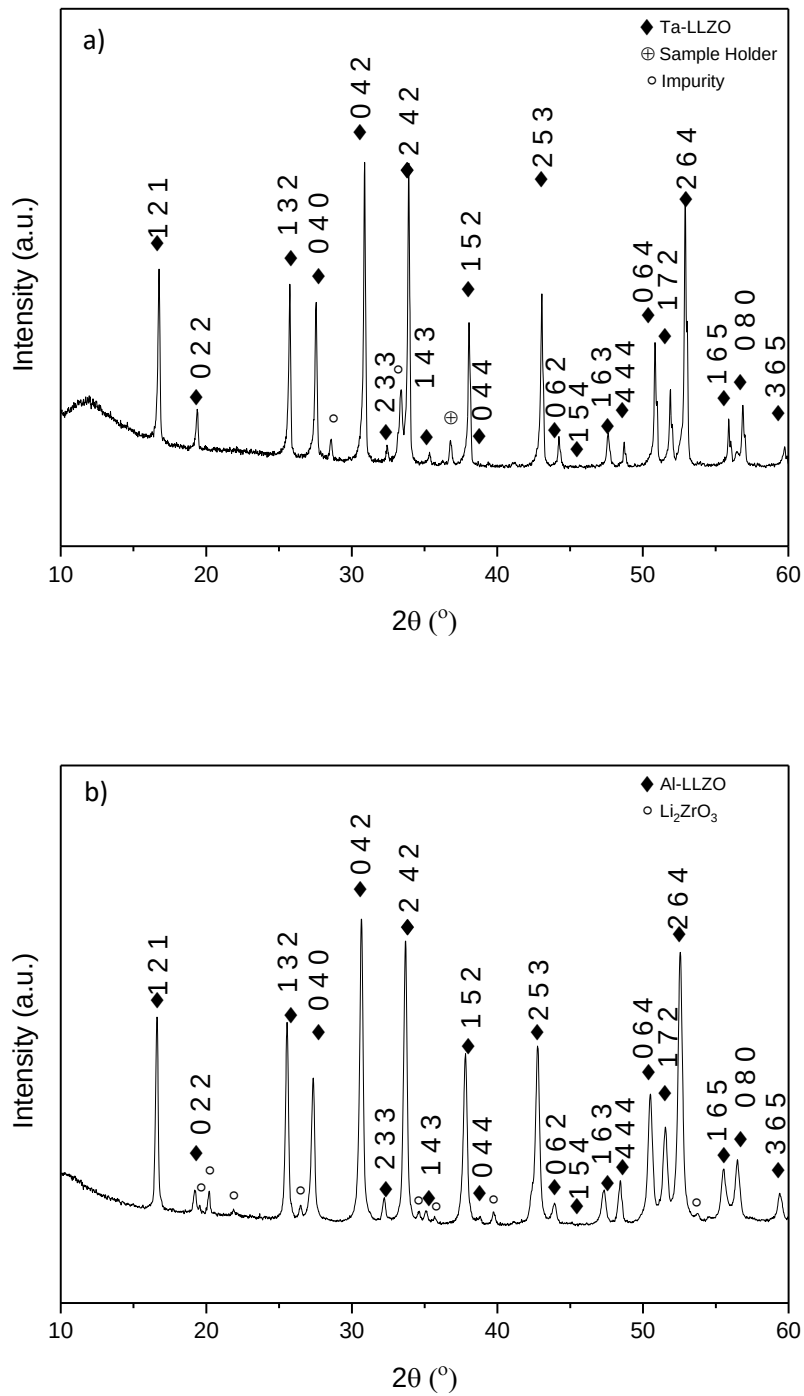


Figure 25 XRD spectra of a) Ta-LLZO 12.5% Li Excess 2 wt% PVB Binder and b) Al-LLZO 12.5% Li excess 2 wt% PVB Binder sintered at 1200 °C for 6 h

Figure 25a shows an almost phase pure XRD spectrum of cubic-garnet Ta-LLZO in Ta-LLZO 12.5% Li excess 2 wt% PVB pellet. The absence of peak splitting of the {022}, {040},

{042}, {242}, etc peaks characteristic of a tetragonal structure further confirms that the sintered pellets were of the higher ionic conductivity cubic-garnet type. This is preferable and crucial for usage as SSE.

Similarly, the absence of tetragonal peak splitting in Figure 25b confirms the phase presence in the Al-LLZO 12.5% Li excess 2 wt% PVB pellets was of the cubic-garnet phase. However, with the Al-LLZO, some Li_2ZrO_3 impurities were present. Further electrochemical analysis, which will be discussed later in this chapter, shows that the small amount of this impurity phase might not affect the conductivity of the pellets too badly, hence further optimization of the synthesis and sintering regime was deemed non-beneficial in view of the time restriction.

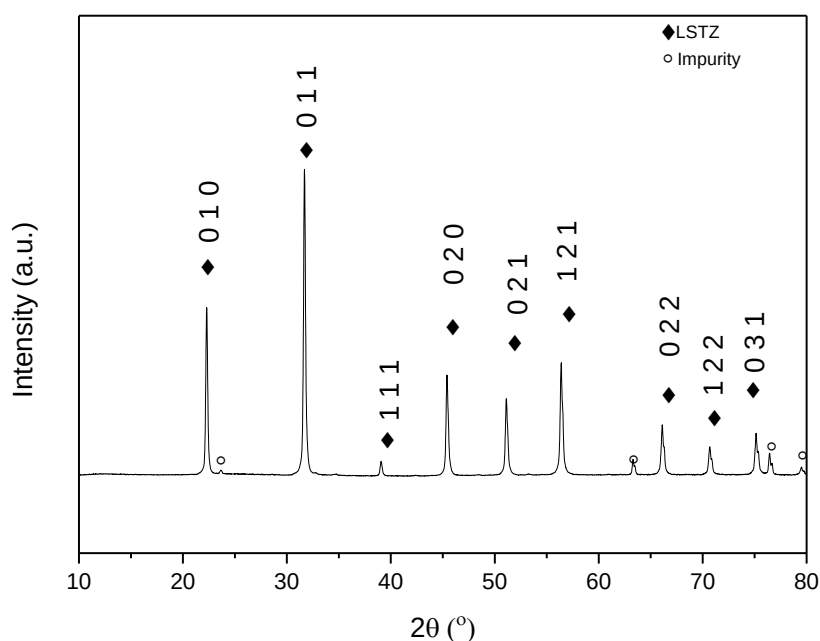


Figure 26 XRD spectra of LSTZ sintered in a conventional tube furnace at 1300 °C for 15 h

LSTZ 10% Li excess pellets have been shown to behave nicely in both the powder processing as well as the sintering step. Figure 26 shows an almost phase pure XRD spectrum of LSTZ in the pellets, with insignificant impurity peaks. However, high sintering temperature well above that of the LLZOs was foreseen to be problematic if layered structure of LSTZ and

LLZO is to be co-sintered. As a result, a plan to lower the sintering temperature of LSTZ by SPS was conceived and deemed necessary to be attempted.

3.3.3 Densification and Microstructure of Pellets by Spark Plasma Sintering

Table 2 Relative density of SPS sintered pellets

Sample	Relative Density of Pellets (%)	Theoretical Density (g/cm ³)
Ta-LLZO 12.5% no binder	98	5.31
LSTZ 10%	98	6.48

In agreement with the literature [6-8], Ta-LLZO and LSTZ sintered via the SPS method yields pellets with higher relative density than can be obtained with conventional sintering, around 98% dense for both.

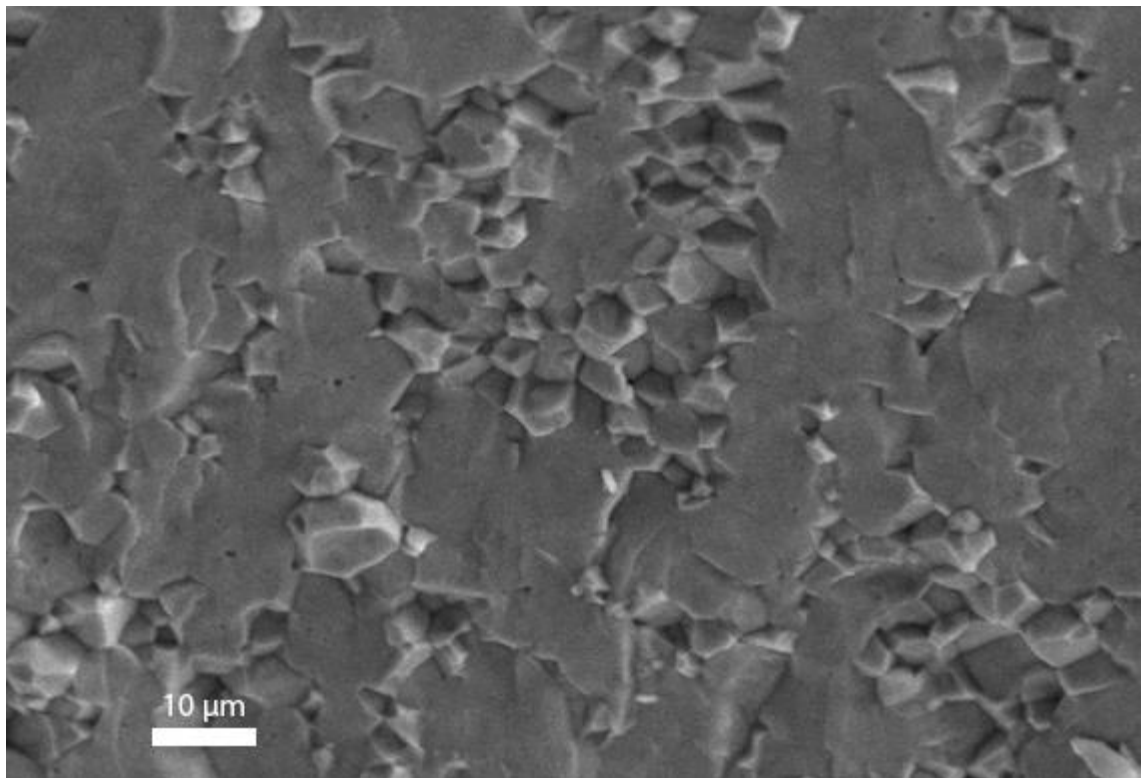


Figure 27 SEM image of a fractured face of a SPS Ta-LLZO sample with 98% relative density.

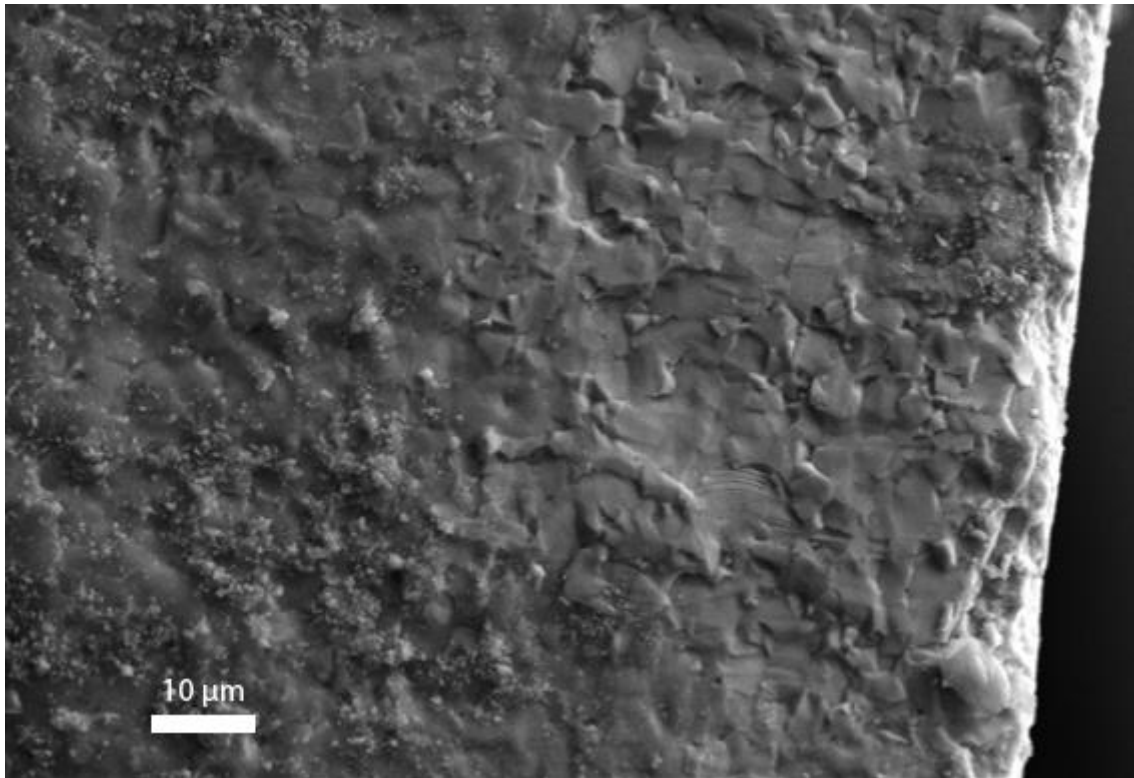


Figure 28 SEM image of a fractured face of a SPS LSTZ sample with 98% relative density.

Figure 27 and Figure 28 show SEM images of unpolished fracture surfaces of Ta-LLZO 12.5% Li excess and LSTZ 10% Li excess sintered using the SPS. Consistent with the high relative density measured by the Archimedes method in Table 2, both images show good densification and little apparent porosity in the pellet. The fracture surface of Ta-LLZO 12.5% Li excess by SPS in Figure 27 shows intergranular fracture, revealing micron-sized faceted grain of the pellet. Figure 28 on the other hand, shows less clearly defined grains, suggesting that the fracture mechanism in the LSTZ 10% Li excess by SPS pellets to be transgranular.

3.3.3.1 Phase Identification

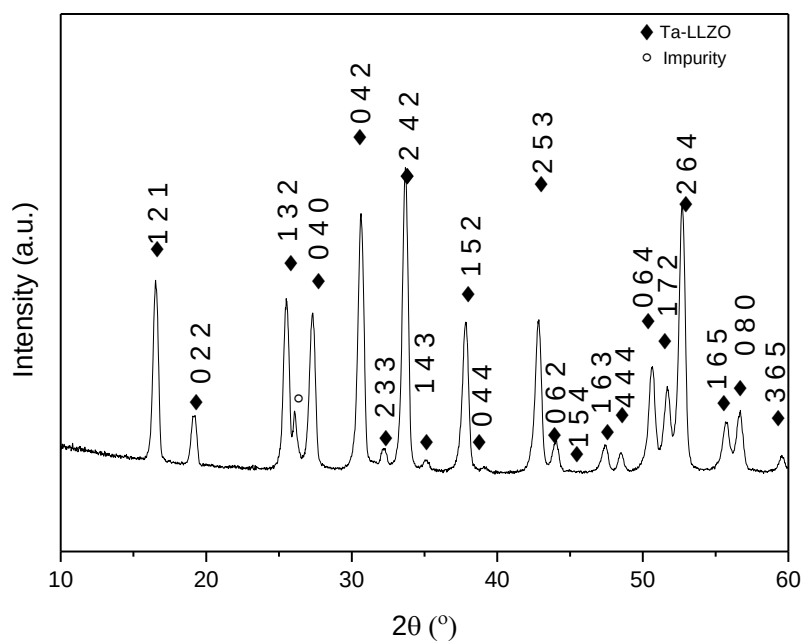


Figure 29 XRD spectra of Ta-LLZO with 12.5% Li excess sintered in a SPS at 1100 °C for 10 min

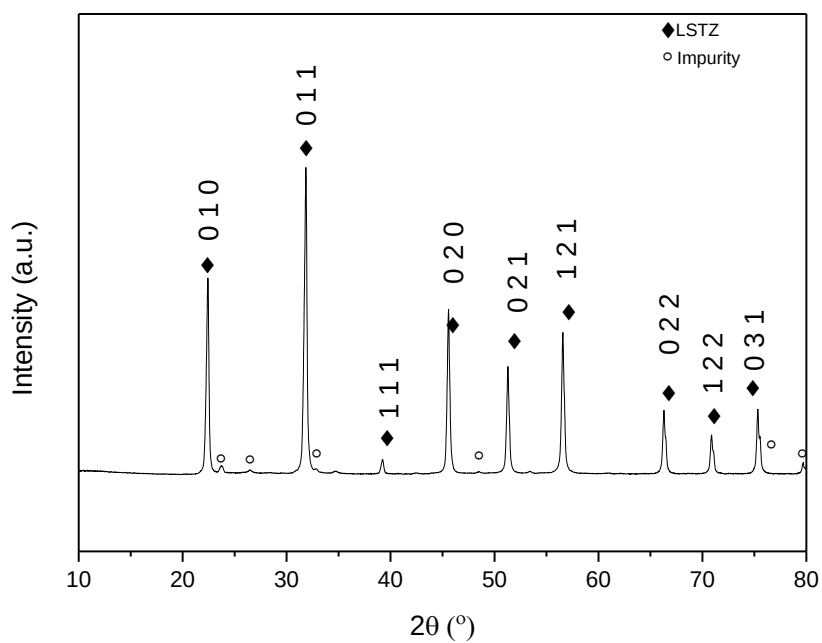


Figure 30 XRD spectra of LSTZ sintered in a SPS at 1100 °C for 10 min

Both Figure 29 and Figure 30 show relatively phase pure XRD spectra of Ta-LLZO and LSTZ respectively. For both samples, a lower sintering temperature and much shorter dwell time of 1100 °C for 10 min were found to be effective in densifying the samples to a high relative density of 98% (Table 2) whilst avoiding impurity phases due to volatilization of Li. Therefore, co-sintering of LSTZ and Ta-LLZO was deemed to be viable and was attempted, as is described in chapter 3 of this thesis.

