# Measurement of the Single Grain Boundary Impedance in Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> Toward Enabling Polycrystalline Solid State Electrolytes

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> > By

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#### Abstract

As society has grown to demand more portable power in segments including, but not limited to, portable computing, communications, power tools, transportation, and grid-scale energy storage, lithium ion batteries have become functionally omnipresent due to their high energy density and long cycle life. The vast majority of these batteries are constructed with a polymer separator that is impregnated with a liquid electrolyte to prevent contact of the electrodes and facilitate the motion of lithium across the battery. While this construction offers an enticing blend of manufacturability, performance, and cost, the liquid electrolytes are also a safety hazard and act as one of the limiting factors for increases in energy density. Generally, the organic liquid electrolytes that are used are highly reactive and do not cope well with high temperatures, which can lead to fires that are difficult and dangerous to extinguish. Additionally, the stability of the electrolyte against electrode materials with high electrochemical potentials is limited, which prevents the integration of new electrode materials that could drive increased energy density. Solid state lithium ion batteries make use of solid electrolytes that can be less reactive, more heat tolerant, and allow for the engineering of interface phases to enable stability against high energy electrodes. One key challenge to the commercial implementation of solid state lithium ion batteries is the low ion conductivity relative to liquid electrolytes, which prevents current solid state batteries from being used in applications with high power demands. A number of ceramic materials have been identified as solid state electrolyte candidates due to their high lithium ion conductivity in the bulk but exhibit low total ionic conductivity in polycrystalline forms due to high lithium ion impedance at the grain boundaries.

It is known that grain boundary energy varies widely with misorientation due to different structural, chemical, and electrical configurations. As such, it is expected that the boundaries separating differently oriented grains might also have different ion conducting behaviors. This has been supported by a number of theoretical studies and has been observed indirectly in experimental work but has not been quantitatively experimentally confirmed. Traditional ion conductivity measurements observe an ensemble response of all grain boundaries in the conduction pathway of a polycrystalline sample, removing any possibility of understanding the individual grain boundary behaviors. This dissertation seeks to develop methods for the quantitative measurement of ionic conduction across single grain boundaries via the epitaxial growth of ion conducting films on substrates with well characterized grain boundaries. To this end, this dissertation includes studies on the following subjects to enable the deposition and characterization of lithium ion conducting grain boundaries: 1) generation of  $Li_{3x}La_{1/3-x}TaO_3$  bulk ceramics for characterization and for use as pulsed laser deposition targets; 2) the effects of deposition parameters on the structure, stoichiometry, and ionic conductivity of epitaxial  $Li_{3x}La_{1/3-x}TaO_3$  films on single crystalline SrTiO<sub>3</sub> substrates; 3) the ionic conductivity of single grain boundaries in  $Li_{3x}La_{1/3-x}TaO_3$  films grown on bicrystal SrTiO<sub>3</sub> substrates; and 4) the synthesis of polycrystalline SrTiO<sub>3</sub> with an average grain size on the order of several hundred microns to enable combinatorial substrate epitaxy of  $Li_{3x}La_{1/3-x}TaO_3$ .

Trials on the synthesis of  $L_{i_{3x}}La_{1/3-x}TaO_3$  ceramics found that the ion conductivity was modified as a function of the lithium ion concentration in the sample due to the formation of a secondary LaTaO<sub>4</sub> phase, driven by the non-stoichiometry of lithium in the sample. Sintering conditions that reliably resulted in dense, polycrystalline Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> were determined and pulsed laser deposition targets were synthesized. During pulsed laser deposition, the background gas atmosphere was determined to change the transfer of lithium from the target to the substrate. Additionally, it was determined that the composition of the target changed significantly during deposition due to preferential ablation of lithium from the target. Commercially procured SrTiO<sub>3</sub> bicrystals were used with epitaxial deposition conditions to generate thin films with grain boundaries that could be quantitatively measured using impedance spectroscopy. It was found that, of the available misorientations, 24°- and 6°-tilt were not highly disruptive to ion conductivity but there was a significant increase in the impedance of the 45°-tilt grain boundary. A process for the generation of polycrystalline SrTiO<sub>3</sub> with large grains was determined based on the requirements that the SrTiO<sub>3</sub> remain insulating. It was found that air sintering followed by reduction annealing and a controlled reoxidation procedure resulted in grains with an average diameter greater than 100 µm without inducing conductive behavior. Finally, results from a related study on LiZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub> thin films are included, where it was determined that the ion conductivity was influenced by a number of competing effects depending on the annealing and synthesis procedures.

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I was lucky enough to happen into the beginning of my research career at Colorado School of Mines under the tutelage of Dr. Geoff Brennecka as an undergraduate. There I began learning what it was to be a researcher and how much I enjoyed the process of discovering something new about the world. I worked at Mines with a talented group of researchers throughout the department and had the opportunity to get my foot into the door of multiple research groups and topics while there. Just prior to graduation, Dr. Brennecka suggested that I apply for a cooperative student internship at Sandia National Labs, where he had worked with Jon Ihlefeld, who would go on to be my advisor. I was among the first students that Jon hired to not only perform research but to build a lab from what were essentially empty rooms when we arrived. In a way, both Jon and I were taking a chance on entering this relationship as I was walking into a new group without much in the way of experimental capabilities, and Jon was essentially hiring me based on one conversation we had over lunch in Albuquerque. Jon's genuine desire to see all of his students succeed has been an inspiration for my own future leadership endeavors. His guidance in shaping me to be a researcher that does good science and is capable of communicating those results has been invaluable. Thank you to Geoff for getting me hooked on research and thank you to Jon for continuing to guide me to become the researcher that I am today, I like to think that both of our gambles have paid off.

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## **Chapter 1: Motivation and Outcomes**

## **1.1 Motivation**

High performance batteries are of great interest due to the increased need for storage and delivery of renewable energy to and from the grid as well as the increasing level of electrification of the transport sector.<sup>1, 2</sup> The current state-of-the-art technology for energy storage in these applications is the lithium-ion battery. Lithium-ion batteries are widely deployed due to their high energy and power density as well as stability of capacity over many charging cycles.<sup>3, 4</sup> At a basic level, a battery must send electrons from its negative terminal (anode) - through the circuit to be powered - to its positive terminal (cathode) and in turn must transport lithium ions from the cathode to the anode through the battery in order to generate this current.<sup>5–7</sup> The medium for transport across the battery is called the electrolyte and its conductivity is key to enabling highpower capable batteries. Common lithium-ion batteries make use of a polymer separator impregnated with an organic, liquid electrolyte between the cathode and anode, which represents a good compromise between cost, ease of manufacture, and performance. However, liquid electrolytes represent both a significant safety concern and have a limited electrochemical stability window. The organic liquids used in current lithium ion battery construction tend to react violently to catastrophic damage to the battery cell including mechanical damage and large current overdraws.<sup>8–12</sup> Both of these situations can lead to fires that have taken lives as well as damaged property. Further, liquid electrolytes have a limited electrochemical window that can prevent their integration with higher energy cathode and anode materials, including lithium metal. Solid state electrolytes offer a potential solution to the safety issue because they have reduced reactivity in air and show good thermal stability.<sup>13</sup> Additionally, several systems have also been shown to be stable in contact with high energy electrodes including lithium metal.<sup>14–16</sup> However, the ion conductivity of most solid state lithium ion conductors is low in the polycrystalline form. This has been observed as a resistive contribution of the grain boundary regions in a number of materials systems.<sup>17–23</sup> Broadly, this increased resistance has been attributed to a combination of structural factors, secondary phases, and space charge regions around the grain boundaries that prevent facile, transverse lithium ion conduction.<sup>24–30</sup> Beginning in the 1970s, the groups of De Jonghe and Nicholson discovered that in  $\beta$ -alumina, there was a pronounced effect of the grain boundaries on the sodium ion conductivity, but this could be mitigated heavily by texturing the ceramics such

that only low-angle grain boundaries were present in the microstructure.<sup>31, 32</sup> The platelet structure of  $\beta$ -alumina was exploited in combination with uniaxial pressing to generate highly textured microstructures that exhibited multiple orders of magnitude improvement in total ionic conductivity compared to their randomly oriented counterparts.<sup>33, 34</sup> Their work confirmed that, not only do the grain boundaries have an outsize effect on the total ionic conductivity of polycrystalline solids, but that grain boundaries can have widely varying properties depending on the change in orientation, structural matching, and electrical and compositional characteristics of each boundary.

To date, there has been very limited characterization of individual grain boundaries. This has come largely as a result of the fact that traditional fixturing for impedance spectroscopy measurements (which are commonly used to characterize ion conductivity) are not sensitive to single grain boundary effects, but to the ensemble effect of all grain boundaries that lie within the conduction pathway. Similar to the bulk sodium ion conductors above, thin film samples have shown marked differences in ion conductivity based on their microstructure, including order of magnitude increases in the conductivity with increased texture<sup>35–38</sup> and results wherein the expected increase in conductivity as a result of doping was overridden by the resultant changes in microstructure driving decreased conductivity.<sup>39</sup> These results paint quite a convincing picture that, not only do grain boundaries have a large effect on the total ion conductivity of a polycrystalline ion conductor, but that different grain boundaries can be expected to exhibit significantly different properties when their configurations are altered. More recently, there have been a limited number of studies that have shown, qualitatively, that this understanding is borne out by single grain boundary measurements using electrochemical strain microscopy (ESM), a form of scanning probe microscopy where an electrical signal is used to excite ion migration and the resulting strain caused by the ionic motion is measured.<sup>40, 41</sup> This gives a qualitative understanding of the high and low conductivity regions of a sample with spatial resolution that can be comparable to that of topographic atomic force microscopy. ESM measurements have been conducted in the  $Li_{1,3}Al_{0,3}Ti_{1,7}(PO_4)_3^{42}$  and  $Ce_{1-x}Sm_xO_{2-\delta}^{43}$  systems. This technique has also been used to demonstrate the difference in electrical response from one grain boundary configuration to another in Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub>. In conjunction with transmission electron microscopy measurements, it was determined that the reduction of titanium, from Ti<sup>4+</sup> to Ti<sup>3+</sup>, in the grain boundary resulted in a resistive Ti-O phase on the order of the thickness of the grain boundary depending on the grain

boundary configuration.<sup>44, 45</sup> This work makes large steps toward the understanding of ion conduction in grain boundary regions, but is limited to qualitative understanding and cannot answer for systems where changes in the coordination number and oxidation state of one of the constituent ions are not expected.

The intuitive understanding garnished from currently available data in the literature has been supported by computational work. The effects of dopant segregation in ion conductors have been modeled and show that a significant impact can be expected due to the change in stoichiometry around the grain boundary.<sup>46</sup> Comparisons of sodium conductivity in oxides and thiophosphates have shown that less dramatic disruptions near the grain boundary should be expected to yield higher ion conductivity across the grain boundary.<sup>47, 48</sup> In zirconia systems, it has been calculated that tilt grain boundaries are able to support ion conduction, but that twist boundaries enable two dimensional ion conduction, therefore providing significantly higher ionic conduction.<sup>25, 49</sup> This work has also extended into the realm of lithium ion conductors, where Symington and co-authors showed that the activation energy for conduction across different, high-symmetry grain boundary configurations could vary greatly, with the lowest activation energy grain boundaries being nearly identical to the bulk and others having as much as a 70% increase in their activation energy compared to the bulk.<sup>50</sup>

This leaves the state-of-the-art study of grain boundary effects on ion conduction with a significant knowledge gap generated by a lack of quantitative, experimental data being available to compare with computational results. While the computational results agree with one another in terms of there being widely varied effects of grain boundaries based on grain boundary structure, the absolute values of calculated materials properties rely on established values of interatomic potentials and thermodynamic properties that are formulated based on idealized theoretical calculations and bulk measurements. The significant deviation from the bulk in the grain boundary region could easily lead to large errors in these values. Development of techniques allowing for experimental data to be tied to quantitative values would allow for significant steps forward in both theory, by providing validation data, and applications, by opening new routes of microstructural engineering, for solid state electrolytes.

## **1.2 Executive Summary of Outcomes**

This thesis will demonstrate the following experimental and analytical outcomes:

- 1. Methods for the production of  $Li_{3x}La_{1/3-x}TaO_3$  bulk ceramics were investigated in pursuit of producing phase-pure ceramic targets for use in pulsed laser deposition.
- 2. The burial powder configuration during the sintering of  $Li_{3x}La_{1/3-x}TaO_3$  was determined to alter the final lithium composition of the ceramics, leading to the formation of varying amounts of a secondary phase, LaTaO<sub>4</sub>, resulting in ionic conductivity that was inversely correlated to the amount of secondary phase present in the microstructure.
- Epitaxial thin films of Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> were deposited by pulsed laser deposition and impedance measurements were performed on nominally single crystalline samples under a variety of conditions.
- 4. The effects of the oxygen to argon ratio in the background gas during pulsed laser deposition on the transfer of lithium from target to substrate was studied. It was found that increasing oxygen content in the background gas led to increased lithium concentration in the resulting film.
- Bicrystal SrTiO<sub>3</sub> substrates were used to template the growth of single grain boundaries in Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> films.
- 6. Quantitative measurements of a set of individual Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> grain boundaries were performed using impedance spectroscopy.
- 7. Electrochemical strain microscopy was measured in the grain boundary regions of the bicrystal  $Li_{3x}La_{1/3-x}TaO_3$  films, but the only observable effects under reasonable experimental parameters appeared to be due to electrostatic and topographic effects.
- 8. Polycrystalline SrTiO<sub>3</sub> with grain sizes on the order of several hundred microns was produced for use in combinatorial substrate epitaxy. These large grain sizes were achieved in a reasonable timeframe by employing an sintering step in air to achieve high density, then an anneal under a reducing atmosphere to encourage grain growth, and, finally, a reoxidation anneal to generate insulating SrTiO<sub>3</sub>.
- The effects of processing methods and temperature were studied in relation to the production and properties of LiZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub> thin films and found to be a function of vapor-phase carrier loss, increased interfacial formation, and dewetting of the bottom electrode.