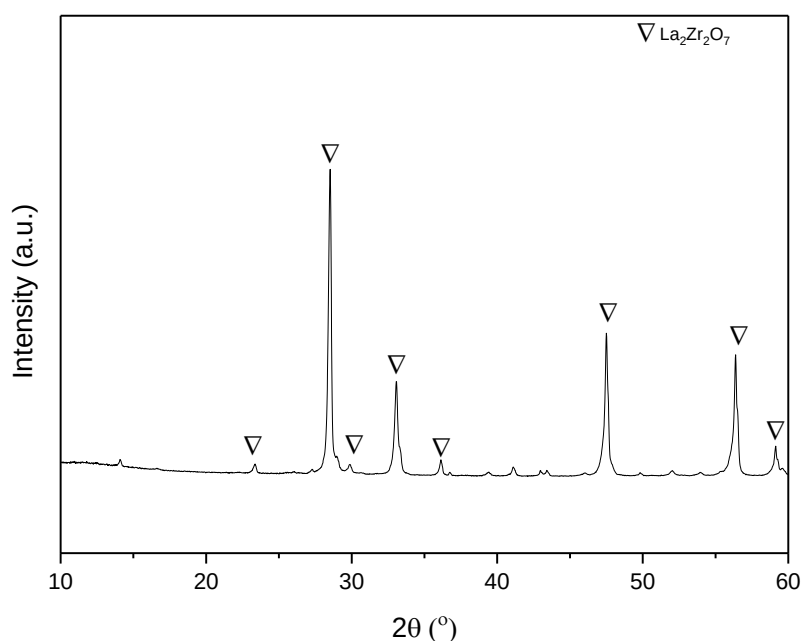


Figure 31 XRD spectra of Al-LLZO with 12.5% Li excess sintered in a SPS at 1100 °C for 10 min

Al-LLZO does not sinter well in the SPS, even with the same treatment as the Ta-LLZO. The lack of mother powder and possibly due to the suboptimal gap between the die set allows Li volatilization, so much so that the pellets are dominated by $\text{La}_2\text{Zr}_2\text{O}_7$ (Figure 31), a Li deficient species commonly seen in LLZO sintering with insufficient Li and excessive Li volatilization [9]. Further optimization and redesign of the die set was required, but unfortunately there was not enough time for this, due to the long turnaround time for ordering a new die set. As a result, attempts at SPS sintering of Al-LLZO were abandoned.

3.3.4 Physical Properties

3.3.4.1 Young's Modulus

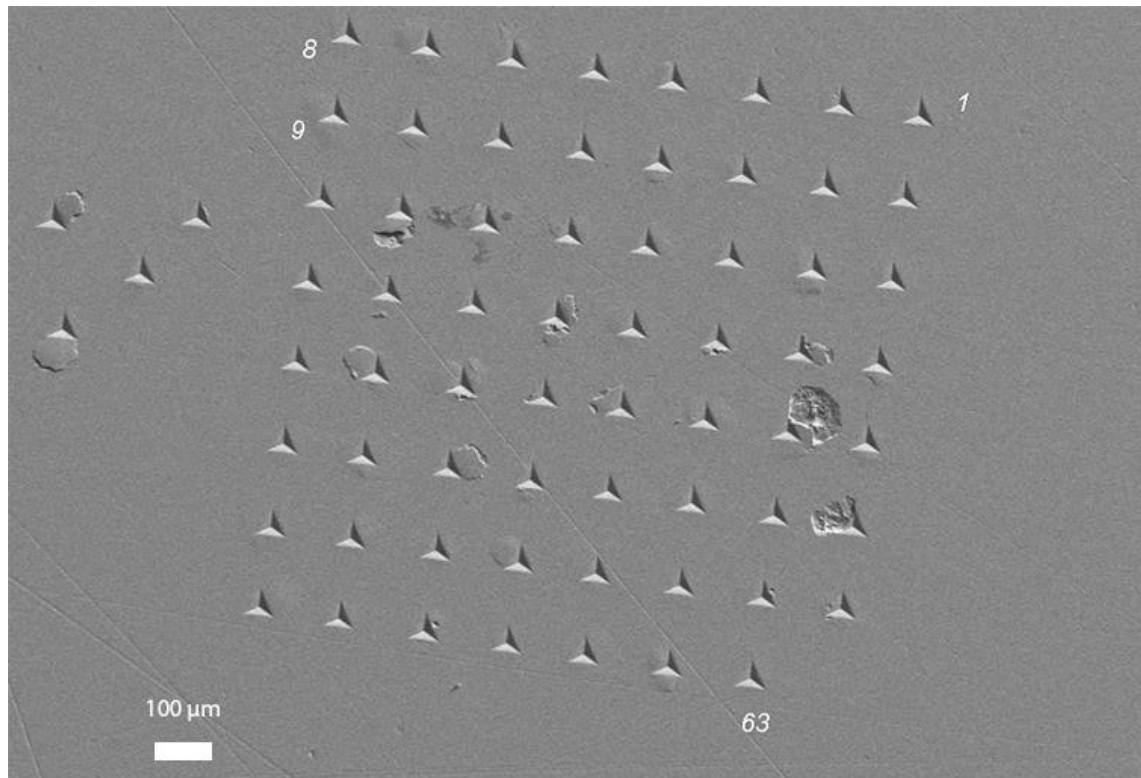


Figure 32 SEM image of nano indents on the polished surface of LSTZ 10% sintered with the SPS

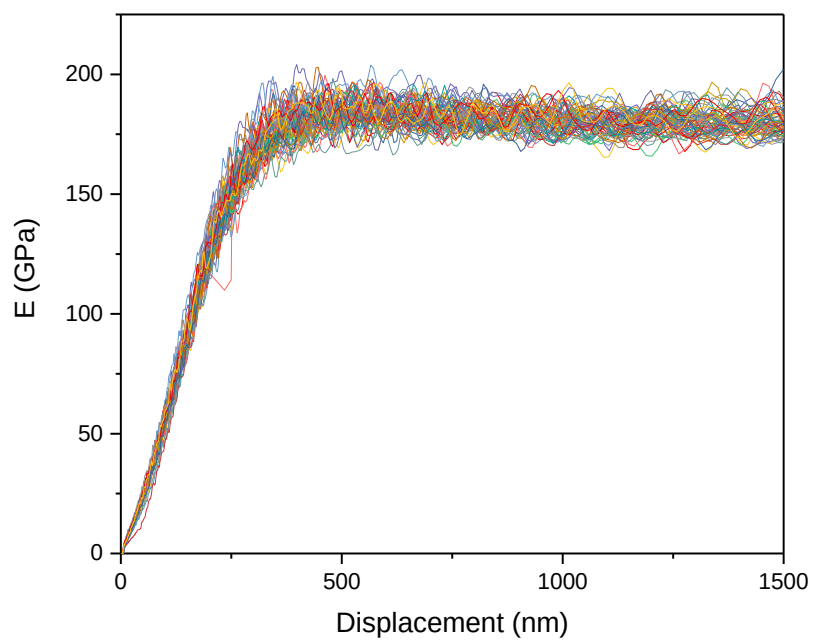


Figure 33 Modulus over tip displacement graph as recorded by nanoindenter

63 individual indents were made on a pristinely polished surface of a high density LSTZ pellet sintered in the SPS (Figure 32). The resulting moduli were plotted against tip displacement in Figure 33. Modulus value plateaued after around 500 nm displacement signifying the bulk value of modulus of the sample had been reached. The mean of hardness and modulus as measured by the nanoindenter was 10 and 181 GPa with a standard error of ± 0.3 GPa and ± 2.4 GPa respectively.

Young's modulus is known to relate to shear modulus by:

Equation 5 [10]

$$\text{Young's modulus} = 2 \times \text{Shear Modulus} (1 + \text{Poisson's ratio})$$

Putting the measured Young's modulus value for LSTZ into Equation 5, assuming a Poisson's ratio of 0.25 typical for oxide ceramics, gives us a shear modulus value for LSTZ to be in the order 72 GPa. This value is exceptionally high compared to the shear modulus of Li metal (4 GPa [11]), hence it should theoretically satisfies Monroe and Newman's criterion for suppression of interfacial roughening [12].

Similar measurements were attempted on Ta-LLZO 12.5% Li excess 2 wt% and Al-LLZO 12.5% Li excess 2 wt% PVB sintered conventionally, however only a few indents were made due to the high porosity of these samples. As a result, the obtained measurements have large standard error and is most likely systematically affected by the presence of pores. Fortunately, prior study on the mechanical properties of Ta and Al doped LLZO has been published by Yu et al. [1], and the published values will be used instead when required.

Table 3 Young's Modulus as measured by Nanoindenter

Sample	Young's Modulus (GPa)	Hardness (GPa)
LSTZ 10% Li excess	181 $\pm$ 2.4	10.0 $\pm$ 0.3
Ta-LLZO 12.5% Li excess 2 wt% PVB	141 $\pm$ 27	8 $\pm$ 3.0
Al-LLZO 12.5% Li excess 2 wt% PVB	108 $\pm$ 26	5 $\pm$ 2.0

3.3.4.2 Thermal Expansion Coefficient

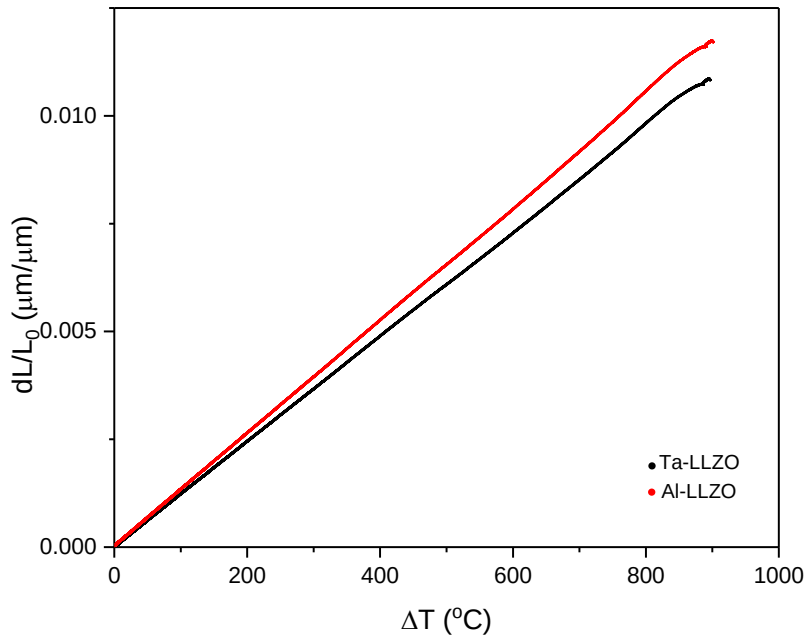


Figure 34 Thermal expansion over temperature change graph for Ta-LLZO and Al-LLZO during cooldown

CTE measurement experiments were done on Ta-LLZO and Al-LLZO pellets stood on its side after grinding the two parallel sides flat. This resulted in initial sample thickness of 6.38 mm and 5.90 mm tall for Ta-LLZO and Al-LLZO respectively. As shown in Figure 34, this configuration resulted in a linear thermal expansion over the measurement temperature, allowing for easy linear fitting to calculate the CTE of each sample using Equation 3.

For this project, the thermal shrinkage of the samples during the cooldown is of main interest, therefore experiments were done recording CTE during the cooling down part of the regime. The values of $1.40 \times 10^{-5} \text{ K}^{-1}$ for Ta-LLZO and $1.14 \times 10^{-5} \text{ K}^{-1}$ for Al-LLZO were obtained.

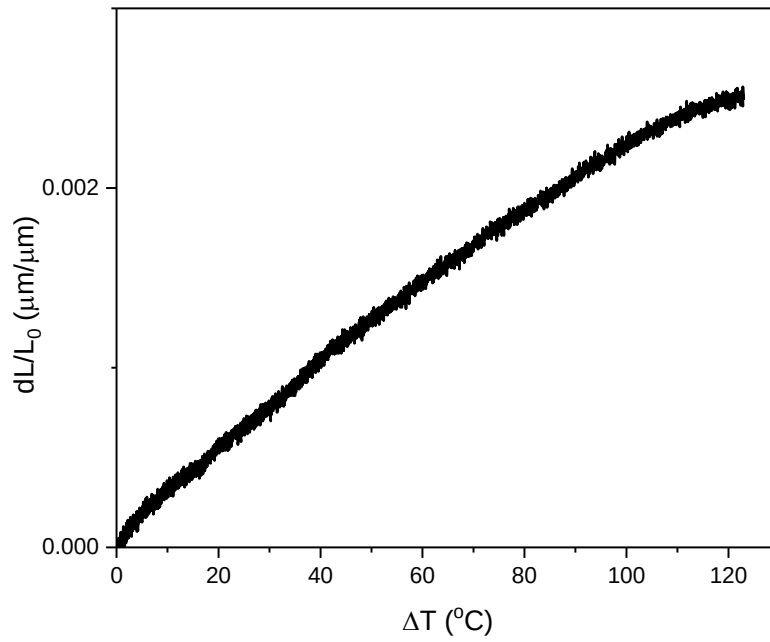


Figure 35 Thermal expansion over temperature change graph for LSTZ during cooldown

CTE measurement of LSTZ using the dilatometer was also attempted. However, due to the thinner sample (1.5 mm), the result of this measurement is to be treated with some caution. The measurement was taken from around 100 °C to 220 °C, as attempts of measurement up to higher temperature was not successful due to instrument breakdown. In view of the LSTZ being unsuitable for the laminates, as will be discussed in the next chapter, repeat measurement of the LSTZ to obtain better result was not attempted. The curve was linearly fitted, resulting in a CTE value for LSTZ of $2.25 \times 10^{-5} \text{ K}^{-1}$. Reports of the measured CTE values are summarized in Table 4.

Table 4 CTE as measured by dilatometer

Sample	Thermal Expansion Coefficient (10^{-5} K^{-1})
Ta-LLZO	1.40 ± 0.2
Al-LLZO	1.14 ± 0.2
LSTZ	2.25 ± 1.0

3.3.5 Electrochemical Properties

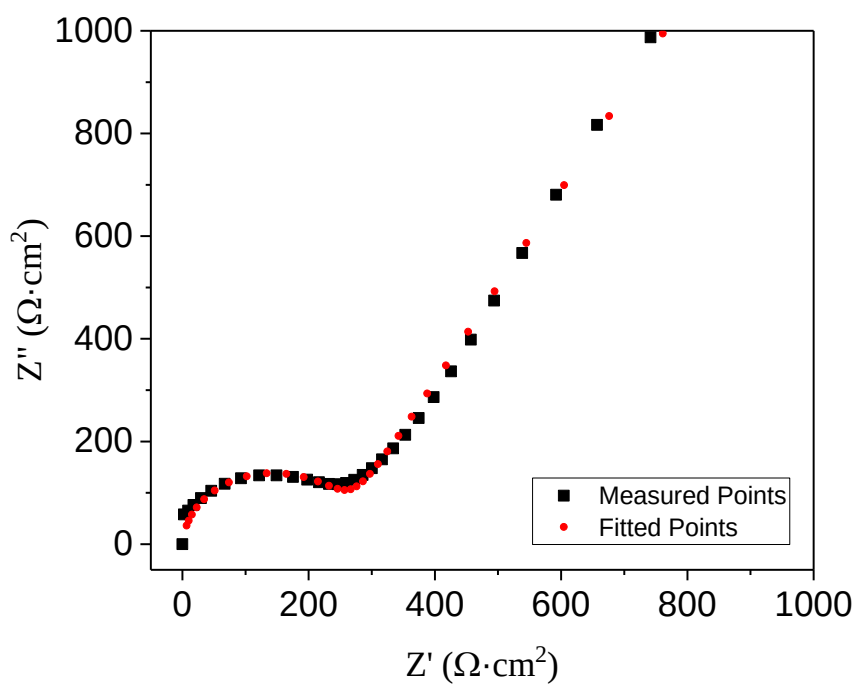


Figure 36 Nyquist plot of EIS measurement for conventionally sintered Ta-LLZO

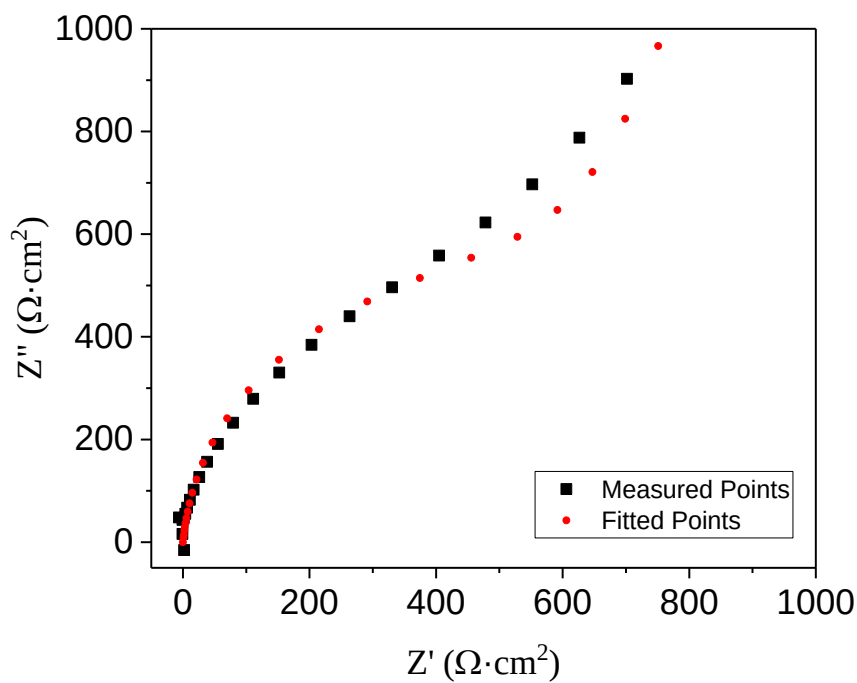


Figure 37 Nyquist plot of EIS measurement for SPS sintered Ta-LLZO

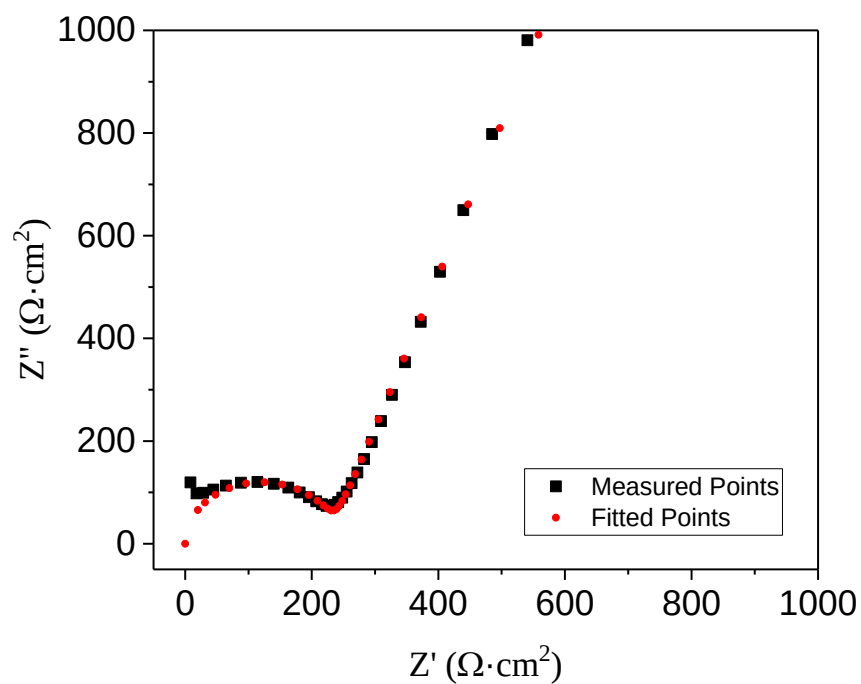


Figure 38 Nyquist plot of EIS measurement for conventionally sintered ALLZO

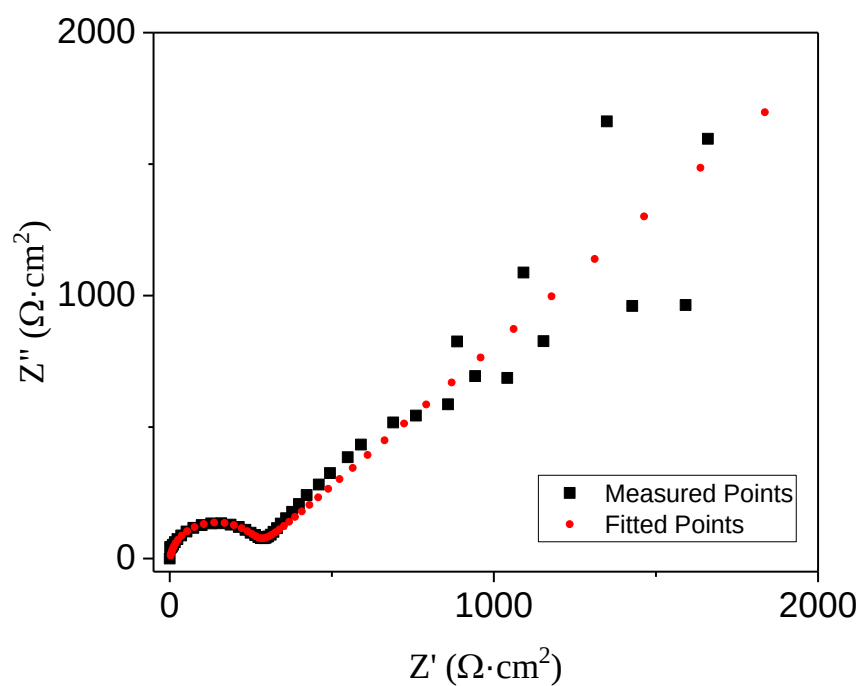


Figure 39 Nyquist plot of EIS measurement for conventionally sintered LSTZ

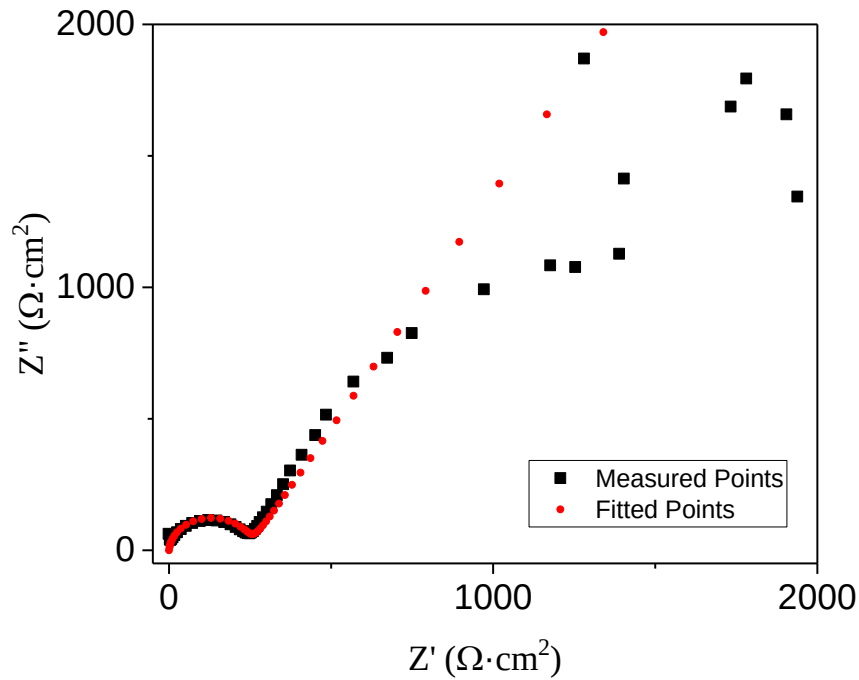


Figure 40 Nyquist plot of EIS measurement for SPS sintered LSTZ

Table 5 Measured conductivity of samples after taking geometry of samples into consideration

Sample	Measured conductivity at 30 °C ($\times 10^{-4} \text{ S cm}^{-1}$)	Surface Area ($\times 10^{-1} \text{ cm}^2$)	Thickness ($\times 10^{-1} \text{ cm}$)
Ta-LLZO 12.5% Li excess 2wt% PVB	4.56	6.05	1.05
Ta-LLZO 12.5% Li excess SPS	4.66	5.03	2.70
Al-LLZO 12.5% Li excess 2wt% PVB	3.85	5.61	0.70
LSTZ 10% Li excess	7.05	7.31	1.80
LSTZ 10% Li excess SPS	7.99	7.85	1.85

EIS measurement results were plotted as Nyquist plots, imaginary impedance over real impedance, in Figure 36 to Figure 40. In general, the resulting calculated conductivities of samples were respectably high in the range of values reported in the literature [13-16], and generally in the 10^{-4} magnitude required for use as SSE, as summarized in Table 5.

For Ta-LLZO sintered by SPS (Figure 37), although the Nyquist plot suggests a resistance significantly higher than the other samples, particularly compared with conventionally sintered Ta-LLZO (Figure 36), the tested sample was also thicker and of a smaller contact diameter. The resulting conductivity of $4.66 \times 10^{-4} \text{ S cm}^{-1}$ for SPS sintered Ta-LLZO is slightly higher than that of conventionally sintered Ta-LLZO with $4.56 \times 10^{-4} \text{ S cm}^{-1}$, owing to the much higher density of the SPS sintered pellets. There is potential that the value for the conductivity of the SPS sintered Ta-LLZO can be even higher, as the sample used for EIS measurement was possibly reduced due to the carbon-rich reducing atmosphere of the SPS chamber, which is a common occurrence for oxide ceramics sintered by SPS. A simple heat treatment in oxygen atmosphere should be able to remedy this, but further optimization was needed considering the potential for volatilization of Li from Ta-LLZO at heightened temperature.

It is also worth noting that the Nyquist plots for LSTZ in Figure 39 and Figure 40 showed a possible secondary semicircle of much lower conductivity at the tail end of the clearly defined semicircle. This might represent the grain boundary contribution to resistivity that is known to be larger in other perovskite type oxide SSE [14], and thus detrimental to the usability as SSE. However, due to the noisy data just adjacent to the tail end, possibly caused by electrode reaction with samples, it was not possible to determine if these are indeed real contributions from grain boundaries. Similar semicircles were not identified as a contribution of grain boundary resistivity in the work by Inada et al. [14], thus it was also not identified as such in this project.

3.4 Conclusion

In this chapter, conventional sintering and SPS were attempted and powders synthesized in the previous chapter were densified to different degrees of density relative to theoretical density. The physical and electrochemical properties of the densified pellets were

characterized and reported. The Young's modulus of LSTZ was reported here for the first time, with a mean value of 181 ± 2.4 GPa, after 63 separate indents were made on the nanoindenter.

Another finding of note is the CTE values of sintered Ta-LLZO and Al-LLZO measured up to a maximum temperature of 1000°C, with values of $1.40 \times 10^{-5} \text{ K}^{-1}$ for Ta-LLZO and $1.14 \times 10^{-5} \text{ K}^{-1}$ for Al-LLZO. A more uncertain value for LSTZ was also measured to be an exceptionally high $2.25 \times 10^{-5} \text{ K}^{-1}$. These values will be important to calculate the maximum possible residual compressive stress in the laminate as will be discussed in the next chapter.

EIS measurements also showed that the pellets made from powders previously synthesized were sufficiently conductive for use as SSE to be comparable with current Li ion batteries [17]. This gave confidence that the densification of green bodies, and synthesis of the powders, had been substantially successful and that trials to make laminated structured pellets should proceed as planned.

3.5 References

1. Yu, S., R.D. Schmidt, . . . D.J. Siegel, *Elastic Properties of the Solid Electrolyte Li₇La₃Zr₂O₁₂ (LLZO)*. Chemistry of Materials, 2016. **28**(1): p. 197-206.
2. Murugan, R., V. Thangadurai, and W. Weppner, *Fast Lithium Ion Conduction in Garnet-Type Li₇La₃Zr₂O₁₂*. Angewandte Chemie International Edition, 2007. **46**(41): p. 7778-7781.
3. Sharafi, A., S. Yu, . . . J. Sakamoto, *Impact of air exposure and surface chemistry on Li–Li₇La₃Zr₂O₁₂ interfacial resistance*. Journal of Materials Chemistry A, 2017. **5**(26): p. 13475-13487.
4. Kumar, P.J., K. Nishimura, . . . H. Suzuki, *A novel low-temperature solid-state route for nanostructured cubic garnet Li₇La₃Zr₂O₁₂ and its application to Li-ion battery*. RSC Advances, 2016. **6**(67): p. 62656-62667.
5. Huang, X., Y. Lu, . . . Z. Wen, *Manipulating Li₂O atmosphere for sintering dense Li₇La₃Zr₂O₁₂ solid electrolyte*. Energy Storage Materials, 2019. **22**: p. 207-217.
6. Zhu, H. and J. Liu, *Emerging applications of spark plasma sintering in all solid-state lithium-ion batteries and beyond*. Journal of Power Sources, 2018. **391**: p. 10-25.
7. Baek, S.-W., J.-M. Lee, . . . Y. Park, *Garnet related lithium ion conductor processed by spark plasma sintering for all solid state batteries*. Journal of Power Sources, 2014. **249**: p. 197-206.
8. Xue, J., K. Zhang, . . . B. Luo, *Spark plasma sintering plus heat-treatment of Ta-doped Li₇La₃Zr₂O₁₂ solid electrolyte and its ionic conductivity*. Materials Research Express, 2020. **7**(2): p. 025518.
9. Geng, H., K. Chen, . . . C. Nan, *Formation Mechanism of Garnet-Like Li₇La₃Zr₂O₁₂ Powder Prepared by Solid State Reaction*. Rare Metal Materials and Engineering, 2016. **45**(3): p. 612-616.
10. Callister, W.D. and D.G. Rethwisch, *Materials science and engineering: an introduction*. Vol. 9. 2018: Wiley New York.
11. Harry, K.J., K. Higa, . . . N.P. Balsara, *Influence of electrolyte modulus on the local current density at a dendrite tip on a lithium metal electrode*. Journal of The Electrochemical Society, 2016. **163**(10): p. A2216.
12. Monroe, C. and J. Newman, *The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces*. Journal of The Electrochemical Society, 2005. **152**: p. A396-A404.
13. Shin, D.O., K. Oh, . . . K. Kang, *Synergistic multi-doping effects on the Li₇La₃Zr₂O₁₂ solid electrolyte for fast lithium ion conduction*. Scientific Reports, 2015. **5**(1): p. 18053.
14. Inada, R., K. Kimura, . . . Y. Sakurai, *Synthesis and lithium-ion conductivity for perovskite-type Li₃/8Sr₇/16Ta₃/4Zr₁/4O₃ solid electrolyte by powder-bed sintering*. Solid State Ionics, 2014. **261**: p. 95-99.
15. Thangadurai, V., S. Narayanan, and D. Pinzaru, *Garnet-type solid-state fast Li ion conductors for Li batteries: critical review*. Chemical Society Reviews, 2014. **43**(13): p. 4714-4727.
16. Luo, J., S. Zhong, . . . C.-A. Wang, *High Li⁺-conductive perovskite Li₃/8Sr₇/16Ta₃/4Zr₁/4O₃ electrolyte prepared by hot-pressing for all-solid-state Li-ion batteries*. Solid State Ionics, 2019. **338**: p. 1-4.
17. Horii, M., R.J. Christianson, . . . J.C. Bachman, *Modeling the effect of electrolyte microstructure on conductivity and solid-state Li-ion battery performance*. Journal of Power Sources, 2022. **528**: p. 231177.

Chapter 4 Laminate Sintering

4.1 Objective

The previous chapters establish that for this project, phase pure powders of Ta-LLZO, Al-LLZO, and LSTZ were successfully synthesized and densified by means of conventional tube furnace sintering and SPS. Having laid the groundwork, the project now seeks to address the main question: is it possible to make laminated SSE, and what effects does it have to the electrochemical and physical properties compared to monolithic SSE pellets? Furthermore, can these modifications in the laminated SSE inhibit dendritting?

In parallel, Will Connolly, a Part II student in our lab [1] has also attempted to address these questions. His attempt of sandwiching a composition of Ta-LLZO and Al-LLZO was however unsuccessful, as conventionally sintering the laminated green body resulted in catastrophic delamination and cracking in the pellet. Learning from his thesis, it was established early that delamination due to differences in CTE and/or rate of shrinkage during sintering needs to be addressed if laminated SSEs are to be made.

Fortunately, looking back even further, our research group have had some expertise in making a laminated ceramic structure of a different composition. In one publication, Dancer et al. were able to fabricate alumina – silicon carbide two-layered composites by introducing pressure to the sintering step, by mean of hot pressing [2]. Therefore, some insights from those previous projects will be incorporated, and an innovative solution will be suggested and explored in this chapter of the project.

4.2 Experimental Methods

4.2.1 Order of layers

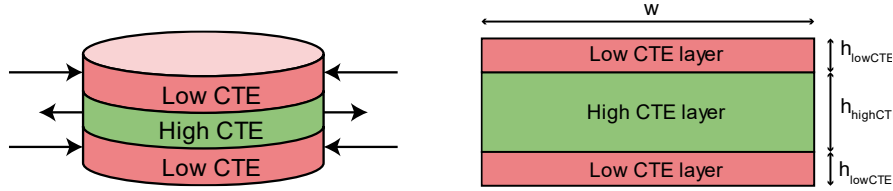


Figure 41 Schematics of the layers in a 3-layer laminated ceramic pellets

In order to induce compressive stresses on the outer layers of the 3-layered laminates during cooling down from sintering temperature, the outer layer must be a composition possessing lower CTE compared to the middle layer, as shown in Figure 41. As determined in the previous chapter (Table 4) in decreasing order of CTE: LSTZ > Ta-LLZO > Al-LLZO. Two compositions of laminates will be attempted here, Ta-LLZO – LSTZ – Ta-LLZO and Al-LLZO – Ta-LLZO – Al-LLZO.

Having established the order of the layers in the laminate, it is possible to calculate the maximum allowable compressive stress (and tensile stress) that the layers in the laminate will experience. The residual stress due to CTE mismatch involves differences in strain caused by the different capacity for shrinkage during cool down, such that the higher CTE layer wants to shrink more but is held back by the lower CTE layer's lower shrinkage. This mismatch in strain can be put into mathematical terms as:

Equation 6

$$\epsilon_{Thermal\ lowCTE} + \epsilon_{Residual\ lowCTE} = \epsilon_{Thermal\ highCTE} + \epsilon_{Residual\ highCTE}$$

In Equation 6, there are two terms of strains for each of the laminate layer. The first, $\epsilon_{Thermal}$, explains the change in length due to thermal expansion, such that:

Equation 7

$$\epsilon_{Thermal} = \alpha \Delta T$$

α here denotes the CTE of each respective layer and ΔT denotes the change in temperature, mainly from sintering temperature to room temperature.

The second term in Equation 6, $\epsilon_{Residual}$, denotes the elastic contribution due to the biaxial residual stress induced in the laminate. This term can be further expanded into:

Equation 8

$$\epsilon_{Residual} = \frac{\sigma_{Residual}}{E_{Residual}} (1 - \nu)$$

As customary, for each respective layer $\sigma_{Residual}$ denotes the residual stress magnitude, $E_{Residual}$ the Young's modulus, and ν the Poisson's ratio, which can be estimated to be 0.25 for oxide ceramics, where actual data is not available. Combining Equation 7 and Equation 8 into Equation 6 gives:

Equation 9

$$\alpha_{lowCTE} \Delta T + \frac{\sigma_{lowCTE}}{E_{lowCTE}} (1 - \nu) = \alpha_{highCTE} \Delta T + \frac{\sigma_{highCTE}}{E_{highCTE}} (1 - \nu)$$

In addition to Equation 9, the forces in the low CTE layers must cancel out with those in the high CTE layer if the laminate is to achieve equilibrium. From this condition we can also derive:

Equation 10

$$2F_{lowCTE} + F_{highCTE} = 0$$

$$F = \sigma h w$$

with F denoting the acting force, h the thickness of the respective layer, and w the width of the pellet. Rearranging Equation 10, with w_{lowCTE} and $w_{highCTE}$ cancelling out, gives us:

Equation 11

$$\sigma_{highCTE} = - \frac{2(\sigma_{lowCTE} h_{lowCTE})}{h_{highCTE}}$$

Substituting Equation 11 into Equation 9 gives us the generalized equation for the compressive stress induced by the CTE mismatch as:

Equation 12

$$\sigma_{lowCTE} = \frac{(\alpha_{highCTE} - \alpha_{lowCTE})\Delta T}{(1 - \nu)} \times \frac{h_{highCTE} E_{highCTE} E_{lowCTE}}{(h_{highCTE} E_{highCTE} + 2h_{lowCTE} E_{lowCTE})}$$

Table 6 Young's modulus of Ta-LLZO and Al-LLZO pellets from the literature [3]

Sample	Young's Modulus (GPa)
Ta-LLZO	153.8 ± 2.7
Al-LLZO	150.3 ± 2.2

Putting in Young's modulus values from Table 3 in chapter 3 for LSTZ and Table 6 for Ta-LLZO and Al-LLZO, as well as CTE values from Table 4, we get the maximum possible residual stresses due to CTE mismatch when $h_{lowCTE} \ll h_{highCTE}$ upon cooldown from 1200 °C. It is important to note that the Young's modulus values from the literature is for fully dense materials, therefore the maximum values presented in Table 7 below does not take into consideration the porosity which tends to reduce the value of the Young's modulus of the samples.

Table 7 Maximum compressive stress possible due to CTE mismatch

Laminate	Maximum compressive stress in a low CTE layer (MPa)
Ta-LLZO – LSTZ – Ta-LLZO	20×10^2
Al-LLZO – Ta-LLZO – Al-LLZO	5.9×10^2

4.2.2 SPS Sintering of Laminated Ceramics

SPS die sets were first prepared by putting in 0.5 g of low CTE powder into a graphite foil lined SPS die (Figure 18). Another plunger was used to tamp down and partially compact this layer inside the die, before 1.5 g of high CTE powder was carefully put inside the die. This layer was again tamped down with a plunger before the final layer, 0.5 g of low CTE powder, was added into the die. The die was then assembled as in section 3.2.3.