# **Chapter 2: Background Information**

## 2.1 Mechanisms of Ion Conduction

## 2.1.1 Defect Chemistry and Equilibrium

In ionically bonded solids, atoms and defects can be described by the site that they occupy within the crystalline lattice and the charge that they possess relative to the ion that would occupy that site in the ideal lattice. This information is commonly conveyed through Kröger-Vink notation as illustrated below:

$$S_j^{\bullet} \text{ or } S_j' \tag{2.1}$$

where *S* represents the species (e.g. atomic symbol or V for vacancy) that is occupying site *j* within the crystal. The relative charge is given by the superscript, where 'represents a positive elementary charge and ' represents a negative elementary charge; these symbols can be repeated to indicate multiply charged defects and an *x* can be used to indicate neutral species.<sup>1, 2</sup> In general, there are three classes of sites that are observed in real lattices, those being cation sites, anion sites, and interstitial sites. The total defect chemistry of a material system is governed by three rules: 1) conservation of mass, 2) conservation of electroneutrality, and 3) conservation of the ratio of sites in the crystal.<sup>3</sup> Any formation or annihilation reaction involving defects must be balanced according to these rules. As an illustrative example, one can consider the sodium chloride rock salt structure. In the case of a pure material with no impurity atoms, only a few intrinsic defects exist as illustrated in the reaction equations below:

$$nil = Na_{Na}^{x} + Cl_{Cl}^{x} \stackrel{NaCl}{\longleftrightarrow} Na_{i}^{\bullet} + Cl_{Cl}^{x} + V_{Na}^{\prime}$$
(2.2)

$$nil = Na_{Na}^{x} + Cl_{Cl}^{x} \stackrel{NaCl}{\longleftrightarrow} Na_{Na}^{x} + Cl_{i}' + V_{Cl}^{\bullet}$$
(2.3)

$$nil = Na_{Na}^{x} + Cl_{Cl}^{x} \stackrel{NaCl}{\longleftrightarrow} Na_{gas}^{x} + Cl_{gas}^{x} + V_{Na}^{\prime} + V_{Cl}^{\bullet}$$
(2.4)

$$nil = Na_{Na}^{x} + Cl_{Cl}^{x} \stackrel{NaCl}{\longleftrightarrow} Na_{Na}^{x} + Cl_{Cl}^{x} + e' + h^{\bullet}$$
(2.5)

where the left-hand side of the arrow represents the inputs, which are simply the existing elements of the crystal structure in this case and can also be designated as nil when there are no external additions being treated. It is common for these equations to be written with only nil on the lefthand side of the arrow with an implied supply of each species on its own equilibrium site. Above the arrow, the number of parent structure basis units involved in the reaction is indicated and to the right of the arrow the products are indicated. Equations (2.2) and (2.3) represent the cation and anion Frenkel defects, where an atom is displaced from its equilibrium site into an interstitial site and the charge is compensated with a vacancy. Equation (2.4), on the other hand, represents a Schottky defect, were equal numbers of cation and anion vacancies are formed to maintain electroneutrality. In this case the extra atoms are represented as sublimating away from the crystal, but vacancies could also form on the surface without the loss of mass from the system. Finally, Equation (2.5) represents the intrinsic ionization of an electron within the material, which would most likely be caused by application of external stimuli to provide the ionization energy.

Expanding this example to include impurity atoms broadens the available reaction pathways that could be considered. For example, if magnesium or oxygen infiltrated the crystal, it might be compensated as below.

$$O_{2(gas)} \stackrel{4 \, NaCl}{\longleftrightarrow} 4Na_{Na}^{x} + 2O_{Cl}' + 2V_{Cl}^{\bullet}$$

$$OR$$

$$O_{2(gas)} \stackrel{4 \, NaCl}{\longleftrightarrow} 4Na_{Na}^{x} + 4V_{Cl}^{\bullet} + 2O_{i}'' + 2Cl_{2(gas)}$$

$$(2.6)$$

$$Mg \stackrel{2 \text{ NaCl}}{\longleftrightarrow} Mg_{Na}^{\bullet} + V_{Na}' + 2 C l_{Cl}^{x}$$

$$OR \qquad (2.7)$$

$$Mg \stackrel{\text{NaCl}}{\longleftrightarrow} Mg_{Na}^{\bullet} + e' + C l_{Cl}^{x}$$

While the Equations (2.6) and (2.7) do not form an exhaustive list of the possible compensation mechanisms they do illustrate the fact that there are many possible mechanisms for compensating aliovalent dopants/impurities in an ionic crystal. In most cases, one of the many possible mechanisms will dominate the compensation response for a given set of external conditions ( $pO_2$ , temperature, etc.) in a material leading to a dominant defect type. The expected dominant defect can be narrowed down by examination of the crystal and electronic structure of the material. The free space within the crystal often prohibits the formation of interstitial defects, particularly in the case of anions, which have significantly larger ionic radii as a result of the extra electron(s) in their

electron cloud. With respect to electronic structure, the large band gap found in some ionic solids leads to very large formation energies associated with the generation free electrons and holes. Of course, there are exceptions to both of these statements, such as the fact that some structures have enough free volume to accommodate interstitial anions such as fluorites<sup>4, 5</sup> and the T\* structure.<sup>6</sup> It is worth noting that some defects, can act as neutral defects, when the associated excess charges are localized. Equations (2.8) and (2.9) show both the charged and neutral vacancy cases for a metal-oxide (MO) in a reducing environment.

$$nil \stackrel{MO}{\Leftrightarrow} M_M^x + V_0^{\bullet\bullet} + 2e' + \frac{1}{2}O_{2(gas)}$$
(2.8)

$$nil \stackrel{MO}{\Leftrightarrow} M_M^x + V_O^x + \frac{1}{2}O_{2(gas)}$$
(2.9)

The neutral vacancy maintains zero net charge by virtue of the electrons that were previously ionizing the oxygen atom being localized to the site of the vacancy by its apparent charge, while the charged vacancy would occur in the case that the electrons are excited such that they are able to become delocalized and move throughout the crystal.<sup>7–9</sup>

The inclusion of defects within a crystal structure is commonly treated, in terms of thermodynamics, as one would approach a solution. In this manner, the defect species can be considered the solute while the crystal itself acts as the solvent. Following this line of thinking and applying the conservation rules set out for defect reactions above, can yield a schematic illustration of how different defect concentrations interact with one another and the environment surrounding the crystal. The resultant log-log plot of defect concentrations is commonly referred to as a Brouwer or Kröger-Vink diagram, especially if the x-axis represents the partial pressure of oxygen.<sup>10–14</sup> This complex interaction can be schematically solved by developing a system of equations that relates each defect of interest to one another in addition to applying the constraint of electroneutrality of the system. This process is best illustrated with an example, such as addressing the possible defects in a metal oxide of the form  $M_2^{3+}O_3^{2-}$  in oxidizing, neutral, and reducing atmospheres. Building a Brouwer diagram starts with writing the possible defect reactions and then applying the well-known mass action law to develop relationships between the concentration of species involved in the reaction and the thermodynamic reaction constants.<sup>15</sup> It is important to note that the mass action law formally ties the activity of the species to the reaction

constant, but in the case of small concentrations, the activity and concentration are equivalent. It has also been shown that, in solids, relatively large concentrations of defects can continue to behave in the ideal, non-interacting manner necessary for this assumption to hold.<sup>13</sup> In the case of the example compound M<sub>2</sub>O<sub>3</sub>, the expected defect reactions and the corresponding mass action laws are shown in Table 2.1 along with the combined electroneutrality condition for all defects. For the purposes of this example, it is assumed that the dominant ionic defects in M<sub>2</sub>O<sub>3</sub> are Schottky-type vacancy pairs. In the equations below,  $E_g$  is the band gap energy and  $\Delta H$  represents the enthalpy of formation for the Schottky vacancy pair.

Defect Type	Defect Reaction	Mass Action Law	
Intrinsic	$M_2 O_3$	$n * p - K' a \frac{-E_g}{kT}$	(2, 10)
Electronic	$nu \iff e + n$	$\frac{1}{1} = K_I e^{-K_I}$	(2.10)
Intrinsic Ionic	$M_2 O_3 Q V''' + Q V^{\bullet}$	$\left[V_{M}^{\prime\prime\prime\prime}\right]^{2}\left[V_{O}^{\bullet\bullet}\right]^{3}$ $W_{I}=\frac{-\Delta H}{\sqrt{2}}$	(2 11)
(Schottky)	$nll \iff 2V_M + 3V_0$	$\frac{1}{1} = K_{Sch}e^{\kappa T}$	(2.11)
Extrinsic	$0^{x} \stackrel{M_2O_3}{\longleftrightarrow} V^{\bullet \bullet} + \frac{1}{2} 0 + 2a$	$n^{2}[V_{0}^{\bullet\bullet}](pO_{2})^{\frac{1}{2}}$	(2, 12)
Reduction	$U_0 \longleftrightarrow V_0 + \frac{1}{2}U_{2(gas)} + 2e$	$\frac{1}{1} = K_n$	(2.12)
Extrinsic	$3 M_2 O_3 M_3 N_4 M_4 + 2 O_4 + C_4$	$p^{6}[V_{M}^{\prime\prime\prime}]^{2}*1 - K$	(2 13)
Oxidation	$\overline{2}^{O_{2(gas)}} \longleftrightarrow 2V_{M} + 3O_{0} + 6$	$n \qquad \frac{3}{(pO_2)^2} = n_p$	(2.13)
Electroneutrality	$n + 2[U'''] - n + 2[U^{\bullet\bullet}]$		(2.14)
Condition	$n + 2\lfloor v_M \rfloor = p + 3\lfloor v_0 \rfloor$		(2.17)

Table 2.1: Expected Defect Reactions for M<sub>2</sub>O<sub>3</sub> Metal Oxide

In the case where most defects generated by slightly oxidizing or slightly reducing conditions are electronically compensated, the near stoichiometric region would exhibit the behavior n = p, where n is the concentration of delocalized electrons and p is the concentration of delocalized holes. From this condition, and the intrinsic electronic mass action law expression, it can be seen that, in the near stoichiometric region, the value of n and p have a constant value proportional to their reaction constant  $K'_{I}$ .

$$np = K_l \text{ and } n = p \therefore n = p = (K_l)^{\frac{1}{2}}$$
 (2.15)
With this knowledge, an extrinsic reduction reaction occurring in the near-stoichiometric region can be considered by combining equations (2.12) and (2.15):

Similarly for an oxidation reaction in the near-stoichiometric region, equations (2.13) and (2.15) can be combined to yield:

$$[V_0^{\bullet\bullet}] = \frac{K_n}{K_l} * pO_2^{-\frac{1}{2}}$$
(2.16)

$$[V_M''] = \left(\frac{K_p}{K_I^3}\right)^{\frac{1}{2}} * pO_2^{\frac{3}{4}} \propto pO_2^{\frac{3}{4}}$$
(2.17)

which completes the set of equations necessary to understand the dependence of defect concentrations on the oxygen partial pressure in the near-stoichiometric region. Further from stoichiometric conditions, different sets of defects can be expected to dominate the electroneutrality condition. The modified electroneutrality conditions for a heavily reducing and heavily oxidizing environment are shown in the set of equations (2.18) and (2.19), respectively.

$$2[V_0^{\bullet\bullet}] = n \tag{2.18}$$

$$3[V_M'''] = p (2.19)$$

Combining equations (2.12) with (2.18) results in a set of equations describing the concentration of oxygen vacancies and free electrons in the heavily reducing region:

$$[V_0^{\bullet\bullet}] = \left(\frac{K_n}{4}\right)^{\frac{1}{3}} * pO_2^{-\frac{1}{6}} \propto pO_2^{-\frac{1}{6}}$$
(2.20)

$$n = (2K_n)^{\frac{1}{3}} * pO_2^{-\frac{1}{6}} \propto pO_2^{-\frac{1}{6}}$$
(2.21)

Applying the mass action laws laid out in equations (2.10) and (2.11) to equations (2.20) and (2.21), the dependence of the metal vacancies and free holes can be derived:

$$[V_M''] = \left(\frac{K_{Sch}K_n}{4}\right)^{\frac{1}{2}} * pO_2^{\frac{1}{4}} \propto pO_2^{\frac{1}{4}}$$
(2.22)

$$p = \frac{K_I}{(2K_n)^{\frac{1}{3}}} * p O_2^{\frac{1}{6}} \propto p O_2^{\frac{1}{6}}$$
(2.23)

Similarly, combination of equations (2.10), (2.11), (2.13), and (2.19) results in analogous relationships for heavily oxidizing conditions.

$$[V_M''] = \left(\frac{K_p}{729}\right)^{\frac{1}{8}} * pO_2^{\frac{3}{16}} \propto pO_2^{\frac{3}{16}}$$
(2.24)

$$p = \left(9K_p\right)^{\frac{1}{8}} * pO_2^{\frac{3}{16}} \propto pO_2^{\frac{3}{16}}$$
(2.25)

$$[V_0^{\bullet\bullet}] = \left(\frac{\sqrt{27}K_{sch}}{\left(K_p\right)^{\frac{1}{4}}}\right)^{\frac{1}{3}} * pO_2^{-\frac{1}{8}} \propto pO_2^{-\frac{1}{8}}$$
(2.26)

$$n = \frac{K_I}{\left(9K_p\right)^{\frac{1}{8}}} * pO_2^{-\frac{3}{16}} \propto pO_2^{-\frac{3}{16}}$$
(2.27)

The relationships found in equations (2.16) through (2.27) can then be represented on a log-log plot of concentration versus the partial pressure of oxygen, providing insight into the formation of vacancies and their relative concentrations in a material. The example solved above is shown in Figure 2.1(A). Using the same methodology, with the assumption of the dominant defects in the near-stoichiometric region being ionic in character results in the solution presented in Figure 2.1 (B). Finally, this methodology can be extended to cover the case of dopants or impurities as shown in Figure 2.1(C). For the first two solutions, it is assumed that there are negligible contributions from impurity or dopant species and that the concentrations of the intrinsically generated defects are much greater than the concentration of impurities in the system. This is, of course, not true in many real materials, but can be easily addressed by considering the expanded electroneutrality condition generated by the impurity/dopant atoms.

$$3[V_M''] + n = [D_M^{\bullet}] \tag{2.28}$$

There will always be some region over which the dopant concentration is dominant in the defect formation in the material and this region can be broken down to electronically dominated (i.e.  $n \approx [D_M^{\bullet}] \gg 3[V_M^{\prime\prime\prime\prime}]$ ) and ionically dominated (i.e.  $3[V_M^{\prime\prime\prime\prime}] \approx [D_M^{\bullet}] \gg n$ ) regions. It is also assumed that the dopant concentration is constant because, in the case of a free standing material, there is not a source or sink for the dopant metal ions and at the relatively low temperatures of interest there it is not expected that there will be significant mass transport of the dopant species. In the case of an electrolyte in a battery cell, the concentration of the mobile ion may change as a function of the environment as defects are formed and the electrode materials could act as a source or sink to generate charge balance. From these limiting equations and assumptions, the same methodology laid out above can be applied to solve for the concentrations of different defects in relation to the dopant concentration.



Figure 2.1: Brouwer diagram solutions to the  $M_2O_3$  system for the cases of (A) electronically dominated intrinsic defects, (B) ionically dominated intrinsic defects, and (C) a donor doped condition.

#### 2.1.2 Classical Ion Transport

Diffusion of ions within solid materials is possible as a result of the open space within a structure. In the most basic form, diffusion can occur even in elemental solids, at any temperature above absolute zero. In order for an atom to move in a solid two things are required, the atom that will move and an open space for the atom to move into. The first is easily satisfied as solid materials contain on the order of 10<sup>22</sup> atoms/cm<sup>3</sup>, while the second is satisfied even in ideal materials due to the expected vacancy defects generated by thermodynamic processes. Thermodynamic theory predicts that intrinsically generated vacancies will occur even in an otherwise perfect material due to the reduction in Gibbs free energy driven by the increased entropy derived from having vacancies present.<sup>16, 17</sup> From Boltzmann's work on statistical thermodynamics, the entropy of a system can be calculated as:

$$S = k \ln(\Omega) \tag{2.29}$$

where S is the entropy, k is the Boltzmann constant, and  $\Omega$  is referred to as the thermodynamic probability or statistical weight. The value of the thermodynamic probability is equivalent to the number of microscopic states that are compatible with the macroscopic state of the system. In an elemental crystal where all sites are filled with a single atom, this value is 1. However, by introducing just a few defects, its value increases to be on the order of the number of atoms in the system. The vacancies increase the number of possible configurations of the atoms in the material, leading to increased entropy and decreased Gibbs free energy. Consider the equation for Gibbs free energy:

$$\Delta G = \Delta H - T \Delta S \tag{2.30}$$

where  $\Delta G$  represents the change in Gibbs free energy,  $\Delta H$  represents the change in enthalpy, *T* is the absolute temperature, and  $\Delta S$  is the change in entropy,<sup>18, 19</sup> it is clear that increasing entropy reduces the Gibbs free energy revealing that generation of vacancies is part of the expected equilibrium of any material. While vacancies are commonly the most energetically favorable position for a mobile ion to occupy, interstitial sites are also available in many situations due to the small size of common mobile ion species such as protons and lithium. With these ingredients present, the process of ion motion becomes apparent: an atom can hop into an adjacent vacancy position resulting in a net flux of material, as illustrated in Figure 2.2. Under different ambient conditions, the availability of sites for transport and the dominant charge carrier in a material can change. This can be schematically illustrated by considering the Brouwer diagrams from Figure 2.1, where following the profile generated by the highest concentration line across the range of  $pO_2$  values gives an indication of what defects might be available to participate in the charge transport in a material.



Figure 2.2: Schematic illustration of the fundamental units of ionic diffusion through a solid, crystalline lattice. A vacant site provides a new place for the atom to reside resulting in equal, but opposite fluxes of vacancies and atoms in the solid. Without an external driving force, the direction of these hops is random.

At the microscopic scale, the motion of ions in a solid is described by random walk diffusion, which is analogous to Brownian motion in liquids and gases. Random walk diffusion can be quantified by the following equation:

$$D_r = \frac{a^2 \nu}{b} \tag{2.31}$$

where  $D_r$  is the random walk diffusion coefficient, *a* is the distance of the hop between two neighboring sites, *v* is the jump frequency of the mobile ions, and *b* is a geometric factor determined by the dimensionality of the ion migration (*b*=2, 4, or 6 for 1D, 2D, or 3D motion, respectively). The jump frequency can be further described in terms of the Gibbs free energy of activation ( $\Delta G_a$ ) by:

$$\nu = \nu_0 \exp\left(-\frac{\Delta G_a}{kT}\right) = \nu_0 \exp\left(\frac{\Delta S_a}{k}\right) \exp\left(-\frac{\Delta H_a}{kT}\right)$$
(2.32)

where  $v_0$  is the attempt frequency (including both successful and unsuccessful hops), k is the Boltzmann constant, T is the absolute temperature, and  $\Delta S_a$  is the entropy of activation, and  $\Delta H_a$  is the enthalpy of activation, more commonly referred to as the activation energy  $(E_a)$ .<sup>20, 21</sup> The value of the activation enthalpy depends on the nature of the defect that accommodates ion motion. In the case of intrinsically generated vacancies, this will include the enthalpy of defect formation as well as the migration enthalpy. However, in the case of extrinsic defects generated by doping, the concentration of defects is dominated by vacancies formed to accommodate the inclusion of the dopant atoms. In this case the activation enthalpy can be approximated as the migration energy alone, assuming that there is no trapping between the dopant defect and the mobile ion. If there is trapping between the mobile ion and the doping defect, this energy must be included in the consideration of the activation enthalpy. As implied by the name, random walk diffusion, in the absence of some external driving force, this motion does not have a preferred direction and will not result in the net migration of mass.

For classical diffusion considerations, the most common driving force is the chemical potential driven by a concentration gradient.<sup>22, 23</sup> The behavior associated with this diffusion mechanism can be measured by the tracer diffusion coefficient (D\*) by introduction of a rare isotope, then measuring diffusion progress as a function of time and fitting the data to Fick's laws. This tracer diffusion coefficient is traditionally used to describe the motion of ions at relatively long length scales compared to those described by the random diffusion coefficient ( $D_r$ ).<sup>23, 24</sup> Ion conduction follows the same principles, but the driving force is an electrical field, which acts on the charged ions and results in an energetic advantage to the forward hop compared to a backward hop. This causes the ions to preferentially move in the direction of the electric field for positively charged ions and opposite the electric field for negatively charged ions. On the macroscopic scale, the net flux of ions constitutes the ionic current that is measured when an ion conductor is subjected

to an electric field. The migration associated with ion conductivity is characterized by a long-range diffusion coefficient ( $D_{\sigma}$ ).

In most cases, the three diffusivity values defined above will not be equal because the motion of ions in a material can rarely be fully described by single, uncorrelated hopping events. The relationship between the random diffusion and tracer diffusion coefficients is defined as the tracer correlation factor,  $f = D_*/D_r$ , which effectively shows the efficiency of tracer diffusion with respect to random walk diffusion. This value is tied to the correlation between forward and backward hopping of atoms, where in most cases, the mobile ion will have a larger chance of making a backward hop instead of a second forward hop.<sup>23, 25</sup> Similarly, the Haven ratio is defined as  $H_R = D_*/D_{\sigma}$  and can give some indication of the level of correlation between mobile ions during the conduction process. Unfortunately, direct interpretation of the Haven ratio requires a significant amount of knowledge about the system because of the large number of factors that play into the final value.<sup>26</sup> Combination of these two equations gives a direct relationship between the random walk diffusion discussed in Equations (2.31) and (2.32) and the long rage diffusion:

$$D_{\sigma} = \frac{f}{H_R} D_r \tag{2.33}$$

The value of the long range diffusion coefficient can also be calculated directly from the ion conductivity of the material by applying the Nernst-Einstein relationship:<sup>27–29</sup>

$$D_{\sigma} = \frac{\sigma kT}{n^2 Z} \tag{2.34}$$

where  $\sigma$  is the ion conductivity, k is the Boltzmann constant, T is the absolute temperature, n is the number of mobile carriers, and Z is the charge of those carriers. Combining Equations (2.31) through (2.34) allows for the development of a relationship between the ion conductivity and the activation energy of migration:

$$\sigma = \frac{f}{H_R} \frac{a^2}{b} \frac{n^2 Z}{kT} \nu_0 \exp\left(\frac{\Delta S_a}{k}\right) \exp\left(-\frac{E_a}{kT}\right)$$
(2.35)

This equation is often further simplified by gathering all terms that are not temperature dependent into a single prefactor termed  $\sigma_0$ . This simplification is not exact because some of the prefactor terms, such as *n*, *f*, and *H<sub>R</sub>*, can have a temperature dependence but will generally hold for measurements within a single system.<sup>26</sup> With the above, Equation (2.35) takes on the familiar form of the temperature dependent conductivity that is used in conjunction with an Arrhenius type analysis for the determination of the activation energy of ion conduction:<sup>30</sup>

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{2.36}$$

By extracting the slope of a plot of product of the absolute temperature (*T*) and measured value of conductivity ( $\sigma$ ) against the inverse of the temperature (1/*T*), the activation energy can be calculated. Notably, if multiple slope regimes are observed in this analysis, it can further indicate that the mechanism of ion conduction has changed. For example, ion migration through new sites may become available with the application of increased temperature allowing the ions to more easily transit larger energy barriers. This could also indicate a phase transition has occurred resulting in a completely new conduction pathway being opened to the mobile ions.

#### 2.1.3 Crystal Structure Effects on Ion Migration

Perhaps the most widely cited structural factor related to the motion of ions is the lattice volume or the size of the bottleneck.<sup>81–88</sup> Common intuition would suggest that increasing the lattice volume, with the assumption that the number of atoms in a unit cell stays constant, would lead to increased free volume in the structure, reducing the barriers to migration throughout the crystal. The ion migration bottleneck is defined as the part of the ion migration pathway with the smallest cross sectional area leading to a high energy position in the migration pathway.<sup>39</sup> By similar logic, expanding this bottleneck should straightforwardly reduce the ion migration barrier and lead to a concomitant increase in ion conductivity, which is found to be the case in a number of studies.<sup>83, 86, 87</sup> On the other hand, expansion of the lattice can lead to changes in the energy landscape of the crystal or change the site energies within the crystal leading to complex, counterintuitive relationships between expansion of the lattice/bottlenecks and ion conductivity.<sup>34, 35, 38, 40, 41</sup>

The coordination environment of both the fixed lattice and mobile ions throughout the migration pathway can also have significant effects on the mobility of ions. Maintaining an advantageous coordination for the mobile ion throughout the migration pathway has been shown to significantly reduce the activation barrier. For example, in spinel structures with a divalent mobile ion (e.g. magnesium), the mobile ion sits at a tetrahedral (four-fold) site, which is not a

preferred coordination for magnesium, however it was shown that in MgSc<sub>2</sub>Se<sub>4</sub> spinel, the migration pathway for magnesium includes an intermediate eightfold coordination site that significantly reduces the activation barrier height during migration.<sup>42</sup> Conversely, lithium conducting structures that exhibit migration pathways with only tetrahedral coordination (BCC anion frameworks) are found to have lower migration energies than those with varying coordination throughout their migration pathways (FCC and HCP anion frameworks).<sup>40</sup>

A common feature in materials with high ion conductivity is a significant level of disorder in the mobile ion sublattice, the fixed sublattice, or both. Disorder can also lead to distortion of the bonding environment for specific atoms, leading to changes in the energetic barrier to ion motion. For example, lithium atoms in some materials have been shown to preferentially sit in the distorted portions of the lattice rather than the traditionally occupied sites of the lattice.<sup>93, 94</sup> The distortion around these sites tends to reduce the strong preference for the ordering of the mobile ions, allowing motion with a smaller energetic barrier. Even without strong distortion, prevention of the ordering of the mobile ion sublattice has been shown to significantly increase ion conductivity in some materials. Several promising ion conducting materials undergo an order-disorder transition, commonly observed as an evolution from lower symmetry to higher symmetry with increasing temperature, that leads to increases in ion conductivity not predicted by the Arrhenius-type relationship between ion conductivity and temperature that is laid out in Equation (2.36). Notably the lithium garnet,<sup>45, 46</sup> sodium closo-borate,<sup>47, 48</sup> and the archetypal silver-halide type systems<sup>99, <sup>100</sup> exhibit this behavior.</sup>

As briefly discussed in Section 2.1.2, vacancies and interstitial sites are a primary part of the ion migration process in solid materials. Both vacancies and interstitial defects can be generated as an intrinsic property of the material, or as a result of extrinsic factors such as doping. The type and arrangement of defect sites determine the value of the jump distance (*a* in Equation (2.31)). Furthermore, the formation energies of the different defects can change the observed value of the enthalpy of migration and are, therefore, related to the mobile ion concentration in any given material. However, in many cases, the relationship between defect concentration and mobile ion concentration is not one-to-one.

#### 2.1.4 Concerted Ion Migration

To this point, the basic mechanism that facilitates ion conductivity in solid materials has been established in a material under the assumption that mobile ions move independently of one

another because of a low concentration resulting in negligible interactions between individual ions. This case works well as a simple model to build understanding but in many technologically relevant ion conducting materials, the concentration of mobile ions is significantly higher than what could be considered dilute. The increased concentration leads to more complicated factors affecting the motion of ions in these materials. For example, ion motion can become correlated as a result of Coulombic interactions between mobile ions.<sup>26</sup> Two complimentary, seminal models exist to explain the details of this process of ion motion in the presence of interacting mobile ions. The coupling model, proposed by Ngai, considers disordered materials and generalizes the application of classical mechanics to the relaxation processes surrounding the movement of ions and describes a "slowing down" of the relaxation time as a result of the interactions between mobile ions.<sup>51–54</sup> The results can effectively recreate ion conductivity measured as a function of frequency and, in fact, can link a number of disparate measurements to a single understanding of constrained ion motion.<sup>55</sup> However, the coupling model does not provide a direct description of the space and time aspects of the atomic scale motions. The jump relaxation model was developed soon after to explain the same slowing of the relaxation phenomenon in ion conducting materials. Although the mathematical formalisms differ, the author explicitly considers the jump relaxation model to be complementary to the Coupling model, because they explain the same phenomenon and give similar results.<sup>56, 57</sup> Importantly, the jump relaxation model provides a straightforward physical picture of the energy landscape the leads to correlated ion motion.