The assembled SPS die set was then sintered inside the SPS in vacuum with a regime similar to that in section 3.2.3: a heating rate of 100 °C/min ramps up to 1000 °C with constant 20 MPa pressure, before a ramp up to 1100 °C with slower heating rate of 50 °C/min and 40 MPa then a dwell for 10 min. The die set was then allowed to cool down naturally, without applied pressure. This cooling rate can predictably be lower than the heating rate, as it took around 2 h for the die set to be at a temperature safe for handling.

4.2.3 Weighted Sintering of Laminated Ceramics

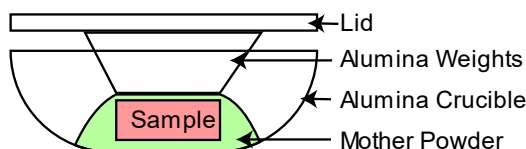


Figure 42 Cross sectional illustration of the weighted sintering setup

As it was obvious that the external pressure exerted in SPS sintering helps in preventing delamination of the laminates, a simpler, innovative method was devised for this project for the sintering of laminated SSE pellets in a conventional tube furnace. Laminated green body pellets were first prepared by uniaxial pressing. First, 0.3 g of Al-LLZO 12.5 %Li excess 2 wt% PVB was put into a 10 mm steel die. The hydraulic press was used to tamp down this first layer by applying the minimum pressure possible, just until the pressure gauge indicator needle started to lift off zero. A second layer of 0.9 g Ta-LLZO 12.5% Li excess 2 wt% PVB was put in and tamped again with the press. A final layer of 0.3 g Al-LLZO 12.5

%Li excess 2 wt% PVB was then carefully put into the die, and the pellet was subjected to 120 MPa pressure to form the laminate pellet. The formed pellets were then transferred into a vinyl sleeve and put inside a CIP chamber with 300 MPa pressure, identical with the step in section 3.2.1.

After the laminated green bodies were formed, they were put inside an alumina crucible with a bed of Al-LLZO mother powder. More mother powder was put on top of the pellets to fully cover the laminate pellets. Some alumina weights were then piled up on top, such that 12.5 kPa of pressure was applied to the pellets. An alumina lid was then put on top of the weights (Figure 42), before transferring the crucibles into a conventional tube furnace. The samples were then sintered with 5 °C/min heating rate, with a 1 h debinding step at 600 °C, up to a temperature of 1200 °C for 6 h dwell time.

As a control, monolithic pellets of 1.5 g Al-LLZO 12.5% Li excess 2 wt% PVB were also sintered using this technique to confirm that differences in the laminate's properties were not caused by the different sintering technique.

This technique was found to be useful for sintering of Al-LLZO – Ta-LLZO – Al-LLZO laminates, as each constituent in this laminate was shown to densify at the same temperature and dwell time. In addition, this method is potentially more effective in preventing lithium loss, especially in Al-LLZO, as mother powder was able to be used, just like in a conventional sintering setup.

4.2.4 Characterization

4.2.4.1 Electron Microscopy

Laminates were sectioned vertically using a slow speed saw with a diamond tipped wafering blade (Isomet, Buehler) to expose the cross-sectional face. Cross-sections and surfaces of pellets to be observed under the SEM (Evo, Zeiss) were then polished with silicon carbide pads and oil-based diamond suspension paste to the same standard as in section

3.2.4. Pellets were then put on SEM stubs and sputtered with 0.5 nm carbon (ACE600, Leica) before being inserted into the SEM.

4.2.4.2 Phase Characterization

XRD scans similar to that in section 3.2.5.2 of the laminates and control Al-LLZO pellets were conducted to verify the phases in the pellets surface.

EDX maps were made using an SEM mounted EDX detector (Oxford Instruments on Zeiss Merlin) to track the elemental compositions on the surface of pellets as well as cross sections of laminates.

4.2.4.3 Polishing

Sintered sample pellets were ground and polished, with similar technique as in section 3.2.4, to eliminate risks of impurity surface reaction layer. Weighted sintered samples were ground to 2.7 – 3.0 mm thickness, to be as consistent as possible for future electrochemical tests.

4.2.4.4 EIS

Similar sample preparation processes to section 3.2.5.4 were followed for polished samples of Ta-LLZO – LSTZ – Ta-LLZO, Al-LLZO – Ta-LLZO – Al-LLZO, and the control sample of Al-LLZO with Au blocking electrode. Also similar to the EIS procedure previously done for monolithic samples, continuous sweeps from 35 MHz to 5 Hz were done with 10 points per decade at 30 °C.

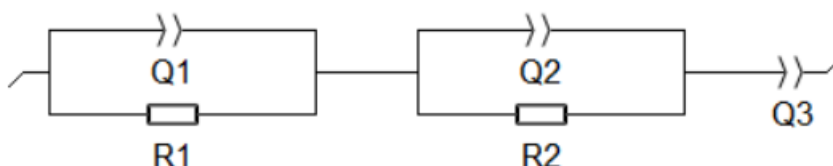


Figure 43 Diagram of Equivalent circuit used for Nyquist plot semicircle fitting. Q1, Q2 and Q3 represent constant phase elements while R1 and R2 represent resistors.

A modified equivalent circuit (Figure 43), slightly different from that of the monolithic samples in the previous chapter was used for the fitting of the resulting Nyquist plot. The modification was an addition of a parallel set of resistor (R2) and constant phase element (Q2) to take into account the extra layer of different SSE components present in the laminates.

4.2.5 Presence of Residual stress

Accurate quantification of residual stress in a laminated ceramic is difficult, as any modification before and during measurement done to the sample might affect the stress in the pellet to maintain equilibrium. A straightforward method, using Vickers indentation, was attempted in this project and measures the residual stress by measuring how much resistant the laminated pellets are to cracking compared with the non-laminated pellet. Anstis et al. evaluate the analysis of radial crack length to quantify fracture toughness in 1981 [4].

A series of Vickers indents were made on Al-LLZO – Ta-LLZO – Al-LLZO before a load of 0.3 kg for 15 s was chosen to be most appropriate. It was found that higher load caused spalling, another route by which energy might be dispersed, and thus was not ideal for radial crack length measurement. Sites where porosity can be avoided, both for the indents and the potential cracks, were chosen as porosity might affect the overall fracture behavior and skews the result of the measurement.

The resulting indents and cracks they cause were observed under optical microscopy (Axioskop 2 MAT, Carl Zeiss) immediately and SEM microscope (EVO, Zeiss) later. For SEM specimens, a similar sample preparation of mounting onto SEM stubs and coating with carbon to section 3.2.5.1 was followed.

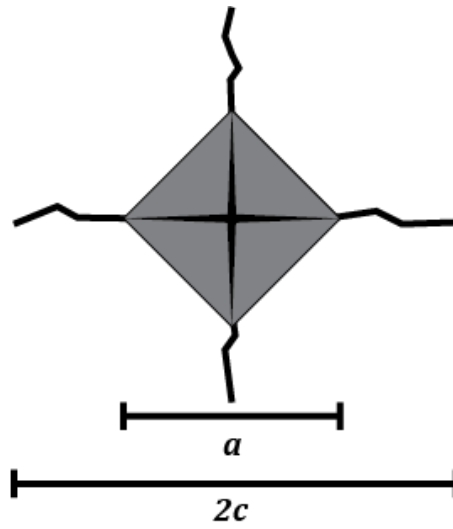


Figure 44 Illustration of a Vickers indent and the corner cracks.

Measurements were taken from the images of the indents. Taking the average of the indentation diagonals gives a value for a , while an average of the crack lengths as measured from the center of the indent gives us a radial crack radius c , as shown in Figure 44. From these measurements, the hardness and fracture toughness of the sample can be calculated, as evaluated by Anstis and Chantikul et al. [4], by Equation 13 and Equation 15:

Equation 13

$$H = P/\alpha_0 \left(\frac{a}{2}\right)^2$$

Hardness calculation by Equation 13 is quite straightforward. Hardness, denoted by H , can be calculated by dividing the tip load of the indenter (P) by a constant (α_0) and the square power of half the indentation diagonal. This equation can also be better understood as dividing the tip load by the area of the indent, such that $\alpha_0=2$ in Equation 13, so that:

Equation 14

$$H = 2P/a^2$$

Fracture toughness (K_c) can be calculated as the indentation plastic zone contribution to the stress intensity factor at crack arrest. Equation 15 describes this in

relation to a material independent constant ($\S_V^R$) and crack radius at equilibrium (c) and is dependent on the square root of Young's modulus over hardness, giving:

Equation 15

$$K_c = \S_V^R \left(\frac{E}{H} \right)^{\frac{1}{2}} \frac{P}{c^{\frac{3}{2}}}$$

The value for $\S_V^R = 0.016$ is usually accepted based on averaging of experimental values of well-behaved materials [4].

To get the fracture toughness of laminated ceramics, where compressive residual stress is assumed to be present, an additional term to account for the residual stress contribution to stress intensity factor needs to be introduced to Equation 15. This thermal residual stress contribution is given by Equation 16.

Equation 16

$$K_a = 2\sigma_a m(c/\pi)^{\frac{1}{2}}$$

The thermal residual stress intensity factor (K_a) describes the contribution of the residual stress (σ_a), and is also dependent on the edge correction constant ($m=1.12$) for semicircular crack.

K_a can be combined into Equation 15 as both contributions to K are mode I, which leads to Equation 17.

Equation 17

$$K_c = \S_V^R \left(\frac{E}{H} \right)^{\frac{1}{2}} \frac{P}{c^{\frac{3}{2}}} + 2.24 \sigma_a \left(\frac{c}{\pi} \right)^{\frac{1}{2}}$$

Due to the presence of pores in the samples tested, the Young's modulus value from the literature (Table 6), which assumes almost full density, must be adjusted for the effect

of the porosity. The relation between porosity with Young's modulus has been studied [5], and can be calculated with Equation 18.

Equation 18

$$E = E_0 \exp(-bp)$$

E_0 represents full density Young's modulus, b an empirically fitted parameter which has been found to be around 4 for oxide ceramics with 0 – 40% porosity [5], and p is the porosity of the materials. Porosity can be assumed to be the complement to 1 of the relative density of the sample.

4.2.6 Galvanostatic Cycling

For galvanostatic cycling experiments to be conducted properly with reliable results, the samples being tested (SSEs in this case) need to be conductive enough to allow for ion migration under DC current. On view of the low conductivity achieved in Ta-LLZO – LSTZ – Ta-LLZO laminates, galvanostatic cycling experiments were done only on Al-LLZO – Ta-LLZO – Al-LLZO and the corresponding Al-LLZO controls.

Prior to galvanostatic cycling, pre-ground samples of Al-LLZO – Ta-LLZO – Al-LLZO and control Al-LLZO were again polished inside a glovebox with grade 800, 1200, and 2400 silicon carbide pads, as well as 1 μ m diamond lapping film, to remove any Li₂CO₃ surface layer that might be present due to the pellet's contact with air. After a sufficiently mirror-like finish was achieved, the samples' thickness was measured. The samples were then dipped into 1 M HCl for 10 s to react any remaining Li₂CO₃ surface impurity.

Acid treated samples were then assembled into metallic Li|sample|metallic Li cells, using Kapton tapes as masks such that a 3 mm diameter interfaces between the metallic Li electrodes and the samples were maintained. Copper tapes were then put in contact with the Li metal electrodes, as interfaces to connect with the potentiostat. This setup of assembled cells was then subjected to a 170 °C heat treatment for 1 h on each side with 200

g weight put on top, as it was found that the heat treatment allows for better contact of the metallic Li with the SSE. Mylar pouches were then used to seal the samples in vacuum, to protect the cell from the air atmosphere.

EIS measurement was taken of the assembled and sealed metallic Li symmetrical cells. A continuous sweep from 5 MHz to 5 Hz was done, with 10 points per decade, to measure the interfacial impedance between the SSE and the Li electrodes. Afterwards, the pouch cells were connected to a potentiostat (VMP-3, Biologic) and a GCPL (Galvanostatic Cycling with Potential Limitation) protocol was conducted to investigate the critical current density before cell failure occurred. The cell was charged and discharged to 0.1 mAh cm^{-2} every half cycle starting from 0.01 mA cm^{-2} increasing by 0.01 mA cm^{-2} for every cycle until failure.

The cell assembly and galvanostatic measurement for the control Al-LLZO was carried out by Marco Sinicalchi with treatment as closely to the laminate as possible.

4.3 Results and Discussions

4.3.1 Ta-LLZO – LSTZ – Ta-LLZO laminates

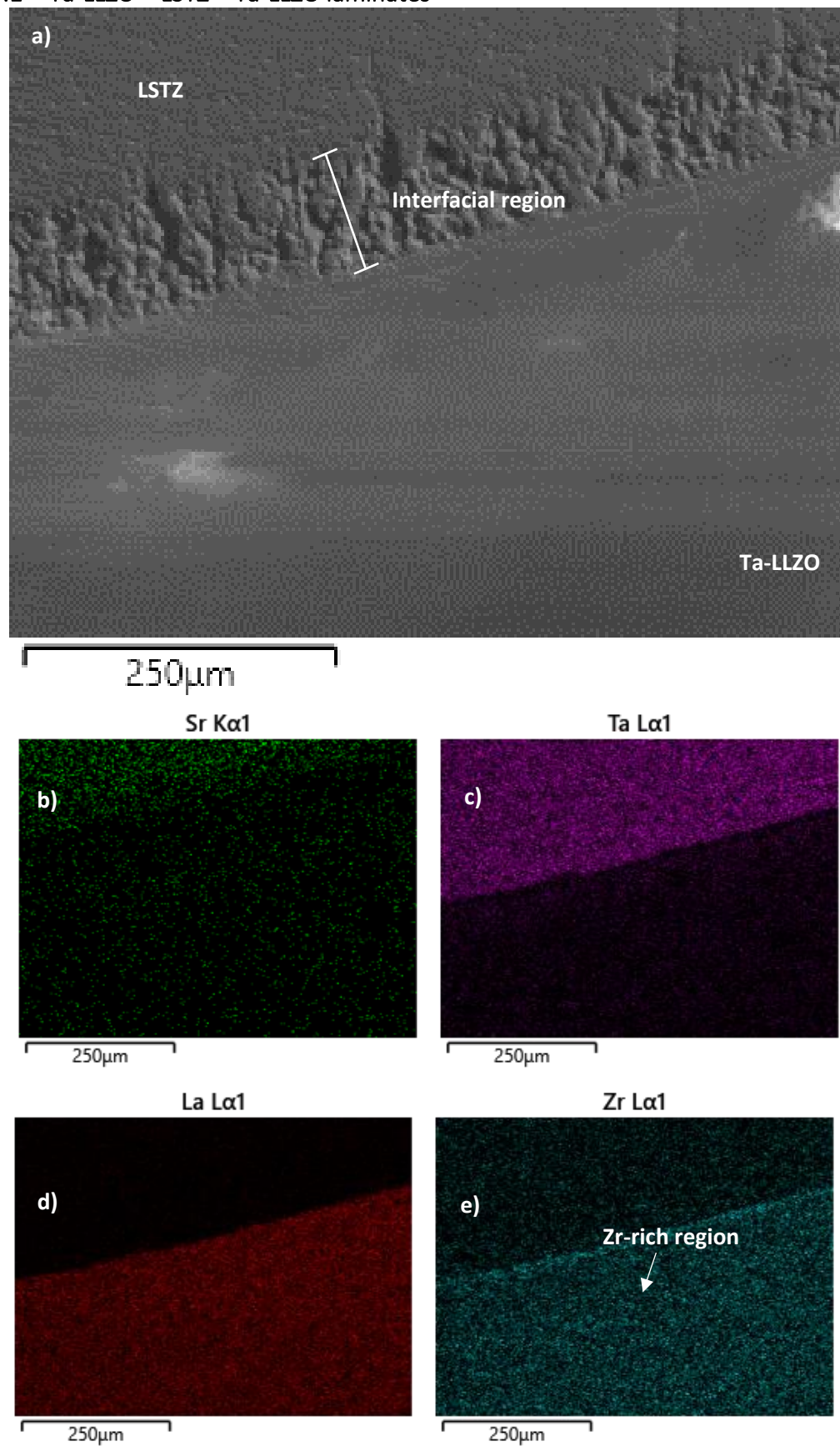


Figure 45 EDX map of Ta-LLZO – LSTZ – Ta-LLZO cross section on the

s

Figure 45 shows an SEM image and the corresponding EDX maps of a polished cross-section of SPS sintered Ta-LLZO – LSTZ – Ta-LLZO (LAM1). In the electron microscope image, the $1 \times 10^2 \mu\text{m}$ thick interface region between Ta-LLZO and LSTZ can clearly be distinguished by the presence of a less densified region, due to the suboptimal bonding of the 2 distinct layers. Elemental mapping further shows a clear segregation between the layers, with the Ta rich region representing LSTZ and La rich region representing Ta-LLZO. However, Figure 45a shows a gradual decrease of Sr starting in the less dense interface region, suggesting possible Sr migration into the Ta-LLZO that should be Sr free. Regardless, owing to the noisy signal for Sr, it was not certain if migration of Sr into the Ta-LLZO occurred.

The EDX map also shows another interfacial layer closer to the Ta-LLZO layer, represented by a line of very bright Zr signals Figure 45e. This Zr rich interfacial layer might well be a reaction layer formed at high temperature during the sintering process of the laminates. Unfortunately, as Li atomic number is generally too light to be accurately detected and quantified by EDX, accurate quantification of the elemental composition of this reaction layer by EDX was not possible.

The danger of having an interfacial layer formed by reaction in a laminated ceramic is that it might possess unpredictable properties detrimental to the purpose of the laminate. Having considered that, the ionic conductivity of LAM1 was measured by EIS, to investigate whether it still preserves the high ionic conductivity of the constituents.