The jump relaxation model supposes that there are two superimposed potential fields that determine the equilibrium site of a mobile ion: the periodic lattice potential and the "Coulomb cage" potential, which is generated by repulsive interactions with other nearby, mobile ions. A schematic Coulomb cage configuration is shown in Figure 2.3(A), with the superimposed potentials shown in Figure 2.3(B). Notably, the energy barrier associated with a forward hop ( $\delta_f$ ) is significantly higher than the energy barrier for the ion to "back-hop" to its original position ( $\delta_b$ ). Because the energetic state at site A<sub>1</sub> is elevated, the system is expected to relax to a lower energy state, which can be accommodated by two mechanisms. The first is the "back-hop" where the lower energy barrier is overcome, and the mobile ions that form the Coulomb cage where the other mobile ions experience correlated motion to shift the position of the Coulomb cage energy minimum to accommodate the original ion's motion. The relaxing energy landscape as a function

of time is illustrated in Figure 2.3(C), where the lattice potential is fixed in space, but the motion of the Coulomb cage potential shifts the total potential such that  $\delta_f(t)$  and  $\delta_b(t)$  become equal, resulting in the situation illustrated for t=0 when the relaxation completes and equilibrium is achieved again.<sup>56–59</sup> Further refinement of the jump relaxation model was made by the introduction of the concept of mismatch and relaxation (CMR)<sup>60</sup> and MIsmatch Generated Relaxation for the Accommodation and Transport of IONs (MIGRATION) models.<sup>61–63</sup> These extensions of the jump relaxation model consider that the back-hop and the motion of the cloud are proportional to one another throughout the relaxation process, while the core mechanism remains the same. The resulting model variations show small improvements to the already strong fits to real data that were generated using the jump relaxation model.



Figure 2.3: Schematic representation of the processes of the jump relaxation model. (A) The simplified structure of an ion conductor in two dimensions with mobile ions (orange) sitting on a sublattice formed within a lattice of fixed ions (blue). The motion of the central ion is used as the starting point for the model. (B) The combination of the potentials generated by the lattice and the Coulomb cage that is generated by the locations of the other mobile ions.  $\delta_f$  represents the energy barrier to a forward hop from site  $A_0$  to  $A_1$  and  $\delta_b$  represents the energetic barrier for a back-hop from site  $A_1$  to  $A_0$ . (C) The time evolution of the potential in the case that a back-hop does not occur. As time progresses from t=0 (when the ion moves to the site  $A_1$ ), the surrounding mobile ions move, leading to a shift in the Coulomb cage potential position, changing the ratio of  $\delta_f$  and  $\delta_b$ .

#### 2.1.5 Fast- and Super- Ionic Conductors

Fast ion conductors are, in particular, enticing for technological applications. This class of materials is defined as solids that have ion conductivity values that approach or exceed the values of their liquid ion conducting counterparts.<sup>59, 64</sup> Fast ion conductors have potential applications as wide ranging as fuel cells, solid state batteries, electrochemical membranes, sensors, and solid state hydrogen storage.<sup>31, 65–69</sup> Given this wide range of potential applications, there has been extensive research into the mechanisms that allow for fast ionic conduction in some materials and what predictors could be used for screening of these materials.<sup>120–122</sup>

As with all conducting materials, the conductivity of a fast ion conductor can be generalized with the equation:

$$\sigma = \sum_{j} n_j Z_j \mu_j \tag{2.37}$$

where  $n_j$  is the number density of charge carrier j,  $Z_j$  is the fundamental charge of charge carrier j, and  $\mu_j$  is the mobility of charge carrier j. This equation is summed over all the available charge carriers in a system to achieve a good estimate of the total conductivity of any given material. In general, the value of  $Z_j$  is fixed, leaving the manipulable variables in this equation to be the number of charge carriers and the mobility of those charge carriers. Both of these considerations are crucial to the high ion conductivity that is observed in fast ion conducting materials.

Large numbers of charge carriers are one key descriptor for fast ion conductors.<sup>73–76</sup> Contrary to the electronic conduction case, where an electron can move freely within any band that is not fully filled, for an ion to become a charge carrier, it must be able to diffuse within its microscopic environment. Depending on the level of concerted motion of ions and the ratio of the concentration of mobile ions and mobile ion vacancies, vacancies or mobile ions may be more appropriate for consideration in Equation (2.37). This can lead to the counterintuitive effect of having a decrease in the stoichiometry of the mobile ion actually result in greatly increased conductivity.<sup>73, 76</sup> This effect can also be highly non-monotonic as the interplay between the vacancy and mobile ion concentration is not straightforward.<sup>127, 128</sup>

Of similar concern for some materials is the dimensionality of the ion conduction path. Some materials exhibit only one- or two- dimensional conduction pathways, which can be blocked by defects or dopants in the material.<sup>79–83</sup> This calls on the importance of having an interconnected, or percolating, path of defect sites that can be occupied by the mobile ion throughout the material. Considerable work has been performed in pursuit of understanding these percolating pathways in different materials such as argyrodites,<sup>84</sup> which form percolating lithium ion paths when the lattice can be made to disorder; garnets,<sup>85</sup> which make use of a highly conductive pathway between octahedral sites that are accessible upon the inclusion an overabundance of lithium in the structure; and in sulfide-based materials,<sup>40</sup> which exhibit large variations in the activation energy for lithium ion motion depending on the percolating pathway that is available in a given crystal structure.

The final consideration gleaned from Equation (2.37) is that the mobility of the charge carriers must be high. In recent decades, one of the key reasons for high mobility in fast ionic conductors has been found to be the frustration of the energy landscape.<sup>86</sup> While there is not a well settled nomenclature in the literature, the concept of frustration refers to a number of mechanisms that generate a relatively flat energy landscape throughout the material. This flat energy landscape is counter to the common illustration of the energetic landscape of an ionic, crystalline solid that can be seen at the top of Figure 2.3(B), which is generated by the enthalpic stabilization of atomic positions as a result of strong electrostatic interactions between cations and anions. In superionic conductors with frustrated energy landscapes, then it can be expected that the materials are at least partially stabilized by an entropic contribution to the free energy. Keeping in mind that liquids are mostly entropically stabilized, this is further evidenced in studies of silver and copper halide materials which, in some cases, show evidence of a superionic transition being interrupted by melting.<sup>49, 75, 87–89</sup> The entropic contribution that appears to be present as part of energy landscape frustration can be generated by dynamic properties of the lattice, by chemical properties of the lattice constituents, or by the intrinsic structural properties of the material. Dynamic frustration occurs as a result of some part of the lattice dynamics having a similar relaxation frequency to that of the ion motion. For most phonons, the frequency is so much greater than that of ion motion that the ion effectively experiences an average value of the effect. In the case that the frequency would be significantly lower than that of ion motion, within the reference frame of the ion, the lattice is static. Only when the frequencies are similar, can the associated vibrations create situations with significantly reduced migration barriers.<sup>90, 91</sup> The well known "paddlewheel" effect observed in a number of ion conductors with orientationally disordered polyanion species are one example of this effect. The rotational frequency of the disordered polyanions coincides with the ion frequencies associated with ion migration.<sup>92, 93</sup> Chemical frustration of the lattice can occur as a result of bonding with mixed character or through interaction with natural dipoles found in some structures, particularly those with polar, polyatomic ions. Bonds that have some covalent character appear to fluctuate in and out of covalent bonding, which reduces the barrier to migration.<sup>94–96</sup> This can be further characterized as an anion polarization distribution, which shows a multimodal character indicating a mixture of covalent and ionic bonding characters. The same analysis can be applied to polyanions, where the structure of the polyanion generates different bonding environments depending on the location of the migrating cation's position relative to the

polyanion.<sup>97, 98</sup> Finally, structural frustration of the energy landscape occurs as a function of the competition between local and global preferences for mobile ion site occupancy. Wide ranging factors (e.g. temperature, ion size, stoichiometry, crystal structure/symmetry, vacancy/interstitial size and shape, and static sublattice order/disorder) can combine to result in no statistical preference for the sites that the mobile ions occupy on their respective sublattice. This results in a significant contribution to the entropic stabilization of the material via the large number of configurations available to the materials.<sup>43, 99–101</sup> In all cases, the frustration of the landscape significantly reduces the activation energy associated with the mobile ion migration from Equation (2.32), in turn increasing the ease with which the ions to contribute to macroscopic conductivity.

## 2.2 Grain Boundary Structure and Properties

The majority of materials systems exhibit crystalline structure at room temperature under both equilibrium and non-equilibrium conditions.<sup>102</sup> While studies of crystal structure can often be made under the assumption that the lattice is effectively infinite due to the minute scale of atoms and their motion, it is exceedingly rare for macroscopic-scale materials to be made up of a single crystal, especially without the intervention of humans in the materials synthesis process. Perhaps the most ubiquitous naturally occurring single crystal is quartz, which can be found as very large, single crystals in places where the material has been allowed to grow very slowly (e.g. caves). On the other hand, manufacturing of single crystals has long been of interest to the electronics industry, leading to the development of very mature processes that can produce single crystalline boules on the order of tens to hundreds of millimeters in diameter and meters in length.<sup>103</sup> These processes have been developed for silicon, GaAs, CdTe, many other III-V semiconductor compounds, metals, and a number of oxides. While this is an impressive feat of engineering, there are few materials that are commercially available as single crystals due to limitations of various growth processes. A number of methods allow for single crystal synthesis across a broad range of compositions, including but not limited to the Czochralski method, <sup>103, 104</sup> the optical floating zone method,<sup>105</sup> the Bridgman-Stockbarger method,<sup>106, 107</sup> chemical vapor transport,<sup>158, 159</sup> and microwave/arc melting.<sup>110, 111</sup> However, all of these result in significantly higher cost for the resulting single crystal materials compared to their polycrystalline counterparts. This leaves the majority of technologically relevant and naturally occurring materials as polycrystalline, meaning that they are composed of many smaller crystals, each with a spatial orientation unique from its

neighbors. While it is straightforward to envision two small crystals, also commonly termed grains, with their principal axes rotated in space with respect to one another, it is then necessary to consider the interaction between the two misoriented crystals where they intersect. The surface separating two misoriented crystals is termed the grain boundary and is one of the most common two-dimensional defects in materials. The misorientation of crystals and a schematic grain boundary are illustrated in Figure 2.4, where it becomes obvious that the properties of the crystalline material are not likely to persist in the grain boundary region due to its highly modified stoichiometry, bonding, and structural organization.



Figure 2.4: Schematic representation of an arbitrary grain boundary in a rock salt structured material. (A) Illustration of full crystals relative orientations to one another. (B) Detail view of the grain boundary region between crystal A and crystal B, where the grain boundary plane (edge illustrated as pink line) is the (110) plane of crystal A and the (130) plane of crystal B.

#### 2.2.1 Grain Boundary Geometry and Energies

In the absence of processing in the solid state, the distribution of the orientation of grains in a polycrystalline material are derived from the many points at which the crystalline phase nucleated. In the case of cooling from a melt, at temperatures sufficiently below the solidification temperature, homogeneous nucleation will become energetically favorable, where a multitude of nuclei will form within the supercooled liquid. Because these nuclei are formed from the disordered atoms within the liquid, there is no energetic driving force for the nuclei to have similarly aligned crystal lattices. In this simple example it can then be expected that the nuclei will grow to the point where they impinge upon each other, generating a network of grain boundaries throughout the solid, with wholly random misorientations between grains. Close examination of the distribution of atoms in the grain boundary region shown in Figure 2.4 may reveal that although the stoichiometry and bonding environment for atoms at the boundary is likely to be altered, there are also likely to be some low energy sites, such as the shared green atom near the top of the boundary plane, which is able to maintain approximately the same bond lengths as in the perfect crystal. This implies that there will be energetically favorable and unfavorable grain boundary orientations, thus necessitating a method of referring to their relative orientations in space.

Defining the relative orientation of multiple coordinate systems (i.e. the principal axes of two lattices) has been a mathematically solved problem for hundreds of years. Euler's work showed that any rotation of the axes in question can be uniquely defined by three parameters as long as they are independent from one another.<sup>112</sup> The classical form for defining the rotations in space is to use a 3×3 matrix of rotational components. These matrices are extremely convenient in cases where mathematical operations must be computed as they have well defined interactions in the framework of linear algebra; however, they do not provide any straightforward way of visualizing the rotational components from the values of the matrix components. Euler also showed that these three independent parameters could be defined using a set of three angles defined by starting with the reference axes and performing specific rotations to arrive at the new axes. For clarity, the reference axes will be referred to as the X-, Y-, and Z-axes, with the rotated axes being the X'-, Y'-, and Z'-axes. The first rotation  $(\phi_l)$  is taken to be the rotation of the original axes around the Z-axis, the second rotation ( $\Phi$ ) is performed around the X'-axis as it was positioned by the first rotation, and the final rotation ( $\phi_2$ ) is performed around the position of the Z'-axis after rotations  $\phi_1$  and  $\Phi$  have been completed. This results in  $\Phi$  representing the angle between the Zand Z'- axes and the  $\phi_1$  and  $\phi_2$  represent the angle between the X- and X'-axes and the intersection between the X-Y and X'-Y' planes. These angles are diagrammed in Figure 2.5 for more clarity than can be achieved in text.<sup>113, 114</sup> The final common method for representing the misorientation between two grains uses an axis vector that is defined in both the reference crystal and the rotated crystal such that a single rotation angle around that axis transforms the reference crystal coordinate system to that of the rotated crystal.<sup>115</sup> The pairing of a defined axis and the rotation angle satisfy Euler's requirement for three independent terms to define the relative orientation of two coordinate

systems, fully defining the relation of one crystal to another. The axis-angle definition of misorientation is perhaps the easiest of the three methods discussed above to visualize, especially in the case of grain misorientations with simple relationships (i.e. those that can use a straightforward crystalline direction as the rotation axis).



Figure 2.5: The process of developing Euler angles for an arbitrary rotation. (A) The XYZ reference axes (dark blue) and the X'Y'Z' rotated axes (orange) before manipulation. (B) Application of the first rotation of  $\phi 1$  around the Z/Z'-axis. (C) Application of the  $\Phi$  rotation about the X'-axis. (D) Final rotation of  $\phi 2$  around the Z' axis. Note that the intersection line of the X-Y and X'-Y' planes is shown in purple.

To this point, several methods of defining the relative misorientation of two grains have been defined, however these definitions only give information on how the lattice of one crystal has been rotated compared to the other. Notably none of these formalisms alone provide any information about the actual intersection of the crystals that forms the grain boundary. To consider this interaction, one additional piece of information is needed: a geometric definition of the intersection between the two grains. This can be accomplished by taking the normal vector of the grain boundary surface. The simplest case would be that of a grain boundary that can be defined by a single, planar intersection. Then the combination of a single boundary normal vector and one axis-angle pair could describe the entirety of the grain boundary. When the normal vector is perpendicular to the rotation axis vector, the grain boundary is defined to be a tilt type grain boundary.<sup>116</sup> Conversely, when the normal vector is parallel to the rotation axis vector, the grain boundary is defined as a twist type grain boundary.<sup>116</sup> These simple cases are illustrated in Figure 2.6(A) and (B) to show the relation between the normal and rotation axis vectors. Most grain boundaries, however, will exhibit a mixture of tilt and twist character as a result of random grain orientation and it is exceedingly unlikely for grain boundary surfaces in a real material to take on a planar form over their entire area.



Figure 2.6: Schematic illustration of the geometric definitions of twist and tilt grain boundaries, in the case of a cubic lattice with a single, planar interface. (A) A pure twist grain boundary, where the rotation axis ( $\hat{t}_R$ ) and the grain boundary normal ( $\hat{n}_{GB}$ ) are parallel to one another. (B) A pure tilt grain boundary, where the rotation axis ( $\hat{t}_R$ ) and the grain boundary normal ( $\hat{n}_{GB}$ ) are parallel to one another. (B) A pure tilt grain boundary, where the rotation axis ( $\hat{t}_R$ ) and the grain boundary normal ( $\hat{n}_{GB}$ ) are parallel to one another.

As a result of the symmetry found in a crystal lattice, certain misorientations can be expected to generate grain boundaries that share common lattice sites. These especially symmetric grain boundaries are referred to most commonly using the coincident site lattice (CSL) formalism.

The CSL formalism defines a  $\Sigma X$  designation for misorientations that include overlapping lattice points, where X is an integer defined by the ratio of the volume of the primitive cell defined by the coincident sites to the volume of the primitive cell of the basic lattice. As a result of the geometry, the value of X will always be an odd number, with lower numbers indicating that coincidence is more common. This is most readily understood with the use of a diagram as shown in Figure 2.7(A) for the case of a  $\Sigma 5$  CSL in a simple cubic lattice. This is illustrated in two dimensions as every (001) plane in a simple cubic lattice is identical. Coincident site lattices for cubic crystals can be arbitrarily computed by selecting a rotation angle such that the point ( $x_0$ , - $y_0$ ) is rotated to coincide with the point ( $x_0$ , + $y_0$ ), the necessary angle can be calculated as:<sup>117</sup>

$$\theta = 2 \arctan\left(\frac{y}{x}\right) \tag{2.38}$$

This is verified by the  $\Sigma 5$  CSL illustrated in Figure 2.7(A) where the angle of rotation between the blue and orange lattices is given by  $\theta = 2 \arctan\left(\frac{1}{3}\right) = 36.87^\circ$ , which causes the [310] lattice point of the orange lattice to align with the [310] point of the blue lattice, giving  $x_0=3$  and  $y_0=1$ . This generates a tetragonal lattice with the lattice parameters of  $\sqrt{5}a$  in the basal plane and a in the [001] direction. In total this gives a volume of  $5a^3$  for the CSL unit cell, resulting in the value of  $\Sigma 5$ . A schematic illustration of the symmetric  $\Sigma 5$  (100) tilt boundary generated in a simple cubic lattice is shown in Figure 2.7(B). From this illustration, it becomes clear that a periodic array of points can be expected in a CSL grain boundary, where the lattices of the two crystals share certain points along the boundary where the atomic spacing and order is preserved for both crystals.



Figure 2.7: (A) Illustration of the rotation leading to a  $\Sigma 5$  CSL lattice in a simple cubic system. Only the basal planes are shown as the crystals are identical in the [001] (out of plane) direction. A rotation of 36.87° results in the orange lattice aligning with the blue lattice on the origin as well as other points marked by purple circles. The CSL primitive cell basal plane is highlighted in purple and has edge lengths of  $\sqrt{5a}$ . (B) Schematic illustration of the special ordering that may occur in the grain boundary between two crystals that form a CSL. It can be seen that at certain intervals points align, resulting in a special grain boundary with some level of periodicity.

The periodicity that is generated at CSL type grain boundaries would imply a lower energy state following the logic that the crystalline structure is the equilibrium state for most materials. Thus, it could be expected that even in disordered regions, generating periodic structures would reduce the grain boundary energy by approaching the periodic nature of the equilibrium state. A number of researchers have shown that in some cases, grain boundaries with increased symmetry as a result of these overlapping lattice points can have significantly lower energy than a grain boundary with arbitrary orientation.<sup>118–122</sup> For example, the grain boundary energy determined for a range of angles in the aluminum grain boundary systems denoted at the bottom of each panel are shown in Figure 2.8. From this data, it can be seen that for some grain boundary configurations, there are pronounced decreases in the grain boundary energy around orientations that result in a CSL lattice being formed, as in the case of Al(110) Tilt (Figure 2.8(A)) and Al(100)

Twist (Figure 2.8(B)) boundaries. On the other hand, for the Al(100) tilt system shown in Figure 2.8(C), there is only one minor dip in the grain boundary energy that does not correspond directly with a CSL boundary and could be attributed to noise in the measurement.



Figure 2.8: Grain boundary energy as a function of misorientation angle for the symmetric (A) Al $\langle 110 \rangle$  tilt, (B) Al $\langle 100 \rangle$  twist, and (C) Al $\langle 100 \rangle$  tilt grain boundary systems. Special misorientations are indicated by the arrows and are labeled with their coincident site lattice,  $\Sigma$  designation. In panel (C), a small dip in the energy is identified with a question mark to indicate that there is no obvious CSL orientation associated with this angle. The families of planes indicated after the  $\Sigma$  designation indicates the plane of the grain boundary in the coordinate system of each crystal. The solid line does not represent a fit to the data, but a guide to the eye. Data adapted from reference.<sup>118</sup>

With the above, one can consider several categorizations of the possible grain boundaries in a system. First it is worth considering the cusps that are generated in the energy as a function of the misorientation angle between two grains. Under this framework, grain boundaries could be divided into categorizations of singular, vicinal, and general grain boundaries. Singular boundaries are defined as those that represent the minima points along the grain boundary vs. misorientation curve. Vicinal boundaries are those that occur with reduced energy as a result of being of similar misorientation to singular boundaries. Finally, general boundaries are those that occur at the relatively higher energy portions of the energy vs. misorientation curve and do not have any special geometric alignment. Considering the data shown in Figure 2.8 in total, one finds that prediction of the existence of singular grain boundaries is not straightforward from the geometry of the boundary except in the case of misorientation angles approaching  $0^{\circ}$ , where the grain boundary disappears, and the grain boundary energy goes to zero. Thus, for any system, it can be expected that there will be a low energy grouping of misorientations near 0° or any other angle that satisfies the rotational symmetry of the crystal. The boundaries in this region, usually extending from  $0 \pm 15^{\circ}$ , are commonly referred to low angle grain boundaries and can be mathematically and structurally modeled using an array of dislocations due to their facile accommodation by the structure. Furthermore, the energy of low angle boundaries can be calculated using dislocation theory successfully.<sup>123, 124</sup> Misorientation angles larger than ~15° are considered high angle grain boundaries and for the most part will take on the character of the general grain boundary discussed above with grain boundary energy values that are high relative to the low angle grain boundaries, but similar from one general grain boundary to the next.

## 2.3 Grain Boundary Effects on Ion Conduction

Combination of the elements discussed in Sections 2.1 and 2.2.1make it somewhat apparent that the alteration of structure, chemical environment, and energy at the grain boundary can be expected to change the ion conduction behavior in these regions. However, it may be less apparent what effect the changes in the grain boundary vicinity might have on ion conductivity. In fact, depending on the material, both enhanced and diminished ion conductivity has been observed at the grain boundaries of lithium ion conducting materials. When observing the ion conductivity of a bulk ceramic, there are often two observable contributions to the total conductivity: the grain (bulk) conductivity and the grain boundary conductivity. These contributions are effectively in series, as illustrated in Figure 2.9, where it becomes apparent that for a lithium ion to move across the ceramic body, it must cross a number of grain boundaries in the process unless the thickness of the ceramic is less than the grain size. Given this series configuration, the limiting step for ion conductivity in these materials is the slower of the intragranular (bulk) conduction or the intergranular (grain boundary) conduction. While a minority, several compositionally complex perovskites<sup>175–181</sup> and garnets<sup>132–134</sup> have been shown to exhibit elevated lithium ion conductivity in the grain boundary than in the bulk. In the case of elevated conductivity at the grain boundaries, it would be expected that the ions might use the interconnected grain boundaries as an easy path for motion, making a parallel model more appropriate. In the majority of cases, however, the grain boundary presents a significant barrier to ion conduction.<sup>135–143</sup>



Figure 2.9: Schematic illustration of the potential, macro-scale conduction pathway of a lithium ion in a polycrystalline ceramic material. This illustrates in the inevitable need for the lithium ions to transit across grain boundaries during migration.

The increased surface energy at the grain boundaries is largely a result of the structural disruption, relative to the ideal crystal structure, where each ion exists in a coordination and bonding environment that minimizes its energy. At the grain boundary, many if not most atoms exist in a non-ideal coordination or bonding environment that includes dangling bonds as well as

non-equilibrium spacing of ions. This disruption can create several compensating environments, two common versions of which are secondary phases and space-charge regions.

Segregation of impurity atoms at the grain boundaries is a well-studied phenomenon in nearly all disciplines of materials science, from structural metals and corrosion<sup>144, 145</sup> to semiconductors<sup>146</sup> and ion conducting materials.<sup>147</sup> In all cases, it is observed that impurity and dopant atoms have a tendency to coalesce in the region of the grain boundaries. The commonly supplied explanation in metals is that the structural disruption of the grain boundaries provides both expanded and compressed sites that can be filled with impurity atoms without the large strain penalty incurred when the impurities are incorporated into the bulk. In ionically bonded materials, local charge imbalances due to dangling bonds and misplaced atoms can create an environment where it is favorable for aliovalent impurities to reside and provide local charge balance. In ceramics, this process has been observed as the formation of a glassy ceramic phase between grains that can be exploited to increase the density of sintered materials by acting as an aid to mass transport at elevated temperatures.<sup>148–151</sup> At or near room temperature, these glassy phases can be either significant barriers to the transport of ions or a high conductivity pathway.<sup>20, 202, 203</sup> Even in the absence of significant levels of impurities, the bonding imbalance at the grain boundary can lead to the formation of thin layers of secondary phases, particularly in the case of materials with multivalent cations such as titanium.44,45

Aside from the formation of secondary phases and the structural and bonding disruption, perhaps the most widely cited reason for the reduction in lithium mobility in oxide solid electrolyte materials is the formation of a space-charge layer. To complete this analysis, the core of the grain boundary is assumed to take on some charge as a result of the structural disruption or segregation of impurities/dopants. To maintain electroneutrality, this charge must be compensated by a depletion like-signed charges in the bulk-like layer immediately bounding the core of the interface, which is termed the space-charge layer (SCL). The SCL takes on charge as a result of the depletion or accumulation of charged defects, such as those discussed in Section 2.1.1. In most cases, the Poisson-Boltzmann formalism is used, which makes the assumption of dilute, continuum defects, a constant structural configuration up to the interface, and constant mobility of defects in both the SCL and the bulk material.<sup>157, 158</sup>

Under these assumptions, two limiting cases are often considered: the Mott-Schottky case, where the dopant or impurity concentration is fixed to the bulk value up to the interface (this condition also implies complete immobility of the dopant or impurity atom, but this is not the defining condition), and the Gouy-Chapman case, where all relevant defects are assumed to have sufficient mobility such that they are able to achieve equilibrium concentration profiles.<sup>158, 159</sup> Solutions to the Gouy-Chapman case are relatively straightforward under the assumption of just two or three charged defects and lead to the concentration profiles show in Figure 2.10(A).

While the Gouy-Chapman assumptions are useful in the fact that they lead to relatively simple, closed-form equations that can be solved to find the space-charge potential, they are generally limited in their applicability to real, ion-conducting ceramics. In most ion-conducting ceramics, not all species are appreciably mobile at operation temperatures. For example, oxygen conducting materials, such as CeO<sub>2</sub>,<sup>160–166</sup> do not have appreciable levels of cation migration at low temperatures, while lithium conducting ceramics are often selected to only have significant migration of lithium ions and all other species can be considered "frozen" in place at reasonable operating temperatures.<sup>167</sup> This can be treated by making the assumption that the compensating defect is evenly distributed (constant concentration) through the bulk region, up to grain boundary core. This condition may be expected at very high temperatures and could be frozen in by rapid cooling past the temperature where the defect becomes immobile. This is leads to the Mott-Schottky solution and results in concentration profiles as shown in Figure 2.10(B). Slower cooling would imply that there was a period of time where the temperature remained high enough to allow for mobility of all defects, but their transport could be kinetically limited during the cooling process. This case has more recently been treated as the restricted equilibrium case and essentially results in values that lie between the Gouy-Chapman and Mott-Schottky solutions. The restricted equilibrium case has shown to give more accurate estimations of the space charge potential than those given by the most simplified Mott-Schottky solutions.<sup>168–170</sup> An example of the concentration profiles resulting from restricted equilibrium is shown in Figure 2.10(C).

In all three cases illustrated in Figure 2.10, it can be seen that the space charge region is generated by a change in the concentration of the mobile defect in the vicinity of the grain boundary core. For the example given, of a positively charged core, this would result in significant depletion of the positively charged oxygen defects. In the opposite case of a negatively charged core, a positively charged, mobile defect would accumulate in the vicinity of the core with similar effects in terms of increasing the barrier to motion through the space charge region. Interpretation of the space-charge region's effects on ion motion are relatively simply explained by considering

Coulomb forces between charged particles. As an example, consider a mobile lithium defect in the case of both a positively and negatively charged grain boundary core. A positively charged grain boundary core necessitates a depletion of the mobile lithium in the space charge region in order to balance the charge locally which, in turn, is driven by the Coulombic repulsion between the positively charged lithium and the core.<sup>171</sup> Conversely, a negatively charged core will result in increased lithium concentrations in the space-charge region for the opposite reason. Referring back to the discussion of energy landscapes in Section 2.1.5 will make it obvious that the modified potential energy required for the lithium to exist in the space-charge region or become trapped in the space charge region for positively and negatively charged cores, respectively.<sup>172</sup>



Figure 2.10: Schematic representations of the concentration profiles derived from the (A) Gouy-Chapman, (B) Mott-Schottky, and (C) Restricted Equilibrium cases. All solutions exhibit a sharp decrease in the concentration of conducting defects  $[V_0^{\bullet\bullet}]$  in the vicinity of the positively charge grain boundary core.