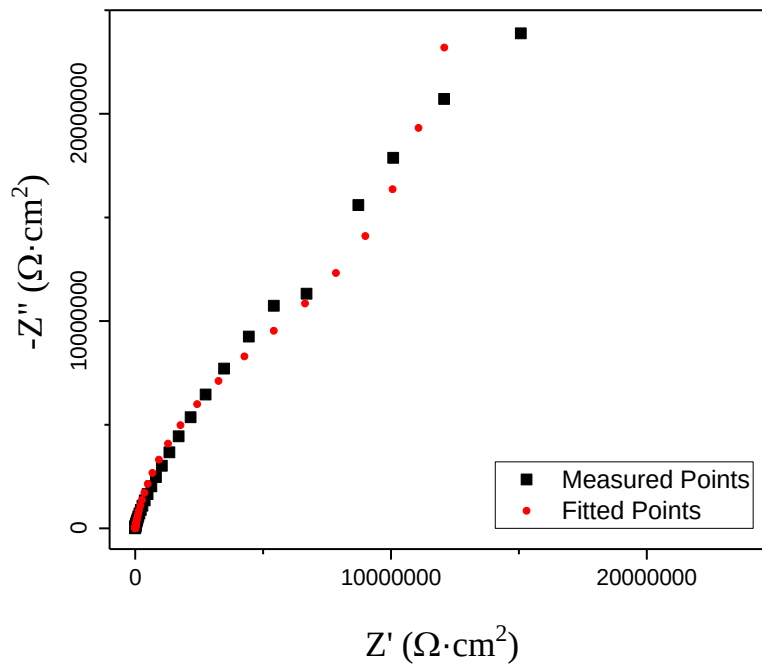


Figure 46 Nyquist plot of EIS measurement for Ta-LLZO - LSTZ - Ta-LLZO

As shown in Figure 46, EIS measurement of LAM1 with Au blocking electrodes reveals a detrimental effect of the lamination process on the impedance of the pellet. Even taking into account the thicker dimension of the specimens (3.5 mm), the overall conductivity of the LAM1 laminate was calculated to be in the magnitude of $10^{-8} \text{ S cm}^{-1}$. Further electrochemical analysis can and should be done to pinpoint the cause of this massive reduction to the ionic conductivity of the LAM1 laminates, but the presence of interfacial reaction layer, as observed in Figure 45e most likely contributed to this loss of conductivity. Formation of this interfacial layer can potentially be avoided by decreasing the sintering temperature and/or dwell time, or by utilizing a different approach such as diffusion bonding separately sintered pellets of Ta-LLZO and LSTZ such that there is less thermal energy for the detrimental reaction to occur.

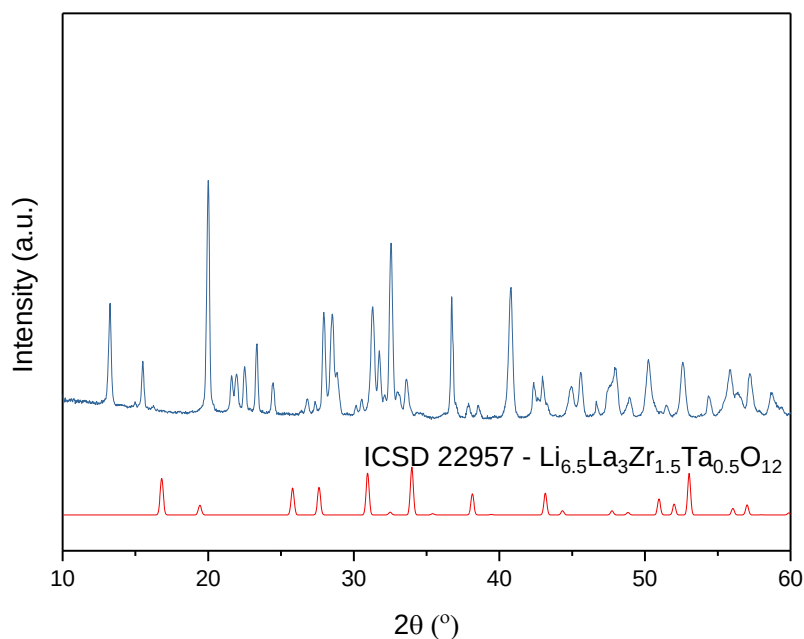


Figure 47 XRD spectrum of SPS sintered Ta-LLZO – LSTZ – Ta-LLZO pellet surface compared with reference peaks belonging to Ta-LLZO

Furthermore, XRD scan of the SPS sintered LAM1 surface also reveals that characteristic peaks of Ta-LLZO were absent. Figure 47 reveals that impurity peaks or combination of impurities peaks dominated the surface of the sample, even after grinding was done to remove potential surface reaction layer. This most likely also contributes to the low ionic conductivity measured by the EIS in Figure 46.

The SPS regime followed for the sintering of this laminate was found to have successfully sintered relatively phase pure monolithic Ta-LLZO pellets. The absence of cubic Ta-LLZO XRD peaks therefore suggested that there might have been some reaction with LSTZ and/or gases evolved during the sintering of said compound, rather than due to Li volatilization caused by the SPS regime. Another possibility might be due to polarization of Li ions caused by diffusion inhibition through the interface of Ta-LLZO and LSTZ when DC current was applied in the SPS. Electromigration due to DC current conduction through the specimen is known to occur [6] and, remembering the high ionic conductivity of the separate constituent layers, might be expected following the sintering of these SSEs. Much more

experimentation, characterization, and optimization of SPS setup and regime, needs to be done before a solid conclusion can be drawn. Nevertheless, to keep in line with this project's interest and time limitation, further experimentation with LAM1 laminates was not attempted in this project.

4.3.2 Al-LLZO – Ta-LLZO – Al-LLZO

4.3.2.1 SPS sintered

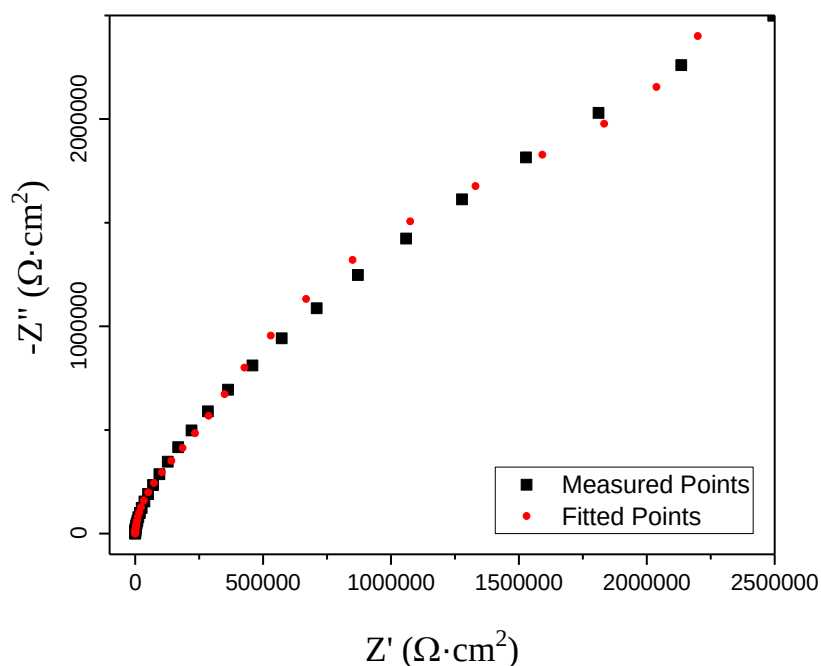


Figure 48 Nyquist plot of EIS measurement on SPS sintered Al-LLZO - Ta-LLZO - Al-LLZO

Intact samples of Al-LLZO – Ta-LLZO – Al-LLZO laminate pellets were successfully sintered by SPS (LAM2). However, as plotted in Figure 48, the LAM2 pellet tested on the EIS with Au blocking electrodes shows very high bulk impedance. Taking into consideration the pellet thickness of 4 mm yielded a measured conductivity in the order of $10^{-7} \text{ S cm}^{-1}$, well below the usual reported value for monolithic LLZOs.

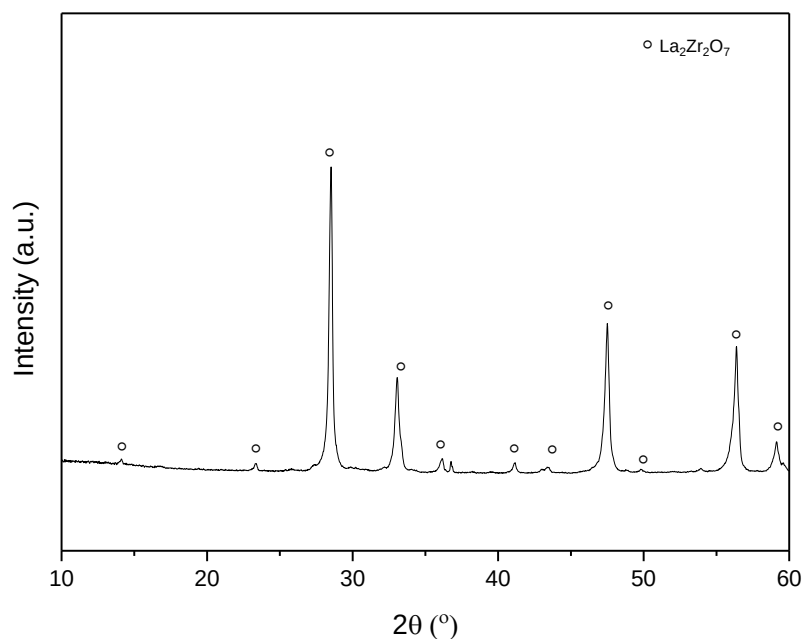


Figure 49 XRD spectrum of Al-LLZO - Ta-LLZO - Al-LLZO laminate surface

To investigate the potential cause of such low conductivity in the LAM2 pellet, an XRD scan of the surface was taken to verify whether the correct phase of cubic Al-LLZO on the outer layers of the laminate was formed. Figure 49 shows that the outer layers of the pellets, which should have been Al-LLZO, was instead dominated by LZO, a competitive phase that was known to form when excessive Li volatilization occurs. Grinding the pellet to remove some more of the outer layer's material maintained the same XRD result, suggesting that the entire low CTE layer of the laminate has indeed formed LZO. This is however not unpredictable, as SPS sintering of monolithic Al-LLZO pellets was found in section 3.3.3 to be difficult to do for the same reason of excessive Li loss. A different idea for sintering the Al-LLZO – Ta-LLZO – Al-LLZO was needed to circumvent this difficulty. In any case, the lack of delamination throughout the SPS experiments has showed that external pressure might be helpful in sintering intact laminates of ceramics.

4.3.2.2 Weighted Sintering

The initial attempt at adding external pressure by means of adding weight on top of the pellets showed promising improvement in keeping the pellets intact. 12.5 kPa was found to be sufficient to keep delamination from happening, while attempts of using lower load of around 6 kPa still resulted in some delamination of the pellets. Higher load was not practical with the setup being used due to space constraint of the furnace tube. Further optimization on the load needed for optimal sintering should be attempted to fully understand the effect of the load on the sintering behavior.

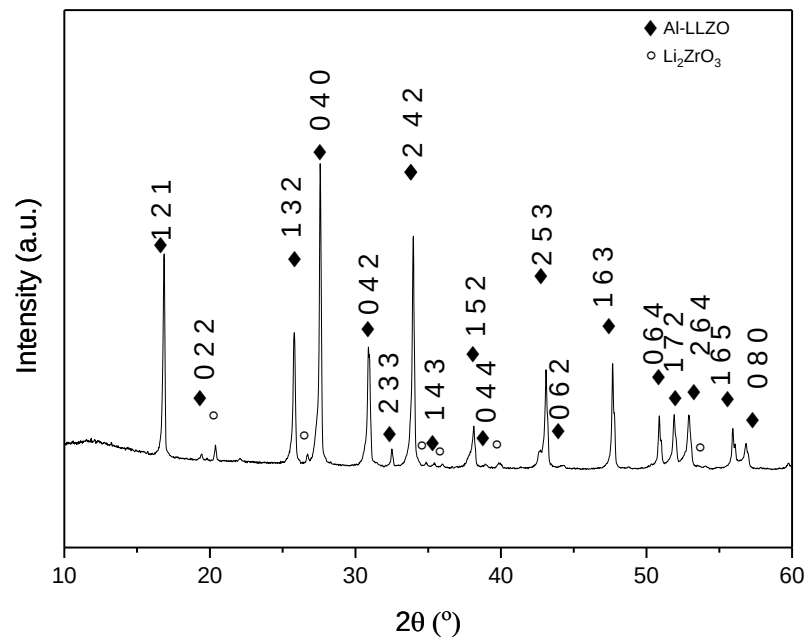


Figure 50 XRD spectrum of LAM3 surface

Figure 50 shows the XRD result of the surface of a polished Al-LLZO – Ta-LLZO – Al-LLZO pellet sintered with 12.5 kPa load (LAM3). The dominant phase in this spectrum is cubic Al-LLZO, signifying that the volatilization of Li was controlled by the mother powder. Consistent with the monolithic Al-LLZO samples in section 3.3.2, minor impurity peaks belonging to Li₂ZrO₃ were also detectable in this scan.

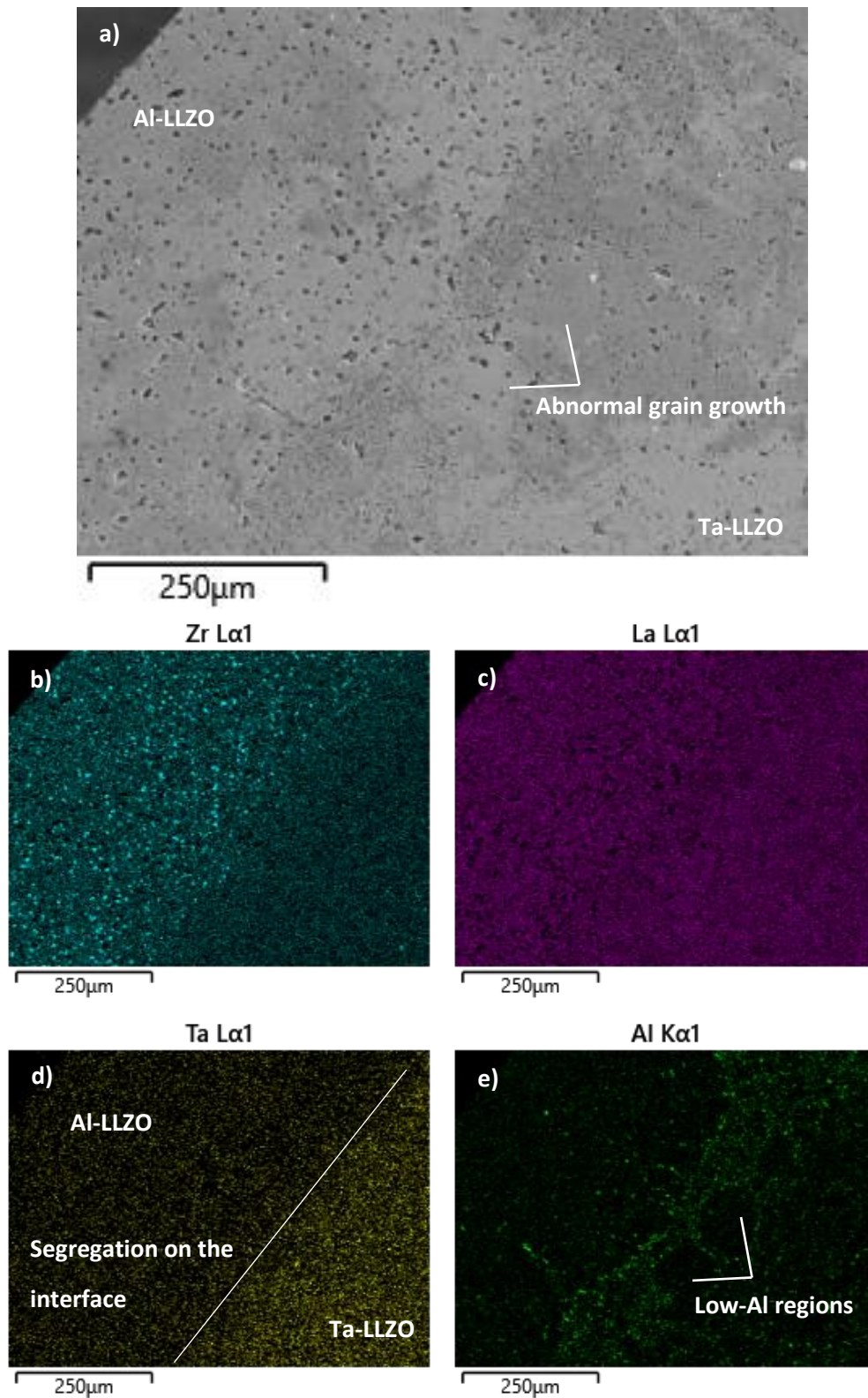


Figure 51 EDX map of Al-LLZO - Ta-LLZO - Al-LLZO cross section on the interface

To investigate the interface of LAM3, a cross sectional EDX map was constructed (Figure 51). The electron microscope image of this map shows no clear segregation or other features as the interface. However, the EDX scan shows a clear line of separation of the Ta-

LLZO layer by the abundance of Ta atoms in the bottom right corner of Figure 51d. This suggests good bonding between the Al-LLZO and Ta-LLZO layers, while maintaining the distinct layers.

Another noteworthy observation is of the Al atoms distribution shown in Figure 51e. Although no Al should be present in the Ta-LLZO 12.5% Li 2wt% PVB powder precursor of the middle Ta-LLZO layer, signals of Al atoms was clearly detected by EDX past the interface into this layer. In addition, the Al atom distribution in the Ta-LLZO layer does not seem to be homogeneous, forming islands of Al-poor grain-like regions. In any case, co-doping of LLZO with Al and Ta simultaneously has previously been reported [7], hence it is logical for Al diffusion into the Ta-LLZO layer to occur and form co-doped phase.

An alternative possible explanation for the highly mobile Al in Figure 51e is grain boundary diffusion of Al. This is further supported by the apparent distribution of Al in the EDX map, where high Al concentration can be seen around 50 μm islands of low Al grain-like regions. The corresponding SEM image shows that these regions are indeed large grain-like region with higher density compared to the surrounding area. These grain-like regions also show bigger, less frequent pores inside it and some smaller pores on the edges, akin to pores trapped inside a grain when grain growth occurs. Turning this observation on its head, this suggest the potential presence of abnormal grain growth in LAM3 which might have been caused by Al atoms diffusion.