## 2.4 Epitaxial Growth of Materials

The term epitaxy, from the Greek for arrangement upon, was introduced in the late 1920s by Louis Royer, who published some of the earliest systematic studies of epitaxy using X-ray diffraction.<sup>173</sup> Royer derived this term by observing that the crystal structures of two materials grew with definite orientational relationships. He was not, however the first to observe this phenomenon, as the earliest observations of epitaxy were in geological studies where naturally

occurring crystals were observed to have the same type of definitional relationship based on their external structures as early as 1836.<sup>174</sup> Royer's name for the phenomenon is quite descriptive in that the basic process of epitaxy is the arrangement of the atoms in the grown layer on top of a substrate in an attempt to minimize the energy of the system. Two major categories of epitaxy are commonly considered in the literature: homoepitaxy and heteroepitaxy. In homoepitaxy, material is grown on a crystalline substrate of the same material. This category is extended to include the deposition of doped layers, meaning that homoepitaxy does not necessarily mean an identical lattice parameter for the substrate and grown layer. Conversely, heteroepitaxy refers to the growth of a material on a substrate that has a significantly different chemical makeup and/or crystal structure.<sup>175</sup> Oftentimes this means that the strain generated in heteroepitaxy is greater than that in homoepitaxy, but this is not guaranteed. Schematic representations of the lattice matching between the substrate and the grown layer are shown in Figure 2.11(A).



Figure 2.11: Schematic epitaxial strain relationships in (A) plan view and (B) elevation view. Depending on the relative size of the substrate and grown layer lattices, the grown layer can be put in tensile or compressive stress. The elevation view in panel (B) shows how misfit dislocations aid in reducing the strain energy in the grown layer for the case of compressive stress in the grown layer.

The difference in lattice spacing between the substrate and the grown layer is referred to as the lattice mismatch and is calculated as:

$$\alpha = \frac{a_s - a_g}{a_s} \tag{2.39}$$

where  $\alpha$  is the mismatch strain,  $a_s$  is the in-plane lattice parameter of the substrate, and  $a_g$  is the in-plane lattice parameter of the grown layer.<sup>176, 177</sup> Note that the value of  $\alpha$  can be positive or

negative, and this sign corresponds to the common convention of referring to compressive stress/strain as negative and tensile stress/strain as positive. A large portion of the excess energy incurred at any epitaxial interface is associated with the strain energy from the lattice mismatch: One or both of the lattices must stretch to accommodate matching of the atomic positions across the interface. For small lattice mismatches, it is possible for this strain to be accommodated coherently across the entirety of the film. For grown layers on the order of 1-3 monolayers in thickness, the Frank-van der Merwe theory has been established to calculate the maximum mismatch for a coherent interface as ~14%.<sup>178, 179</sup> However, when the mismatch is larger or the thickness of the film increases, other defects such as dislocations are formed to relieve some of the strain energy. A misfit dislocation is any dislocation formed such that its Burgers vector has some component in the plane of the interface. Accordingly, the most efficient misfit dislocation, in terms of relieving mismatch strain, would be an edge type dislocation with a Burgers vector that lies wholly within the interface plane.<sup>177</sup> This type of misfit dislocation is illustrated in Figure 2.11(B).

The process of generating misfit dislocations to reduce the strain energy at the interface is referred to as relaxation and can be expected to occur in cases where the strain energy generated by a coherent interface exceeds the energetic cost of generating the misfit dislocation.<sup>180</sup> The cost of generating a misfit dislocation is dependent on an activation energy and is facilitated by the thermal energy present in the materials system. Generally, the activation energy is not determined by the perfect crystal structure, but by other defects or interfaces in the grown layer, referred to as dislocation sources, that significantly reduce the activation energy of dislocation formation. The most common source of misfit dislocations are threading dislocations (dislocations whose line passes through the thickness of the film, clusters of point defects,<sup>177</sup> and the free edge or surface of a film.<sup>178</sup> Additionally, multiple dislocations with "inefficient" (i.e. out of plane) Burgers vectors can interact with one another or the film interface to form new dislocations that are more efficient in relieving strain energy as the film grows.<sup>181–183</sup>

As discussed above, even epitaxial layers that fall below the critical mismatch strain of  $\sim$ 14% are expected to generate misfit dislocations as the thickness of the film increases. This can be interpreted loosely as the grown layer exhibiting increasing stiffness as monolayers are added, which in turn increases the energy associated with the same strain. As such, there must be a critical thickness, at which misfit dislocations can be expected to nucleate. Modeling the critical misfit and thickness has been treated a number of times using different approaches, including the Frank-

van der Merwe model,<sup>178, 179</sup> the Matthews-Blakeslee model,<sup>184–186</sup> and the People-Bean model.<sup>187</sup> The Frank-van der Merwe model focuses heavily on the critical mismatch strain for thin layers with some mention of the critical thickness. The most widely cited model, that of Matthews and Blakeslee, calculates the critical thickness of a single layer epitaxial film to be:

$$h_c = \frac{b}{8\pi f} \frac{1 - \nu \cos^2 \alpha}{(1 + \nu) \cos \lambda} \left( \ln \frac{h_c}{b} + 1 \right)$$
(2.40)

where  $h_c$  is the critical thickness, *b* is the length of the Burgers vector, *v* is the Poisson ratio, *a* is the angle between the Burgers vector and the dislocation line,  $\lambda$  is the is the angle between the slip direction and the direction, in the film plane, that is perpendicular to the intersection of the slip plane and the interface, and *f* is the mismatch as calculated in Equation (2.39).<sup>188</sup> This equation is generally solved numerically, due to the convoluted nature of its analytical solutions.<sup>189</sup> Because many of the values in this expression are constant for a given crystal structure, numeric solutions to the equation are not particularly taxing for modern day computers, allowing one to solve for the expected critical thickness using a range of reasonable values when one parameter is unknown for a system. An example of this type of solution is given for the Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> on SrTiO<sub>3</sub> system in Figure 2.12, where the value of the Poisson ratio was varied between 0.17 and 0.32 in steps of 0.01 and the slip system was assumed to follow that of SrTiO<sub>3</sub>.<sup>190</sup>



Figure 2.12: Solution to the Matthews-Blakeslee equation for the  $Li_{3x}La_{1/3-x}TaO_3$  on SrTiO<sub>3</sub> system of epitaxy. The Poisson ratio for the film material is unknown and was varied between 0.17 and 0.32 to cover a common range of values for cubic oxides. In all cases, the critical thickness in these films can be expected to fall below a value of 250 Å.

While the Matthews-Blakeslee equation accurately represents the formation of misfit dislocations in the case of an equilibrium material, <sup>191–193</sup> the observed critical thickness ( $h_c^{obs}$ ) is often significantly larger than the value calculated by Equation (2.40).<sup>194–198</sup> This is largely due to kinetic limitations on the formation of the misfit dislocations and their mobility throughout the film. This is partially captured by the People-Bean model discussed above, as they approached the calculations by considering the local strain energy's effects on the generation of misfit dislocations.<sup>187</sup> Further studies have been conducted in attempts to understand the kinetically limited case of critical thickness by a number of authors, including UVA's very own, William Jesser.<sup>197–199</sup> While these models tend to give results closer to  $h_c^{obs}$  for real materials, they are still

plagued by relatively large error bars and require significantly more *a priori* knowledge of the system under test, which prevents their adoption on the scale of the Matthews-Blakeslee model.

# **Chapter 3: Experimental Outline and Instrumentation Development**

## **3.1 Experimental Outline**

The work contained in this dissertation seeks to generate a suite of processing and measurement techniques that allow for the characterization of single grain boundary impedance behaviors in pursuit of understanding the fundamental mechanisms for diminished ion conductivity across grain boundaries. As discussed, this has been observed in many materials systems and stands as a persistent challenge to the implementation of solid state lithium ion batteries. Furthered understanding in this area can be expected to enable the generation of polycrystalline, solid state electrolytes with significantly higher total ion conductivity through microstructural engineering techniques, both reducing the costs and improving the capability of solid state lithium ion batteries.

For the most part, the results in this dissertation will be presented in chronological order due to their interdependent nature. The major exception to this trend is the presentation of the data surrounding the processing of  $LiZr_2P_3O_{12}$ . The majority of the  $LiZr_2P_3O_{12}$  data was collected by one of the coauthors on the related paper but was delivered to me with limited organization and had not been analyzed to any meaningful degree. Although the study is not directly related to the bulk of the work in this dissertation, I have chosen to include it here because I spent a significant amount of time generating a cohesive analysis of this data and it was my first foray into published scientific writing. This work was completed during the COVID-19 laboratory shutdown (relatively early in my graduate student tenure) but will be presented as the final experimental chapter of this dissertation to avoid detracting from the  $Li_{3x}La_{1/3-x}TaO_3$  related throughline of most of my study.

The remaining chapters will be presented to illustrate to the reader how the foundations for measuring single grain boundary impedance spectroscopy of  $Li_{3x}La_{1/3-x}TaO_3$  were established, beginning with the development of a process for creating pulsed laser deposition targets of bulk  $Li_{3x}La_{1/3-x}TaO_3$ . Following this work, development on the deposition parameter space was performed to better understand film properties that resulted from changes in the deposition environment. After establishing epitaxial deposition and processing parameters for  $Li_{3x}La_{1/3-x}TaO_3$  on SrTiO<sub>3</sub>, bicrystal substrates were introduced to allow for the growth of single grain boundaries in the  $Li_{3x}La_{1/3-x}TaO_3$  system for characterization of the effects of the grain boundary on ion conductivity. In parallel with the work on the bicrystalline  $Li_{3x}La_{1/3-x}TaO_3$  films, a process was
developed for the generation of polycrystalline  $SrTiO_3$  with grain sizes in excess of 100 µm to act as substrates for depositions that would allow the measurement of multiple grain boundary configurations that are not available commercially as bicrystals. Finally, the preliminary work toward achieving combinatorial substrate epitaxy will be presented.

#### 3.2 The Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> System

The majority of the work in this dissertation will focus on the synthesis and characterization of the Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> (LLTaO) materials system. LLTaO is an A-site deficient perovskite structure that shares a structural configuration with the more widely studied  $Li_{3x}La_{2/3-x}TiO_3$  (LLTiO) materials system.<sup>247-251</sup> The chemical formula A-site deficient LLTaO may be more accurately represented by  $Li_{3x} \square_{2/3-x} La_{1/3-x} TaO_3$ , where the character " $\square$ " represents A-site vacancies in the structure that are necessary to satisfy the charge balance of the system. The titanate material possesses a very high value for bulk ion conductivity but is hindered by high grain boundary resistance in its polycrystalline form.<sup>4, 6</sup> While this initially appears to make LLTiO a strong candidate for the proposed study of single grain boundary effects there are a few key aspects of the structure that discourage its use in this study. Firstly, the titanate material always exhibits ordering of alternating (001)-type planes with lanthanum rich and lanthanum poor stoichiometries, which in turn generates a tetragonal symmetry of space group P4/mmm.<sup>7</sup> Twin boundaries, which are essentially very high symmetry grain boundaries, can be generated in the material as a result of the tetragonal symmetry. The presence of these twin boundaries could potentially be observed in the impedance spectroscopy measurements, convoluting the interpretation of data generated from single grain boundaries.<sup>253</sup> LLTaO can take on the same tetragonal structure, but with values of  $x \ge -0.075$  in Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub>, a cubic, high ion conductivity phase has been observed.<sup>9-11</sup> Furthermore, the cubic form of LLTaO does not exhibit the two dimensional conduction that is observed in the domains of LLTiO as a result of the ordering in the tetragonal phase. The cubic symmetry arises from the ordering of lanthanum rich and lanthanum poor planes breaking down, leading to an equal distribution of lanthanum across all A-sites. The tetragonal and cubic structures are illustrated in Figure 3.1. Both structures have  $a_0$  lattice parameters ( $a_0 \approx 3.91$ Å) that match very well with SrTiO<sub>3</sub> ( $a_0 \approx 3.905$ Å) – a material that can be purchased as both single crystalline and bicrystalline substrates - indicating that epitaxial growth can proceed with fewer defects being generated during the relaxation process than in a more highly strained epitaxial system. Previous

work has shown that the reduction of titanium near the grain boundaries can be a significant driver for the increase in resistance observed at grain boundaries of LLTiO.<sup>12</sup> Because the ions that make up LLTaO are only commonly found to exhibit a single oxidation state (e.g. Li<sup>1+</sup>, La<sup>3+</sup>, Ta<sup>5+</sup>, and O<sup>2-</sup>) it can be expected that observations of the grain boundary in LLTaO will experience far less influence due to changes in the chemical species present in the material.<sup>6, 13</sup>

Mizumoto and Hayashi published several works in the late 1990s surrounding characterization of the ion conductivity of LLTaO. These works discovered the cubic phase of LLTaO and peak in ionic conductivity that is observed in conjunction with the formation of the cubic phase.<sup>9–11, 14</sup> While the cubic phase has exhibited high ion conductivity values, especially in the bulk, LLTaO still lags behind its titanate counterpart in ion conductivity in addition to being extremely refractory, making it less desirable for mass production applications. While LLTaO has been widely passed over as a commercially viable solid state electrolyte due to its somewhat lower ionic conductivity when compared to LLTiO, this combination of factors makes LLTaO an ideal candidate for the study of the fundamental mechanisms that affect ion conductivity in the vicinity of grain boundaries.



Figure 3.1: Illustrations of the (A) tetragonal (P4/mmm) structure and the (B) cubic (Pm3m) structure of LLTaO (Note, x = 0 in the calculated structures shown). Oxygen atoms are represented by red spheres, tantalum by the gold spheres, and lanthanum is represented by green spheres. The occupancy of the lanthanum sites is represented by the portion of the sphere that is filled with green. In (A) it can be seen that the tetragonal structure is very nearly equivalent to a stack of two cubic unit cells in the c-axis direction, but with alternating (001)-type planes containing lanthanum rich or lanthanum poor sites.

# 3.3 Sample Synthesis and Processing

## 3.3.1 Bulk Ceramic Processing

The first major hurdle in the work presented here was discovering a set of processing conditions that would allow for the generation of dense, polycrystalline LLTaO ceramics. Two primary methods were used in the initial attempts toward this goal: combustion synthesis and solid state powder synthesis. The combustion synthesis method was used previously to generate dense ceramics of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>, a garnet-structured lithium ion conductor that is extremely resistant to densification by traditional solid state synthesis methods.<sup>15</sup> Due to the refractory nature of LLTaO it was expected that this method might provide better density than solid state synthesis. The combustion synthesis method state (La(OAc)) as precursors. The general process is to generate

solutions of LiNO<sub>3</sub> dissolved in ethanol and La(OAc) dissolved in propionic acid. The Ta<sub>2</sub>O<sub>5</sub> powder is then suspended in ethanol by stirring and the solutions containing lithium and lanthanum precursors are then mixed into the suspension of tantalum. The ethanol is then driven off under moderate heating, while continuing to stir. This causes the tantalum oxide particle to be coated with a layer rich in lithium and lanthanum as illustrated in Figure 3.2. The advantage of this particle geometry is straightforward in that the coating of each tantalum oxide particle provides a physically closer source of lithium and lanthanum to form LLTaO. In a traditional solid state sintering process, the atoms must diffuse a distance that is on the order of the largest average particle, while in the combustion synthesis that diffusion length is effectively limited to about half the size of the tantalum oxide particles. Although the combustion synthesis processing route has a number of theoretical advantages, it was unfortunately found that it provided inconsistent results in terms of the final density of LLTaO ceramics. The few samples that reached a density greater than 90% of theoretical, are those presented in Chapter 4.



Figure 3.2: Schematic illustration of the coating of tantalum oxide with the layer rich in lithium and lanthanum. This coated particle geometry should minimize the necessary diffusion distance required for the formation of LLTaO during calcining and sintering.

The solid state synthesis processing route will be familiar to anyone with bulk ceramic processing experience. Solid precursors of Li<sub>2</sub>CO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and Ta<sub>2</sub>O<sub>5</sub> were mixed in stoichiometric ratios with the addition of 20 at.% lithium in a bid to account for the lithium losses during calcine, sinter, and pulse laser deposition processes. The precursors were then submerged in ethanol and milled overnight using a ball mill with yttria-stabilized zirconia (YSZ) milling media to mix the

precursors and ensure that no large agglomerates from the powder stock remained. This mixture was then dried at 80 °C for a minimum of 12 hours to drive off the ethanol before calcining at 1285 °C for 12 hours. This resulted in a multiphase powder that was milled again in ethanol with 2 wt.% polyethylene glycol added as a binder. This mixture was again dried at 80°C before being uniaxially pressed to 175 MPa for pellets in a 12.7 mm diameter die and to 85 MPa for pellets pressed in a 31.75 mm diameter die. This resulted in pellets with green density of 45-55% of the theoretical density of LLTaO. Pellets were then stacked inside an inverted crucible with loose powder of the same composition used to separate each pellet. This configuration was selected based on the results presented in Chapter 4, where it was found that burying the pellets in powder of the same composition did not result in significant changes to the lithium content in the sample. However, some powder was used to separate the pellets in order to prevent pellets fusing to one another during sintering. Samples were then heated slowly to 600 °C and allowed to dwell for 4 hours to burn off residual carbonates and the PEG binder. The reactive sintering step was carried out at 1500 °C for 12 hours, with natural cooling of the furnace, resulting in dense, single phase LLTaO pellets.

#### **3.3.2** Pulse Laser Deposition

All epitaxial films discussed in this dissertation were deposited using pulsed laser deposition (PLD). The basic process of PLD is illustrated in Figure 3.3. The PLD process uses the incident energy of the laser to ionize/vaporize the target material and eject it towards the substrate where the thin film will be grown. This technique was commonly cited in historical literature as providing stoichiometric transfer from the target to the substrate.<sup>16</sup> The combination of this purported benefit and a number of experimental parameters to adjust (background pressure, background gas, laser fluence, target compositions, distance from target to substrate (TTS), laser pulse frequency, incident beam angle, substrate and chamber temperatures, etc.) make PLD an ideal choice for the deposition of thin films in research. However, it has not been widely adopted in industry due to low areal uniformity that would prevent single depositions across a large area from having uniform properties. As will be seen in Chapter 5 the stoichiometric transfer from target to substrate is essentially a fiction in the case of materials with significant variations between the masses of constituent ions. Another key consideration is the effect of laser-target interactions. This is a field of study in its own right, but to summarize in the case of PLD, the primary goal of the laser-target interaction is to ablate atoms from the target material and generate a plasma with

stoichiometric ratios of each constituent atom. With large enough fluences, the laser can melt even extremely refractory materials, which can result in molten droplets of the target material being ejected toward the substrate. In most cases these are cooled and solid before reaching the substrate and tend to become large defects in the resulting film. Alternately, the laser can superheat and melt subsurface parts of the target resulting in rapid melting and vaporization that can eject particles on the order of the grain size from the target. Either of these processes involving ejection of larger particles from the target are referred to as bouldering and are not desirable.



Figure 3.3: Schematic drawing of the Ihlefeld group PLD chamber. Target materials are located on a carousel that rotates about multiple axes to allow for raster-motion and rotation of targets and is vertically centered in the chamber. An excimer laser pulse is delivered into the chamber through a window and impinges upon the target to create a plasma plume containing the elements of the target. The plume then travels in a line-of-sight manner to the substrate which is mounted to a heater at the top of the chamber.

Pulsed laser deposition in this dissertation was performed in a custom built vacuum chamber (manufactured by Kurt J. Lesker Co.) containing a substrate heater and a target carousel manufactured by NBM Design and modified to allow for computerized control of the target to substrate distance and target positions, respectively. The chamber is evacuated via a combination of a Pfieffer TPU 170 turbomolecular pump and an RV212 rotary vane roughing pump (Kurt J. Lesker Co.). A Lambda Physik (now Coherent) COMPex 205, KrF excimer laser that outputs 20 ns pulses is used to generate the plasma plume at pulse rates from 1 Hz to 20 Hz. The laser is capable of generating up to ~750 mJ per pulse depending on the recency of the gas fill and losses in the laser column. The laser beam is delivered into the vacuum deposition chamber through a custombuilt optics table (pictured in Figure 3.4(A)) that was assembled and calibrated by me with help from several other members of the Ihlefeld lab group. The beam is redirected three times to allow for entry to the chamber at 45° from vertical and is focused on the center of the target to allow for maximal use target surfaces. The multiple axis target carousel allows the target to be simultaneously rotated about its own axis as well as rotated about the larger axis of the carousel, which allows the user to move the laser beam across the entire surface of the target without altering the optical path.

During the course of my research, I designed and implemented a number of custom fixtures, hardware modifications, and software interfaces to allow for repeatable control and measurement of parameters of the PLD process. The energy density of a focused laser beam would damage a laser energy meter, necessitating indirect measurement of the laser energy used during deposition. The set of fixtures pictured in Figure 3.4(B) are used to repeatably measure the energy of the laser before entering the chamber and after exiting the chamber as well as take measurements of the laser spot size at the target surface without opening the chamber to atmospheric air. Figure 3.4(C) contains images of the motorized axes added to the PLD to allow for automated, repeatable setting of the TTS distance and raster-motion of the targets under the laser beam as well as the computerized control module for these axes built by myself. Finally, Figure 3.4(D) contains several screenshots showing the custom software interface, written in python, that allows for control of the motorized axes, external pyrometer temperature measurement and recording, and laser pulse delivery.<sup>17</sup> Calculation of the correct angular distances to allow for raster-motion based on target size are given in Chapter 4.



Figure 3.4: (A) Image of the custom optical table for delivery of the laser beam into the PLD vacuum deposition chamber. The beam path is illustrated by the arrows along with labels for the mirrors, attenuators, and beam aperture labeled in callout boxes. (B) Custom laser energy and spot size measurement fixtures. (C) Stepper motors attached to the target-to-substrate (TTS) distance and target carousel axes with in-house designed and fabricated adapter plates. (D) Screenshots of the custom software interface written for control of the PLD system in the Ihlefeld lab.

Unless otherwise noted, the standard processing parameters used for the deposition of LLTaO films on SrTiO<sub>3</sub> substrates via PLD in this dissertation are given below in parentheticals associated with each step of the deposition. Targets were generated using the solid state synthesis method discussed in Section 3.3.1, typically with 20 at.% excess lithium compared to the stoichiometric ratios. Targets were loaded onto the target carousel and the system was allowed to pump overnight, typically resulting in a system base pressure of approximately  $5 \times 10^{-7}$  Torr. Single crystal SrTiO<sub>3</sub> substrates (MTI Corporation) were cut or fractured to dimensions of approximately

 $5 \times 5 \times 0.5 \text{ mm}^3$  before deposition. The substrate platen was ground prior to each deposition using 320 grit paper and water to keep as consistent an emissivity as possible for temperature measurement via pyrometer. The substrates were then adhered to the heater platen using conductive silver paint that was cured (~20 minutes, 105 °C) on a hotplate prior to entering the chamber. Laser fluence was characterized by measuring the average energy at the back of the chamber and the front of the chamber then applying the following formula (note that it is assumed that loss at each window is the same):

$$E_{target} = E_{back} + \frac{E_{front} - E_{back}}{2}$$
(3.1)

Laser spot areas were measured by taking the average area of 10 distinct laser spots generated on Zap-It paper held at the level of the target surface by the black, 3D printed fixture in Figure 3.4(B). The substrate and platen are then loaded onto the heater via a transfer arm from the load lock and moved to the TTS height required for the deposition (68 mm, unless otherwise reported). The background gas was then introduced to the chamber (12 sccm O<sub>2</sub>) and the chamber roughing valve was used to control the total background gas pressure (150 mTorr). When the initial setting of the background gas pressure was within ~5 mTorr of the goal pressure, the substrate heater setpoint would be set for the deposition (950 °C). The gas pressure and heater temperature were allowed 40 minutes to reach their setpoints and stabilize before deposition. With a shutter shielding the substrate, 1800 pulses were placed on the target in the deposition atmosphere to clean the surface of any adsorbed material that was not the ceramic of interest. For targets that were used for multiple depositions, the face of the target was ground with isopropyl alcohol until the laser damage track was removed, and then brough to a finish of 600 grit. After the preparation pulses were completed, the sample shutter was opened, and deposition pulses were run (18,200 at 10 Hz). Immediately following the conclusion of the deposition pulses, the substrate heater temperature setpoint was adjusted to 20 °C to cool in the deposition atmosphere. Most films were post-annealed in a tube furnace at 950 °C to improve the crystallinity of the films compared to the as-deposited state.

#### 3.3.3 Electrode Deposition

Lithium-ion blocking metal electrodes (palladium or platinum) were deposited on all samples that underwent impedance spectroscopy measurements. These electrodes were deposited using one of three masking techniques: manual masking for bulk samples, shadow masking for most samples deposited on single crystalline substrates, and photolithographic masking for bicrystal samples and other samples that required precise placement of the electrodes relative to film features. These techniques are illustrated in the panels (A), (B), and (C) of Figure 3.5, respectively. The deposition of the electrodes was performed using DC magnetron sputtering, wherein a plasma is generated within a field near the sputtering target. The plasma constituents are then drawn through the sheath, to impact the target and eject material toward the substrate in the center of the chamber. Which deposits a layer of the target material on regions of the sample that are not masked against deposition. In the case of manual and shadow masking, the masks are then lifted away from the sample and the electrodes are completed. In the case of photolithographic masking, a final liftoff step is performed to remove the mask material and any electrode material that was deposited on the mask.



Figure 3.5: Schematic illustrations of the three methods of electrode generation used for sample preparation. (A) Bulk samples received palladium electrodes and were masked on the curved surface of the pellet with Kapton tape. (B) Most epitaxial samples were coated with platinum electrodes through a shadow mask. (C) Bicrystalline samples and epitaxial samples with specific electrode shape and size requirements received platinum electrodes deposited through a photolithographically defined mask. For depositions using photolithographically defined electrodes, the sputtering gun was moved to a 90° incidence geometry to avoid coating the side walls of the photoresist mask, which would prevent successful liftoff.

Bulk samples discussed here received palladium electrodes via DC magnetron sputtering. The parallel faces of the pellet were ground to a finish of 600 grit using isopropyl alcohol before electrode deposition. The curved surface of the pellet cylinder was masked using Kapton tape as illustrated in Figure 3.5(A). In order to generate parallel electrode geometry on bulk samples, the palladium sputtering process was performed once, then the sample was removed from the chamber and the process was repeated on the opposite side of the pellet. Standard sputtering conditions of 67 W actual power in 5 mTorr of argon were used for all sputtered electrode depositions. Electrode thicknesses were determined based on per-sample needs and varied from ~35 nm for photolithographically defined electrodes to ~100 nm for bulk samples.

For samples deposited on single crystalline substrates, the placement of the electrodes was not crucial beyond ensuring that the full length of the electrode defined in the shadow mask was on the film surface. In all cases it is assumed that the thickness of the film is constant over the  $5 \times 5 \text{ mm}^2$  area of the sample. PLD is expected to generate relatively uniform thicknesses over samples of this size. These samples were placed such that the maximal number of bar electrodes were available on the film surface. The shadow mask employed to produce bar electrodes was developed with varying distances between bar electrodes of a constant size (see Appendix III, IIIi for the specified dimensions of the shadow mask electrodes). On the other hand, it is imperative that electrodes be generated without overlapping the grain boundary region in samples deposited on bi- or polycrystalline substrates. For this purpose, photolithography was used to define electrodes with specific spatial relationships to features of the sample. Ion beam deposited platinum from a dual-beam scanning electron microscope was used to generate precisely placed fiducial markers in relation to the features of interest. These fiducial markers were then used to align a laser microwriter such that the resulting electrodes were positioned correctly in relation to the features of interest. Initially, photolithography processes were carried out by collaborators at Purdue University using a positive-tone photoresist. While liftoff was still possible with this process it was found that a negative-tone photoresist was more suited to generating well formed electrodes. In particular, the positive-tone resist tended to generate ragged edges on the electrode boundary due to parts of the electrode sticking to the upward facing walls and being removed during liftoff.