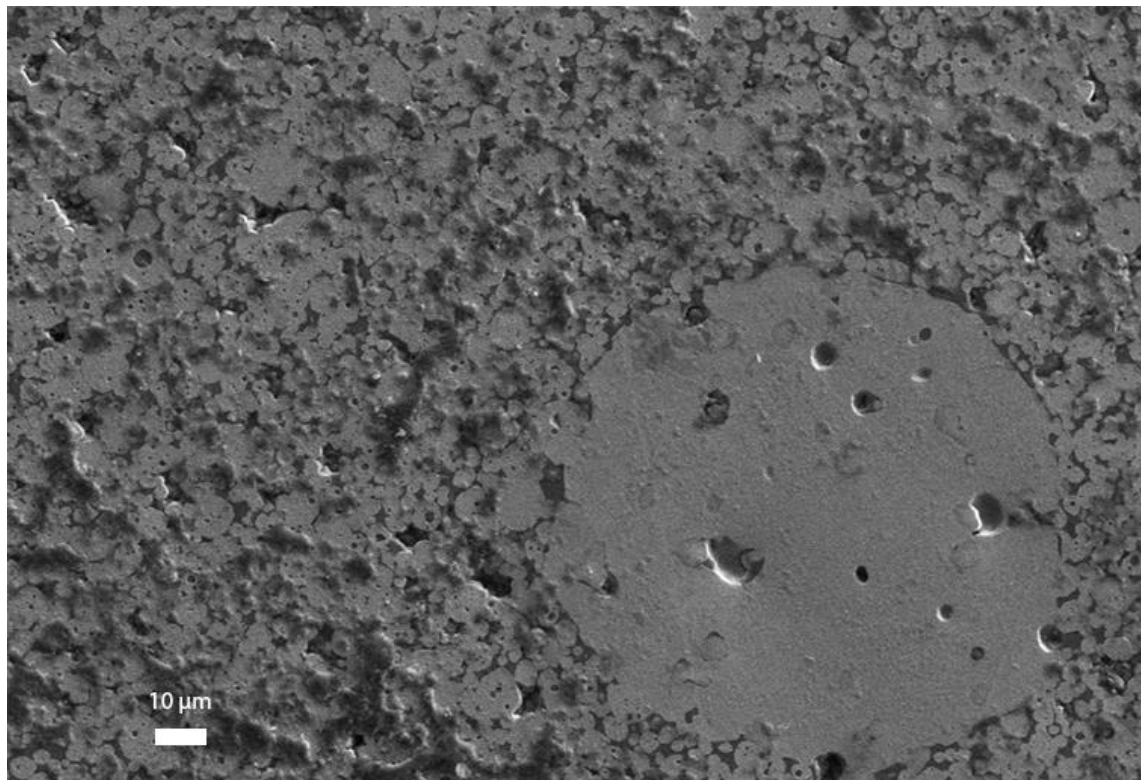


Figure 52 SEM image of Al-LLZO – Ta-LLZO – Al-LLZO sintered by weighted sintering method surface.

SEM image of the surface of LAM3 shows the presence of similarly sized intermittent large grain/grain-like regions on the surface. Figure 52 shows one of these large grain-like structures encompassed by smaller grains and pores. The presence of larger pores trapped inside this large grain-like structure as well as the slightly faceted shapes of the grain greatly supports the argument that this might be abnormal grain growth. The similar size of this abnormal grain growth to that seen in the Ta-LLZO layers in Figure 50, further supports the idea that rapid Al diffusion into the Ta-LLZO layer might be along the grain boundaries. An electron back-scattered diffraction (EBSD) scan should be able to give a conclusive answer to this and should be attempted in the future.

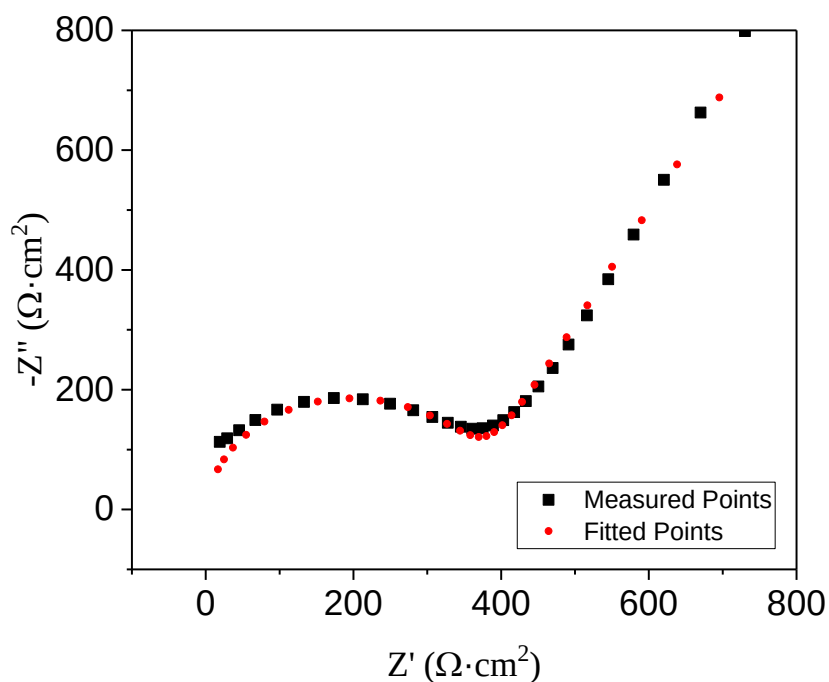


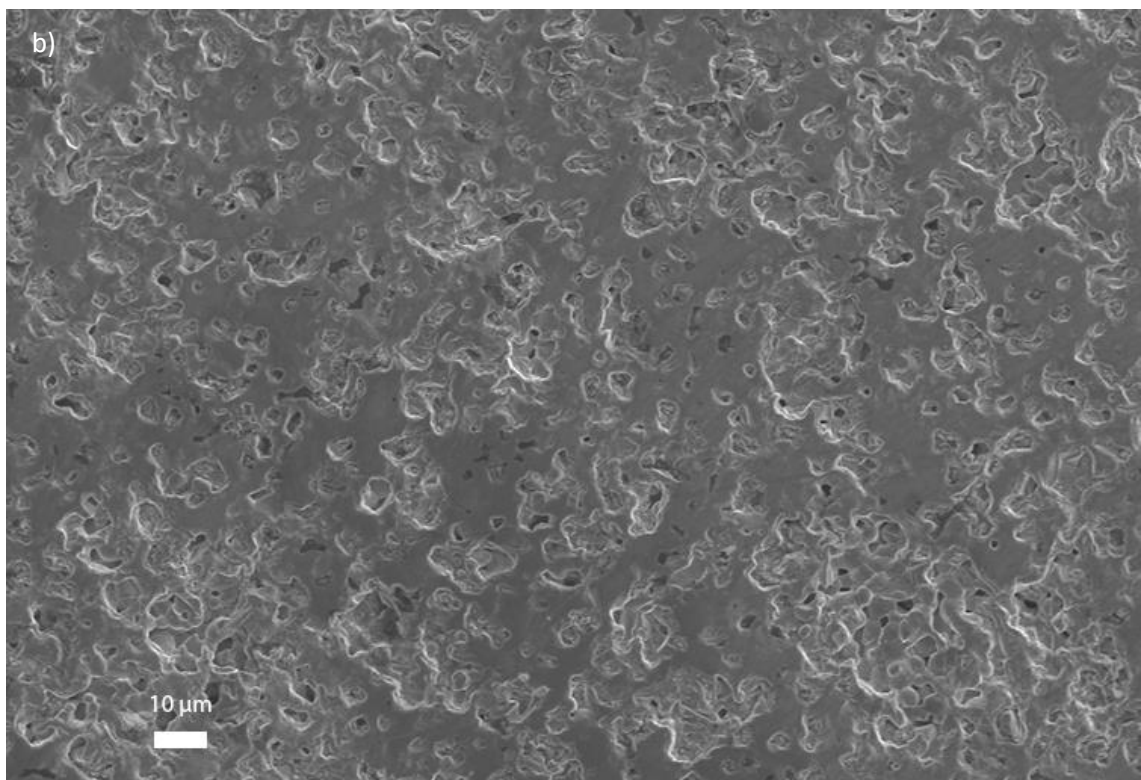
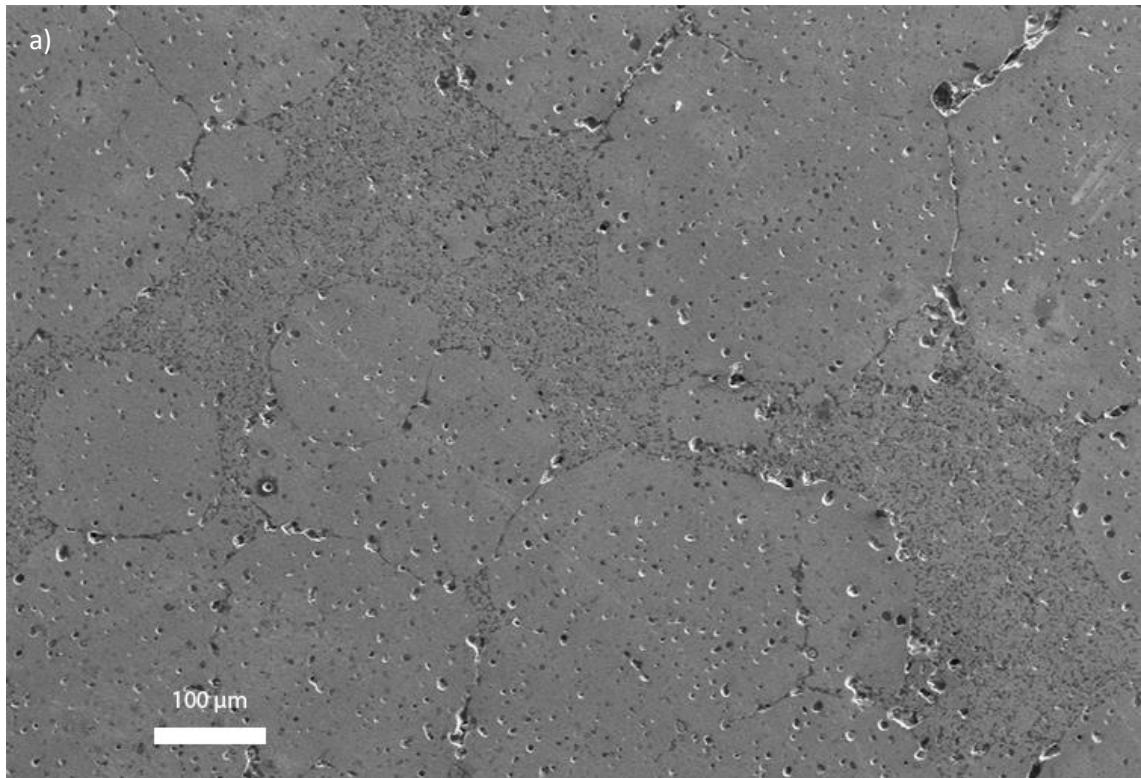
Figure 53 Nyquist plot of EIS measurement on Al-LLZO - Ta-LLZO - Al-LLZO laminate sintered with weighted sintering method

Figure 53 shows the impedance response to the EIS scan on the LAM3 samples with symmetrical Au blocking electrodes. The resulting response forms a widened semicircle, most likely as a total impedance of the Al-LLZO layers and Ta-LLZO layer. The resulting total ionic conductivity of the laminate as measured by EIS, taking into consideration sample thickness of 2.7 mm, is $7.78 \times 10^{-4} \text{ S cm}^{-1}$, almost twice the conductivity of either Al-LLZO and Ta-LLZO monolithic pellets measured in section 3.3.5. The values of ionic conductivities of LAM3, monolithic Al-LLZO 12.5% Li excess 2 wt% PVB and Ta-LLZO 12.5% Li excess 2 wt% PVB pellets sintered conventionally is summarized in Table 8.

Table 8 Ionic conductivity as measured by EIS

Sample	Ionic conductivity (10^{-4} S cm $^{-1}$)	Density (g cm $^{-3}$)
LAM3	7.78	4.9
Al-LLZO 12.5% Li excess 2wt%PVB	3.85	4.6
Ta-LLZO 12.5% Li excess 2wt%PVB	4.56	4.8

4.3.3 Control



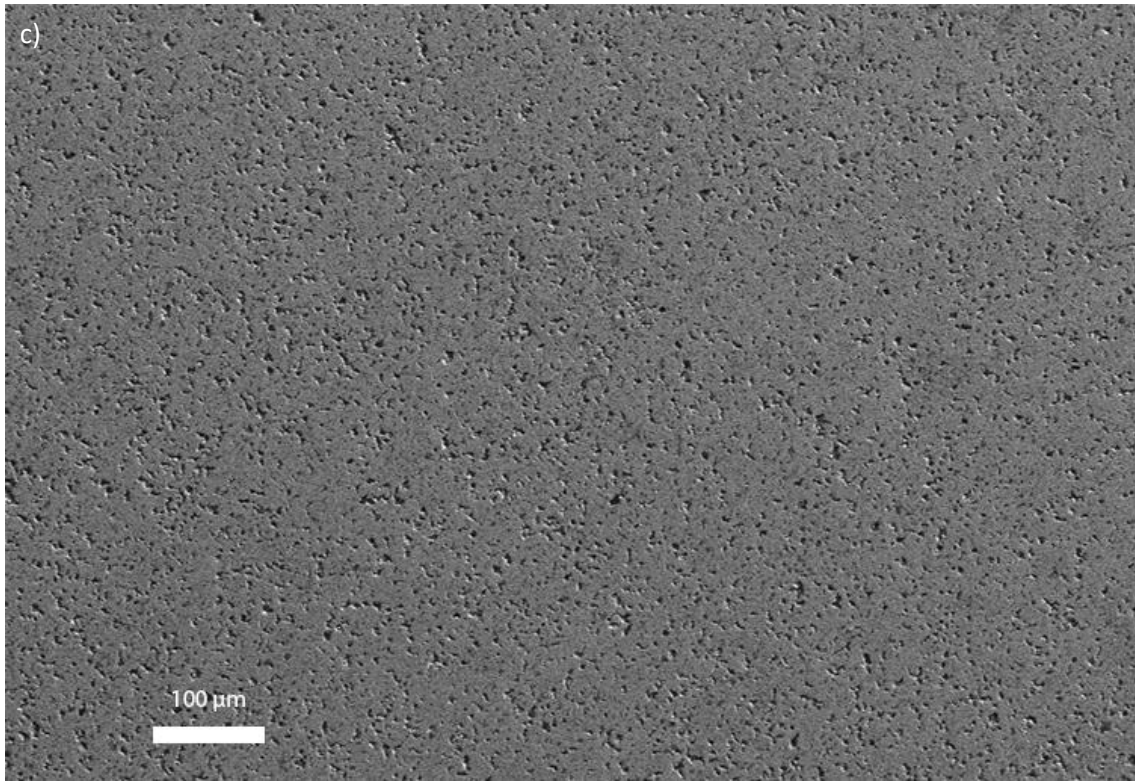


Figure 54 SEM images of a) Al-LLZO control sintered with weighted sintering method b) Al-LLZO 12.5%Li excess 2wt%PVB sintered in a conventional tube furnace c) Ta-LLZO 12.5%Li excess 2wt% PVB sintered with weighted sintering method

To verify the potential cause of the abnormally large grain-like structure in Figure 51, samples of control Al-LLZO sintered with the weighted sintering method, Al-LLZO 12.5% Li excess 2 wt% PVB sintered conventionally (3.3.1.2), and Ta-LLZO 12.5% Li excess 2 wt% PVB sintered with the weighted sintering method was observed under the SEM and presented in Figure 54. The control Al-LLZO and Ta-LLZO sintered with the weighted sintering method was measured to be 4.7 g cm^{-3} and 4.6 g cm^{-3} density wise, not significantly different from samples of the same composition sintered conventionally (Table 8).

Figure 54a clearly shows similarly large grain-like structures up to 200 μm across in the control Al-LLZO sintered with weighted sintering method. In comparison, SEM image of Al-LLZO sintered conventionally (Figure 54b) shows no such abnormal grain growth-like structure, suggesting that this abnormal behavior might have been caused by the modified sintering technique. Porosity is known to pin grain boundaries at lower density, hence the pressure applied might have favoured grain growth by increasing the density. However,

Figure 54c shows that Ta-LLZO sintered with 12.5 kPa external load applied did not form this abnormal grain-like structure, suggesting that this behavior is due to a combination of the applied external pressure and the Al dopant in LLZO.

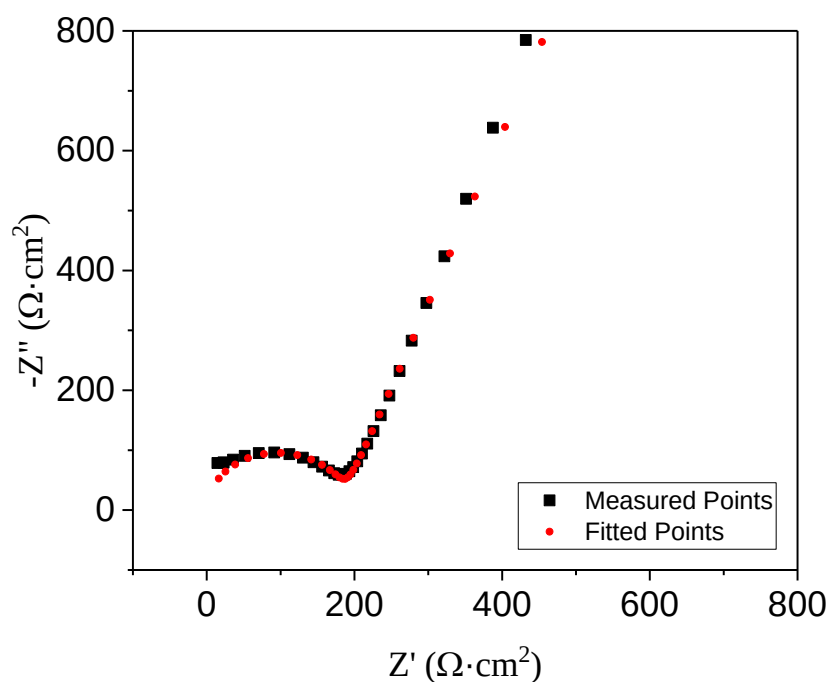


Figure 55 Nyquist plot of EIS scan on control Al-LLZO

Regardless of the difference in microstructure and the presence of the abnormally large grain-like structure, EIS scan of control Al-LLZO (Figure 55) shows conductivity value of $3.98 \times 10^{-4} \text{ S cm}^{-1}$, similar to that for identical sample thickness to that of monolithic Al-LLZO 12.5 % Li excess 2 wt% PVB sintered without external load (Figure 38). This eliminates that the abnormal grain growth found in LAM3 as the factor causing the much higher ionic conductivity recorded in Figure 53.

4.3.4 Residual Stress

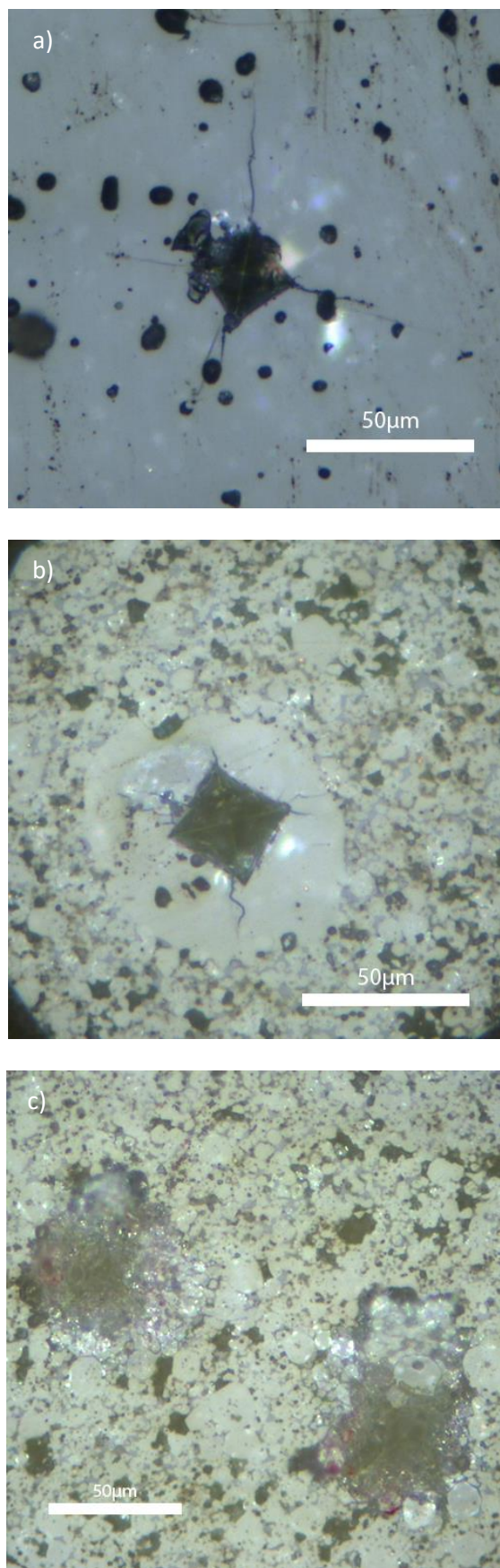


Figure 56 Vickers indent on a) control Al-LLZO b) LAM3 c) LAM3 on porous area

Table 9 Average measurement of *a* and *c* from Figure 43

Sample	<i>a</i>	<i>c</i>
Control Al-LLZO	$32 \pm 1.5\mu\text{m}$	$43 \pm 6.1\mu\text{m}$
LAM3	$37 \pm 0.8\mu\text{m}$	$28 \pm 3.6\mu\text{m}$

Figure 56 shows Vickers indent in the control Al-LLZO and LAM3 as observed under an optical microscope. At a glance, the crack length in Al-LLZO can be seen to be longer than LAM3. This is as predicted if LAM3 is in compressive stress. Inserting the measurements from Table 9 into Equation 14 gives us hardness value for control Al-LLZO and LAM3 as 5.7 ± 0.5 GPa and 4.3 ± 0.4 GPa respectively.

Using these values for hardness and the published Young's modulus value in Table 6 with Equation 15 gives us the apparent fracture toughness values of $0.7 \text{ MPa}^{1/2}$ for the control Al-LLZO and $1.5 \text{ MPa}^{1/2}$ for LAM3. Assuming K_c on the left hand side of the fracture toughness equation in Equation 17 is intrinsic to the material, the difference between the apparent fracture toughnesses of control Al-LLZO and LAM3 is due to residual stress term of the equation. Therefore, rearranging to solve for σ_a gives a value of residual compressive stress in LAM3 to be $126 \pm 23.5 \text{ MPa}$, well under the maximum possible value calculated in Table 7. However, when Equation 12 was used to calculate the residual stress value, with the measured layer thickness of 0.5 mm for each of the Al-LLZO layer and 1.7 mm for the Ta-LLZO layer, the resulting compressive stress value of $282 \pm 11 \text{ MPa}$ is almost twice the experimentally measured value. This discrepancy underlines the shortcoming of the Vickers indent technique for quantification of residual stress in porous ceramic. There is a big potential for error as there are possibility of energy dissipation mechanisms other than the radial crack happening because of the porosity.

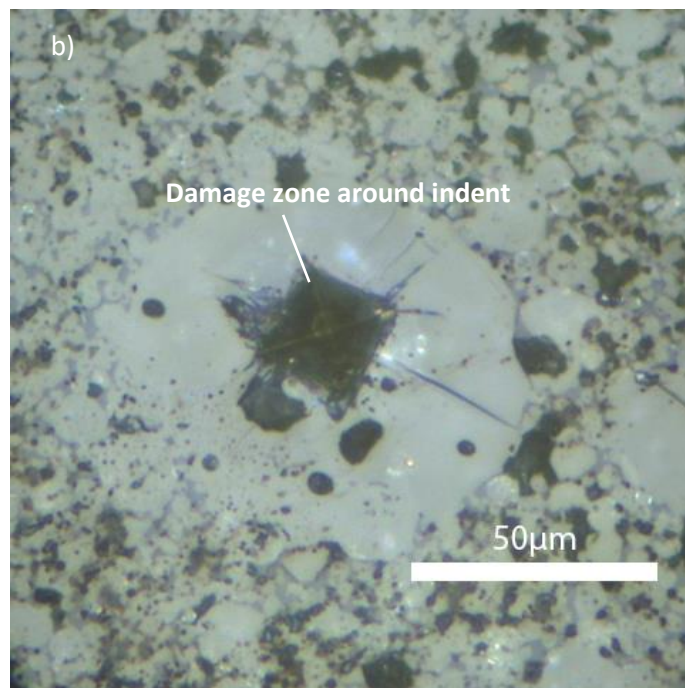
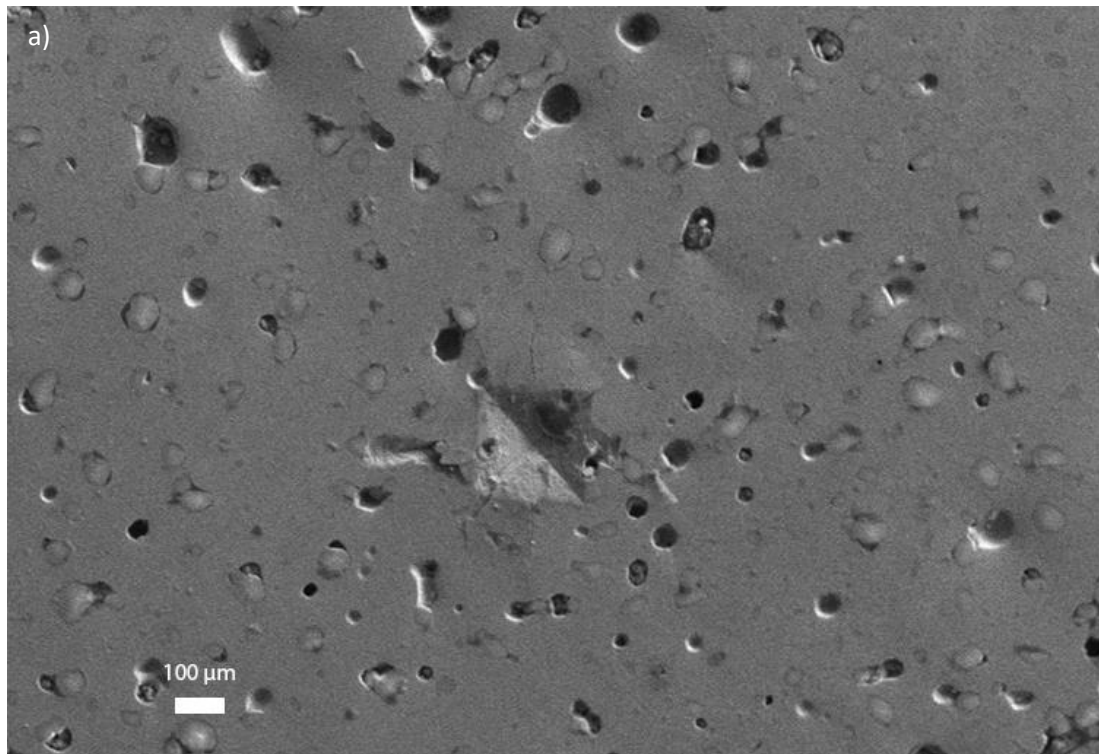


Figure 57 Image of Vickers indent on random location away from edge on LAM3 observed using a) SEM b) optical microscope

In addition to the porosity of the sample and the need to indent on the abnormally large grain-like regions, another reason for the small sample size of this experiment is due to the spalling around indents made randomly on LAM3 away from the edges (Figure 57). This chipping fracture was not found around indents made on control Al-LLZO, hence it was reasonable to assume that the compressive stress prefers this mode of fracture than radial cracks on the corner of the indents. Formation of damage zone around indents and cracks emanating from edges instead of corners of indents on a functionally graded ceramic system have been reported previously [8]. This further supports that compressive residual stress is indeed present in the laminate.

4.3.5 Galvanostatic Cycling

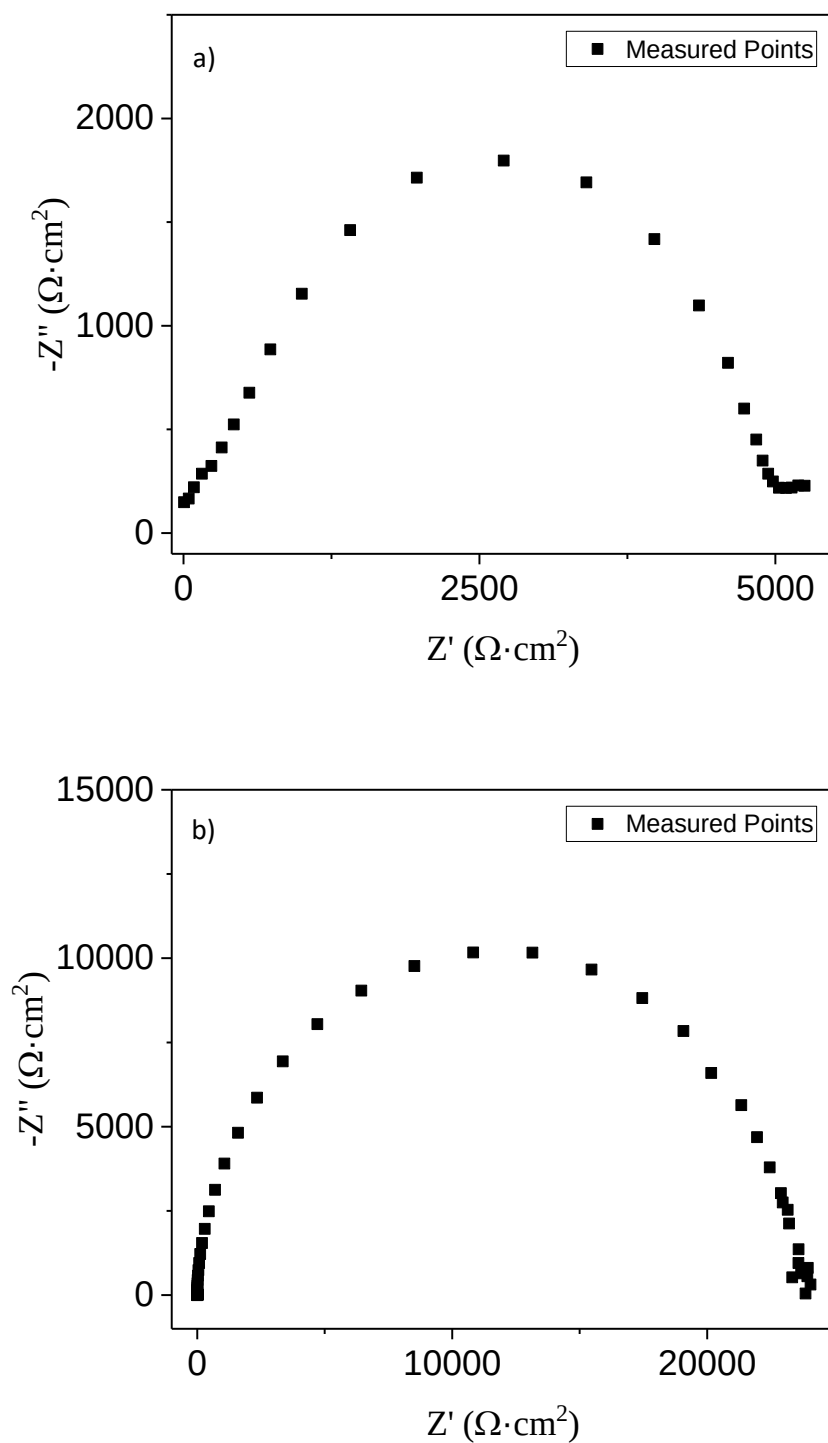


Figure 58 Nyquist plot of EIS scan before cycling for a) LAM3 and b) control Al-LLZO

Figure 58 shows the interfacial impedance between LAM3 and control Al-LLZO with the metallic lithium used as electrodes in a symmetrical cell. Even after acid and heat treatment, which was shown to be able to suppress interfacial impedance in Ta-LLZO to a very low level [9], it is evident that the interfacial impedance in both LAM3 and control Al-LLZO is significantly larger than the bulk impedance of the electrolytes. Even then, the interfacial impedance in control Al-LLZO is still slightly higher than LAM3 after identical treatment, as can be seen from the larger radius of the semicircle in the Nyquist plot (Figure 58). This high interfacial impedance is problematic for extracting accurate information from a galvanostatic experiment, as the interfacial impedance has been shown to cause polarization in the sample and bad contacts between the electrodes and electrolytes [9]. This could lead to inhomogeneous contact, resulting in extremely high potential in localized areas, such that the contact areas as defined by the Kapton masking tape are no longer valid.

Some potential explanation to the high interfacial impedance of both LAM3 and control Al-LLZO might be due to the porosity of the samples, the abnormal microstructure, or even potential reaction between the electrolyte and the electrode. The acid and heat treatment procedure followed in this project was originally done on Ta-LLZO, and the difference in doping might have caused a significant difference in behavior, particularly during the heat treatment step, as Al dopants in Al-LLZO are known to be less stable against Li [10]. Regardless, cycling of both samples was attempted anyway with low current at lower capacity (normally 0.2 – 0.4 mAh is preferred [11]), to observe if the laminated sample can fare better compared to the monolithic after being subjected to identical treatment.

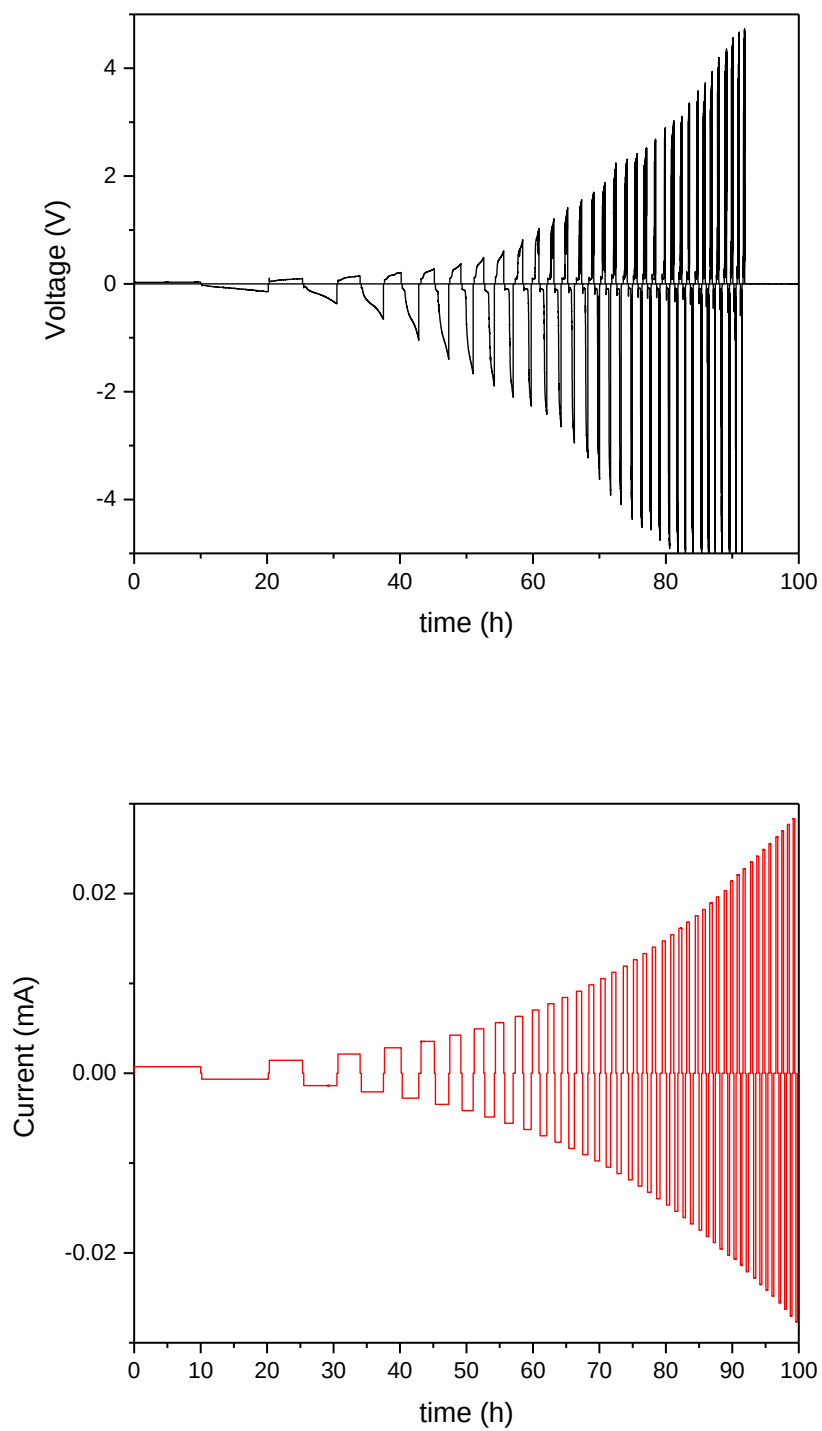


Figure 59 Galvanostatic profile of LAM3 plotting a) voltage vs time b) current vs time charged to 0.1 mAh cm⁻² per half cycle

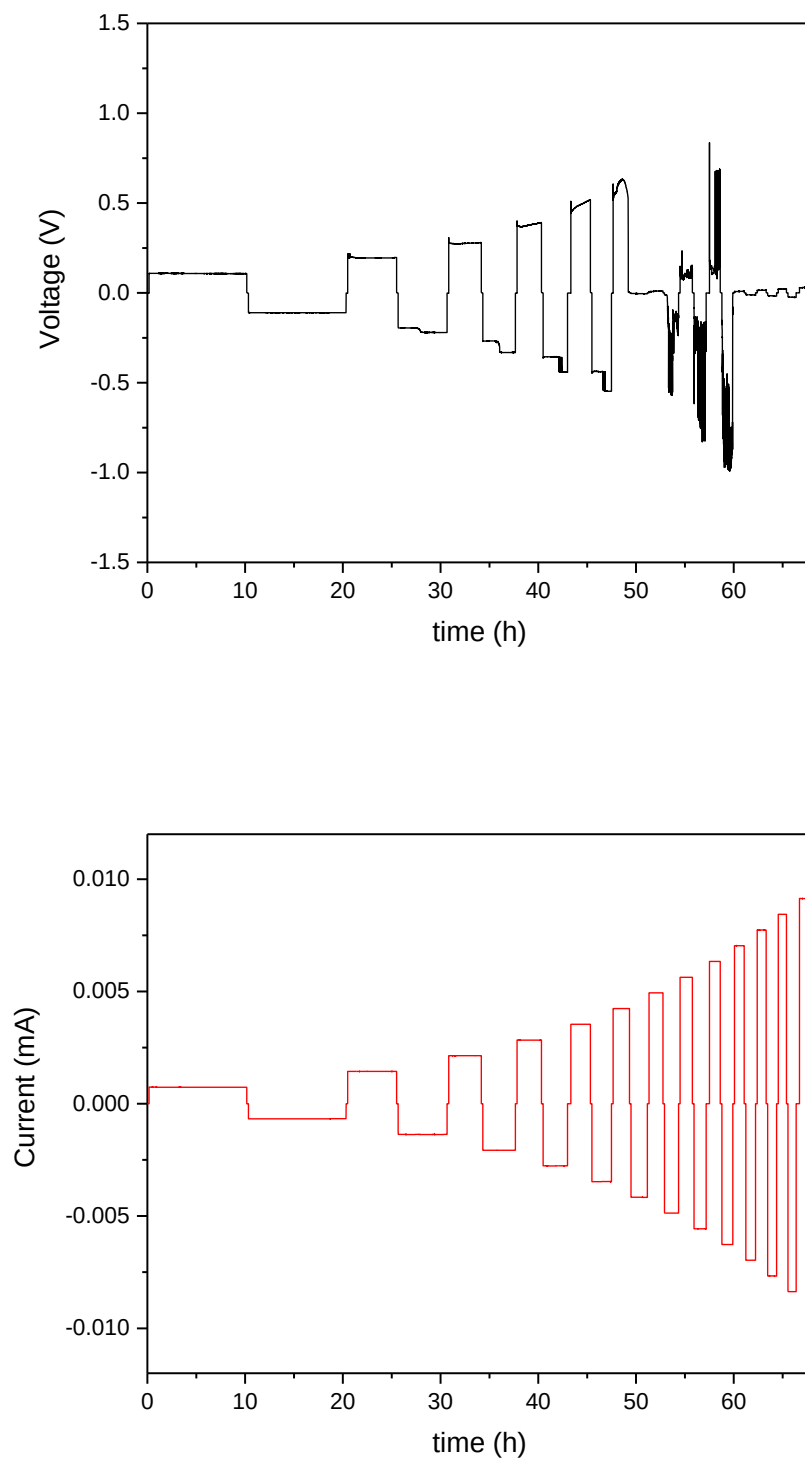


Figure 60 Galvanostatic profile of control Al-LLZO plotting a) voltage vs time b) current vs time charged to 0.1 mAh cm^{-2} per half cycle

Comparing Figure 59 with Figure 60, the control Al-LLZO was shown to fail at around 0.004 mA. On the contrary, LAM3 was shown to endure higher current, and fails at around 0.023 mA after some voltage clipping occurred due to the potential difference reaching higher than the allowed 5 V at around 0.015 mA.

In contrast to the more desirable flat profile of the voltage response at the start for the control Al-LLZO, the voltage response of LAM3 showed some polarization from the beginning. This causes the voltage response to rise instead of plateauing, even though a constant DC current was applied for each half cycle. Although interfacial impedance of LAM3 was shown to be lower than control Al-LLZO, polarization causes the voltage response in each half cycle to be extremely high for LAM3, reaching the voltage limit of the potentiostat at 5 V. This clipping causes the potentiostat to skip to the next half cycle immediately, resulting in asymmetrical charging-discharging capacity.

In addition to asymmetrical charging capacity caused by voltage clipping, the voltage response of LAM3 has also showed asymmetrical discharging profile from the beginning. Further investigation to the cause of this needs to be done to conclusively unearth the cause of this detrimental response but a speculative source to this behavior might relate to the inconsistent plating and stripping of Li.

The fact that LAM3 can resist failure even after some detrimental phenomena have been observed in the voltage response suggests that the concept of utilizing compressive stress in a SSE to inhibit Li dendriting by preventing dendrite penetration might have some merit.

4.4 Conclusion

This chapter of the thesis provides a very viable sintering technique for future investigations of SSE laminates, emphasizing the importance of external load during sintering. An innovative weighted sintering method with 12.5 kPa external weight was

shown to be able to sinter the Al-LLZO – Ta-LLZO – Al-LLZO laminates with good interfacial bonding between the layers, whereas SPS sintering of the laminates needs more optimization due to Li volatilization and potential electromigration of the Li ion. This weighted sintering method resulted in abnormal grain growth in Al containing pellets, which requires further investigation.

Residual stress was also demonstrated to be present in the laminates. Quantification of this should be investigated, using better samples with higher density and other techniques. One of such techniques that was proposed and attempted, but need further optimization, is XRD peak shift measurement from omega scan at high angle, which should be able to give more definite value of the residual stresses in the laminates. Such technique was not able to be attempted in this study due to equipment breakdowns.

Electrochemically, proofs that the laminated structure can be as conductive, or as shown in Table 8 be more conductive than, monolithic pellets should also provide incentive for further investigation of this concept. In addition, galvanostatic CCD cycling reveals that the laminate was able to survive higher potential difference and current compared to the monolithic sample, regardless of subpar interface with the electrodes.

As has been repeated frequently in this thesis, these results are preliminary and serve as initial proof of concept. More thorough investigations need to be conducted to extract definitive quantification of the beneficial effect that the compressive residual stress in the laminate provides. In conclusion, this chapter achieves the objective of this project for laying the groundwork on the viability of laminated SSE and should open the floor for further discussions and investigations of compressively stressed SSEs as a mean of Li dendrite inhibition.

4.5 References

1. Connolly, W., *Part II thesis*. 2021, University of Oxford.
2. Dancer, C.E.J., N.A. Yahya, . . . G. de Portu, *Effect of residual compressive surface stress on severe wear of alumina–silicon carbide two-layered composites*. Tribology International, 2014. **74**: p. 87-92.
3. Yu, S., R.D. Schmidt, . . . D.J. Siegel, *Elastic Properties of the Solid Electrolyte Li₇La₃Zr₂O₁₂ (LLZO)*. Chemistry of Materials, 2016. **28**(1): p. 197-206.
4. Anstis, G., P. Chantikul, . . . D. Marshall, *A critical evaluation of indentation techniques for measuring fracture toughness: I, direct crack measurements*. Journal of the American Ceramic Society, 1981. **64**(9): p. 533-538.
5. Wachtman, J.B., W.R. Cannon, and M.J. Matthewson, *Mechanical properties of ceramics*. 2009: John Wiley & Sons.
6. Olevsky, E. and L. Froyen, *Constitutive modeling of spark-plasma sintering of conductive materials*. Scripta Materialia, 2006. **55**(12): p. 1175-1178.
7. Shin, D.O., K. Oh, . . . K. Kang, *Synergistic multi-doping effects on the Li₇La₃Zr₂O₁₂ solid electrolyte for fast lithium ion conduction*. Scientific Reports, 2015. **5**(1): p. 18053.
8. Asmi, D., P. MaAnurung, and I.M. Low, *6 - Manufacture of graded ceramic matrix composites by infiltration technique*, in *Advances in Ceramic Matrix Composites (Second Edition)*, I.M. Low, Editor. 2018, Woodhead Publishing. p. 121-153.
9. Siniscalchi, M., J. Liu, . . . C.R.M. Grovenor, *On the Relative Importance of Li Bulk Diffusivity and Interface Morphology in Determining the Stripped Capacity of Metallic Anodes in Solid-State Batteries*. ACS Energy Letters, 2022: p. 3593-3599.
10. Wang, C., K. Fu, . . . L. Hu, *Garnet-Type Solid-State Electrolytes: Materials, Interfaces, and Batteries*. Chemical Reviews, 2020. **120**(10): p. 4257-4300.
11. Taylor, N.J., S. Stangeland-Molo, . . . J. Sakamoto, *Demonstration of high current densities and extended cycling in the garnet Li₇La₃Zr₂O₁₂ solid electrolyte*. Journal of Power Sources, 2018. **396**: p. 314-318.

Summary and Outlook

5.1 Summary

Laminated Al-LLZO – Ta-LLZO – Al-LLZO pellets were successfully synthesized from precursor powders and sintered by a weighted sintering method. The pellets were found to be almost twice as conductive as monolithic pellets of their constituent layers. SEM images with EDX maps confirmed that the layers were still distinctly separated, and good bonding between the layers was achieved. Vickers indents of these laminates behaved differently compared to indents made on monolithic Al-LLZO, suggesting that residual compressive stress was present. Galvanostatic CCD cycling to failure showed that the laminates were able to withstand higher currents and higher potential difference between the electrodes compared to monolithic Al-LLZO with similar treatment. All this shows that the concept of laminated SSE has some merit and should attract further investigation.

At the start of this project, to the author's knowledge, no attempt to produce a sintered laminated SSE had been published. Starting from the ground up, in chapter 2 synthesis of SSE powders from appropriate precursors were successfully conducted and optimized. This optimization of the powder synthesis allowed for better control of powders for use in the sintering, as well as giving the author a better understanding of the materials, mainly regarding lithium volatility and air instability. TGA analysis of precursor powders discussed in this chapter also gave a better picture of the gas evolution and stability window for thermal processing of the SSE powders. Ball milling of the calcined powders was also observed to have a huge impact on the particle size of the powders, potentially affecting sintering behavior. Ultimately, it was found that LSTZ with 10% Li excess, Ta-LLZO and Al-LLZO with 12.5% Li excess yielded the most phase pure powders of the precursor compositions attempted due to the Li excess counteracting Li loss during calcination.

Chapter 3 discussed the sintering of pellets from powders synthesized in chapter 2. Compared with commercially purchased powder for Ta-LLZO, the Ta-LLZO powder with 12.5% Li excess synthesized in chapter 2 was found to be able to achieve higher relative density. It was found that the addition of 2 wt% PVB binder allows for higher relative density by conventional mother powder sintering. LSTZ powder was shown to achieve a high enough relative density even without binder addition. SPS was also attempted on the SSE powders, with relatively phase pure pellets of LSTZ and Ta-LLZO successfully sintered to 98% dense. SPS sintering of Al-LLZO was not successful due to excessive Li loss resulting in formation of LZO. Better quality of graphite dies with a narrower gap, as well as more optimizations should allow for high density Al-LLZO to be sintered by SPS.

In addition to the sintering of monolithic pellets, Chapter 3 also investigates the properties of the pellets sintered. Physical property wise, Young's modulus and hardness of LSTZ were successfully measured by nanoindentation on a 98% dense SPS LSTZ pellet. To the author's knowledge, these values of 181 GPa and 10 GPa for Young's modulus and hardness of LSTZ respectively, are the first to be reported. Nanoindentation of Ta-LLZO 12.5% Li excess 2 wt% PVB and Al-LLZO 12.5% Li excess 2 wt% PVB was also attempted, but reliable results were not achieved due to high porosity of the conventionally sintered samples used. CTEs of LSTZ, Ta-LLZO 12.5% Li excess 2 wt% PVB, and Al-LLZO 12.5% Li excess 2 wt% PVB were also measured using a vertical dilatometer, with values of $2.25 \times 10^{-5} \text{ K}^{-1}$, $1.40 \times 10^{-5} \text{ K}^{-1}$, and $1.14 \times 10^{-5} \text{ K}^{-1}$ respectively.

In addition to physical properties, the ionic conductivity of conventionally sintered LSTZ 10% Li excess, Ta-LLZO 12.5% Li excess 2 wt% PVB, and Al-LLZO 12.5% Li excess 2 wt% PVB, as well as SPS LSTZ and SPS Ta-LLZO were investigated using EIS. Respectively, the conductivities of conventionally sintered LSTZ, Ta-LLZO 12.5% Li excess 2 wt% PVB, and Al-LLZO 12.5% Li excess 2 wt% PVB were found to be $7.05 \times 10^{-4} \text{ S cm}^{-1}$, $4.56 \times 10^{-4} \text{ S cm}^{-1}$, and $4.56 \times 10^{-4} \text{ S cm}^{-1}$. Intuitively the higher density pellets made using SPS were shown to be

more conductive. However, the effect of higher density to ionic conductivity was found to be insignificant, with overall measured conductivities of $7.99 \times 10^{-4} \text{ S cm}^{-1}$ for SPS LSZT and $4.66 \times 10^{-4} \text{ S cm}^{-1}$ for SPS Ta-LLZO.

Having successfully synthesized and sintered the SSEs, chapter 4 then delves into the core question of the project. Two arrangements were decided upon based on the CTEs measured in chapter 3, Ta-LLZO – LSTZ – Ta-LLZO and Al-LLZO – Ta-LLZO – Al-LLZO. SPS was attempted to densify these two arrangements by co-sintering the layers but was unsuccessful. The Ta-LLZO – LSTZ – Ta-LLZO laminate was quickly abandoned, as although an intact specimen was successfully sintered via SPS, EDX mapping of the cross section revealed an interfacial reaction layer between LSTZ and Ta-LLZO. An XRD scan of the surface also showed dominant impurity peaks. These facts combined lowered the specimen's ionic conductivity such that it was insufficiently conductive as a battery electrolyte. SPS sintering of Al-LLZO – Ta-LLZO – Al-LLZO specimen was also unsuccessful with the current setup, due to excessive loss of Li from the Al-LLZO layer. Therefore, an innovative weighted sintering technique, where 12.5 kPa pressure was applied to the specimen, was attempted and successfully produced intact Al-LLZO – Ta-LLZO – Al-LLZO laminates. These laminates were found to be almost twice as ionically conductive as the monolithic pellets, at $7.78 \times 10^{-4} \text{ S cm}^{-1}$. Preliminary attempts on galvanostatic cycling the laminate to failure showed that it survived higher current (0.023 mA) compared to similarly treated monolithic Al-LLZO sample (0.004 mA).

Undoubtedly, this project raises some new questions about laminated SSEs that are still yet to be answered. The quantification of the residual stress on the laminates needs better, ideally 100% dense samples; Better samples and sample preparation with optimized setup for the CCD cycling experiment should also be experimented on to fully measure the beneficial effects of the laminates on inhibition of Li dendrites; And of course, better optimization of the sintering techniques, as well as new techniques such as diffusion bonding

of pre-sintered pellets should be investigated to achieve better laminates with less porosity. However, there is only so much that can be done with the time constraint of an M.Res project. Nevertheless, I am satisfied that, in my opinion, this thesis has achieved its primary objective to prove that the concept of laminated SSE for Li ion battery does have merit and should be investigated further.

5.2 Suggestions for future investigations

- On the sintering of the pellets, flash sintering can be an interesting method for SSE. Due to the high ionic conductivity of the SSE even at room temperature, flash sintering of SSE might be achievable at very low furnace temperatures, and potentially even at room temperature. On the flip side, the Li ion conduction in the sample might prove to be detrimental if direct current is used. An attempt to flash sinter Ta-LLZO 12.5% Li excess with AC current was made, however it was not further investigated due to equipment limitation, namely a current-controlled AC power supply.
- On the co-sintering of the laminates, hot pressing or SPS with a better die set with a narrower gap might be able to produce highly dense Al-LLZO – Ta-LLZO – Al-LLZO pellets. An attempt with the SPS for the Ta-LLZO was observed to be able to sinter the SSE up to 98% dense, and reports from the literature on hot pressing states that high density LLZO pellets are achievable. A colleague in another group in Oxford was even able to produce translucent Ta-LLZO on the SPS with a better-quality die set recently. Further optimization on sintering of the laminated SSEs using these techniques might be able to result in similarly dense laminates, allowing for better specimens for the characterization and quantification of both physical and electrochemical properties.

- On the weighted sintering technique to densify laminates, more thorough optimization of the load and equipment to apply the load should be attempted to study its effects on the microstructure of the laminates.
- On the diffusion bonding of SSE laminates, an idea of diffusion bonding pre-sintered SSEs was also attempted. In this attempt, pre-sintered discs of Al-LLZO and Ta-LLZO were ground and then stacked on top of each other before being heated with mother powder under pressure from an air piston. More time was needed to optimize this technique, but early attempts suggested that it is possible to bond the laminates in this way, as long as the starting pre-sintered discs are parallel to each other. The main benefit of this technique is in the lower bonding temperature, and the use of pre-sintered, potentially very high density, discs possibly mediating any risks of interfacial reaction layer and resulting in very high-density laminates.
- On the quantification of residual stress on the laminates, higher density samples with less porosity will intuitively result in more reliable measurement by Vickers indentation. In addition, the use of high angle XRD omega scan was attempted, but more time was needed for optimization of this technique due to its high sensitivity and messy high angle XRD peaks of LLZOs.
- On the galvanostatic cycling of the laminates, better, highly dense samples need to be made from start to finish inside a glovebox to eliminate any risk of a bad interface with the metallic Li electrode.
- On the ionic conductivity of the laminates, particularly LAM3, better EIS technique, possibly measuring the conductivity at very low temperature, or other electrochemical measurement techniques need to be attempted to fully understand the impedance contribution of the individual layers. Intuitively, LAM3 should have more impedance, however the results so far have proven that it is in fact more conductive when compared with monolithic samples of its constituent layers. The

mechanism that allows for this higher conductivity should be understood, as it might be important in the design of future SSEs.

- On the cross-sectional image of the laminates, as well as the reactive interfacial layer between Ta-LIZO and LSTZ in LAM1, an EBSD map might be able to identify the phases present. An attempt with the Zeiss Evo mounted EBSD in the David Cockayne Center for Electron Microscopy (DCCCEM) was made, but no clear diffraction signal could be captured, possibly due to suboptimal finish of the surface of the sample, potential presence of impurity surface layer due to reaction with air, or not high enough energy of the electron beam used.
- On the idea of laminated SSEs as a whole, further investigations on the feasibility of laminates of other SSEs should be made. In addition to compressive residual stress, there might be merits in utilizing different classes of SSEs with different stability, conductivity, and properties to inhibit dendrite propagation, as better understanding of the dendriting phenomenon continues to evolve.