The procedure for the production of negative-tone photoresist was newly developed for use in the Ihlefeld group. Surface contaminants were removed using an ultrasonic cleaner with progressive baths of acetone then isopropyl alcohol. After each ~5 minute cleaning step, the samples were rinsed with isopropyl alcohol without drying. Samples were then blown off with

compressed nitrogen to remove dust and debris from the surface. Finally, the samples were cleaned using an oxygen plasma in a Henniker plasma cleaner using 15 sccm oxygen flow, 80% power for 10 minutes. The plasma was observed to take on the purple hue of an argon plasma, even with 100% oxygen inflow after prior users had run argon plasma processes. This required that a 10 minute cycle with the above conditions be run without the samples to purge interior lines of argon. Samples were then transported to the UVA Innovations in Fabrication (IFAB) cleanroom. Here samples underwent spin cleaning, where acetone then isopropyl alcohol were sprayed, in sequence, across the surface of the sample while spinning on a spin coater. Samples were spun until dry then transferred to the Laurell spin coater for photoresist deposition. AZ-nLOF 2020 photoresist was dispensed onto the static sample then spun using a two-step program with spin speeds of 500 rpm, then 2750 rpm, acceleration of 5000 rpm/s, and step times of 30 seconds then 1:00 minutes. After the photoresist mask was spun dry, the back of the sample was cleaned with an acetone-soaked swab. Edge bead removal was not performed due to the size of the samples. Samples were then baked at 110 °C prior to UV exposure for 90 seconds by placing the samples directly on a hotplate. Masks were exposed using a MicroWriter ML3 laser writer (Durham Magneto Optics, Durham, North Carolina) equipped with a 385 nm light source. Example masks produced using the KLayout software package are shown in Appendix III-ii. The best performing exposure conditions used a dosage of 400 mJ\cm<sup>2</sup> and the "Vector multiple objects" algorithm. It was found that the "mask inversion" setting on the MicroWriter ML3 was unreliable, and masks needed to be manually inverted/prepared for use with negative-tone resists in KLayout prior to use. A post-exposure bake was performed at 110 °C directly on a hotplate for 60 seconds as directed by the AZ-nLOF 2020 technical data sheet. Samples were then developed using AZ-300MIF developer for 120 seconds in a static bath then rinsed by placing in a static bath of deionized water for 120 seconds. Electrodes were deposited as above by DC magnetron sputtering. Liftoff was performed by placing the sample into an acetone bath in the ultrasonic cleaner for  $\sim$ 5 minutes.

# **3.4 Measurement Techniques**

## 3.4.1 Impedance Spectroscopy for Measuring Ion Conductivity in Ceramics

Impedance spectroscopy uses a small signal electrical input (generally a sine wave) that rides on some direct current bias value that can be positive, negative, or zero. A schematic depiction

of the technique, as applied to solid state, ceramic materials, is shown in Figure 3.6. Impedance spectroscopy essentially consists of generating an input signal with known amplitude and timing, applying this input signal to the material, and measuring the response signal after passing through the material under test. The response signal will have some combination of a change in amplitude and a change in phase angle (time between a specific point on the input signal waveform and the same point on the response signal waveform) when compared to the input signal.<sup>18</sup> Characterizing this response across a range of frequencies allows for the fitting of the data using an equivalent circuit model. Common electrical components used in equivalent circuit modeling for impedance spectroscopy of solid state ion conductors are:

- Capacitor: Perfectly insulating materials between two electrodes. Ideal capacitors do not allow for the flow of DC current but pass AC current with a phase angle of 90° (voltage trails current) from the input signal.
- 2. *Resistor*: Materials that pass an amount of current that is proportional to the applied voltage. Resistors do not alter the phase angle of the response signal, leaving the peaks of the response signal matched in time ("in phase") with those of the input signal.
- Inductor: Inductors are materials that oppose the flow of current as a result of the back-electromotive-force that is generated by passing current through them. This opposition to current flow leads the current to trail the voltage in an inductive circuit by -90°.
- 4. Constant Phase Element (CPE): Constant phase elements are an empirically driven modification of the capacitor. They add an additional parameter ( $0 \le a \le 1$ ) that essentially gives the "ideality" of the capacitor. For a = 1, the constant phase element reduces to an ideal capacitor. Values of *a* less than one indicate that there is some spread in the value of the relaxation time. The physical origin of this behavior can be a number of things that are related to inhomogeneity of the material under test.<sup>19</sup>
- 5. *Warburg Impedance Element*: A single element in the model circuit that represents a diffusional process in the material system. This is commonly associated with a charge transfer resistance and/or a double layer capacitance. There are multiple forms of the Warburg impedance element that depend on the diffusion situation

being modeled (e.g. solutions for infinite linear diffusion, finite length diffusion, and both transmissive and reflective boundary conditions).

Each of these circuit elements generates a characteristic shape in the complex impedance space. There are two common representations of complex impedance data, the Bode plot and the complex plane impedance plot (also referred to as Nyquist plots and sometimes, errantly, Cole-Cole plots). The characteristic shape of each individual element listed above is shown in Figure 3.7(A) using the complex plane impedance representation. While these shapes are characteristic of each element alone, perhaps the most common shape to observe in the complex plane impedance of a solid ion conducting material is an arc. This is generated by the combination of a resistor and a constant phase element in parallel and is referred to as a ZARC. The resulting data is shown in Figure 3.7(B) and (C) in the complex plane and Bode representations, respectively.



Figure 3.6: Schematic representation of impedance spectroscopy measurement in solid state, ceramic materials. The impedance analyzer (also referred to as a frequency response analyzer) is a device that can generate the input signal (shown in orange) and measure the response signal (shown in purple). The response signal differs from the input signal based on how the material under test modifies it. The impedance analyzer reads the change in the signal amplitude and the change in the phase compared to the input. With these two quantities, the instrument can return values for the impedance and phase angle, giving information about the effective resistance and capacitance of the sample.



Figure 3.7: (A) Characteristic shape generated by each circuit element commonly used in equivalent circuit modeling of solid state ion conductors. Note that the constant phase element (Q1 and Q2) can take on multiple slopes as a function of the value of a. (B) Complex plane and (C) Bode representations of an equivalent circuit model that might be used for a single crystalline ion conductor with different levels of non-ideal behavior represented by different values of  $a_1$ . The complex plane impedance representation is most useful for fitting of the data and interpretation of the characteristic shapes but does not directly represent the frequency data. Each point in the complex plane representation corresponds to a measurement at a specific frequency. On the other hand, the Bode representation allows for direct correlation of the impedance to different frequencies and therefore provides more straightforward information on the relaxation time associated with each response.

One of the key pieces of information that comes from impedance spectroscopy is the response of the material with relation to frequency. Each mechanism contributing to the impedance of the material becomes active in a certain range of frequencies. For example, mechanisms tied to the motion of electron clouds are very fast and tend to be active over the entire range of frequencies accessible to measurement equipment, while polarization of the electrodes via ion transport is very slow leading it to only be accessible at very low frequencies. The quantity tied to this concept is the relaxation time of the charge-motion mechanism. Again, the relaxation time is a quantity that can be determined through fitting of the impedance data. In the case of a ZARC the relaxation time is:

$$\tau = RC = (RQ)^{1/a} \tag{3.2}$$

where  $\tau$  is the relaxation time, *R* is the fit resistance associated with the ZARC, *C* is the psuedocapacitance (capacitance required if the CPE were replaced by a capacitor), *Q* is the CPE value, and *a* is the CPE ideality exponent. The ability to assign parts of the impedance spectrum to specific parts of the sample (i.e. the grain bulk (fast), grain boundary (slower), and the electrode (slowest)) stems from the separation of the time constants for each response being unique. The value of the relaxation time is often temperature dependent allowing for the preferential measurement of faster or slower processes based on the measurement temperature.<sup>20</sup> As the temperature increases, the relaxation times tend to decrease (move to higher frequencies) but also tend to collapse upon one another as a function of the different activation energy associated with each process.

Perhaps the most difficult part of analyzing impedance spectra is determining an appropriate equivalent circuit model. In some cases, the separation of relaxation times between different responses is sufficient that multiple arcs are clearly visible in the complex plane representation of the data. However, it is also possible for the arcs to overlap in such a way that essentially appear to be a single arc.<sup>265</sup> As with any fitting technique, it is possible to fit nearly any data by simply adding many fitting elements to the equivalent circuit but then many of these elements would not have any physical meaning. In these cases, analysis of the distribution of relaxation times (DRT) can be applied to impedance spectroscopy data to give some idea of how many elements are appropriate to include in the equivalent circuit. This technique revolves around solving a Fredholm equation and has been extensively developed and extended with different

regularization techniques<sup>22–26</sup> and levels of statistical analysis.<sup>24, 27–30</sup> After determination of an appropriate equivalent circuit, the data are fit using complex non-linear least squares algorithm to allow for extraction of the resistance value associated with each response of the material. Using the geometry of the sample and the extracted values, the conductivity can be calculated. Performing the same analysis at several temperatures also allows for extraction of the activation energy associated with each response.

In this dissertation, the impedance spectra of polycrystalline bulk samples were measured with an Agilent E4980 LCR meter with a full frequency range of 2 MHz to 20 Hz. For thin film samples, which possessed significantly higher impedance values due to the geometric constraints on their conduction pathways, the combination of a Solartron 1260A frequency response analyzer and Solartron 1296 dielectric interface were used to enable measurement between 10 MHz and 500  $\mu$ Hz as well as impedance values greater than 10<sup>9</sup> Ohms.

## **3.4.2 X-ray Diffraction**

X-ray diffraction (XRD) is one of the primary methods of characterizing the crystal structure and orientation in this dissertation. In XRD, a source generates X-rays with a specified wavelength by exciting electrons in an elemental target. The decay of these electrons to their ground state generates characteristic X-rays based on the material of the target. In all cases, the XRD in this dissertation was performed using primarily copper K $\alpha_1$  radiation. Lab based X-ray sources are not monochromatic, however, so in cases where further filtering optics were not used, reflections associated with adventitious X-rays such as copper K $\alpha_2$ , copper K $\beta$ , or even tungsten K $\alpha$  can be observed in measured patterns. The X-rays are then directed at the target, where they interact with the periodic nature of the electron clouds in a crystalline material. The interactions result in constructive interference between multiple X-rays exiting the sample only at very specific angles corresponding to a phase difference between the two X-rays of an integer multiple of  $2\pi$ . These angles are calculated using Bragg's law<sup>275, 276</sup>:

$$n\lambda = 2dsin(\theta_B) \tag{3.3}$$

where  $\lambda$  is the incident X-ray wavelength, *d* is the real space distance between atomic planes, and  $\theta_B$  is the Bragg angle (the angle where constructive interference occurs). In most cases, the value of *n* can be assumed to be one, but *n* can also take on any other integer value to cover cases where

the phase difference is greater than  $2\pi$ . The arrangement of atoms in each crystal structure determines which sets of atomic planes are capable of generating this constructive interference and, therefore, which atomic spacings are measurable via XRD. Other cases, such as single crystals or strong preferred orientations (texture) may also reduce the number of reflections available for measurement in a given geometry.

This dissertation contains both polycrystalline XRD and single crystalline XRD. Polycrystalline XRD is more straightforward in many ways because, outside of certain processing regimes, it can be assumed that the grains in a sample are randomly oriented meaning that all Bragg reflections will be available for measurement in the standard  $\theta$ -2 $\theta$  instrument configuration. The primary source of error that appears in randomly-oriented, polycrystalline XRD are generated by incorrectly setting the height of the sample, resulting in shifts of the measured Bragg angles across the measurement range.



Figure 3.8: Diagram of a four-circle diffractometer. This geometry gives four independent axes for positioning the sample relative to the beam path. The angle  $\omega$  is formed by the beam and the sample diffraction plane normal (commonly approximately parallel to the sample surface),  $2\theta$  is the angle between the incident and diffracted beams,  $\chi$  is the tilting angle of the sample around the  $2\theta = 0^{\circ}$  beam path, and  $\phi$  is the rotation axis around the diffraction plane normal.

Because the diffraction vector (the difference between the incident and diffracted X-ray vectors) must be normal to the atomic planes being measured, more careful consideration must be taken when performing XRD on single crystalline or heavily textured materials. In the case of much of the XRD characterization in this dissertation, this is accomplished by taking a suite of measurements to allow setting the diffraction vector parallel to the out-of-plane vector of a set of planes in the substrate with known spacing. Strontium titanate provides a well characterized (002) reflection at 46.51° in  $2\theta$  and is used throughout this dissertation for epitaxial sample alignment. After aligning the diffractometer with the substrate reflection, it becomes possible to position the sample and diffractometer such that most peaks are measurable by deviating heavily from the standard  $\theta$ -2 $\theta$  geometry. Alterations to the angles  $\phi$ ,  $\chi$ , and  $\omega$  are most common in accommodating these geometries. A diagram of the angles of interest in a diffractometer is given in Figure 3.8. Although the diffracted beam is drawn here as a single ray, in reality, the diffracted beam forms a cone with its vertex at the point of the incident beam. The Rigaku Smartlab diffractometer is also equipped with an "in-plane" measurement arm, where the detector can effectively be moved in both  $2\theta$  and  $\phi$  independently of the sample  $\phi$  position. This enables the measurement of a number of geometries that would be difficult or impossible to access on a more typical diffractometer by moving the detector throughout the diffraction cone.

X-ray diffraction measurements in this dissertation were performed across a combination of a Malvern-Panalytical X'Pert and Panalytical Empyrean diffractometers for polycrystalline diffraction and some out-of-plane diffraction from epitaxial samples. The majority of the XRD experiments (including out-of-plane measurements) performed on epitaxial samples utilized the Rigaku Smartlab system of diffractometers, which offer more capabilities for the measurement of thin film samples than the Panalytical instruments available in the University of Virginia Nanomaterials Characterization Facility (NMCF). Notably, the beam monochromators, fifth axis, and area detectors available in the Smartlab diffractometer were used frequently.

## 3.4.3 X-ray Reflectivity

X-ray reflectivity (XRR) allows for the non-destructive measurement of the thickness of thin film samples. X-ray reflectivity measurements are performed in the same diffractometers as XRD but make use of a different physical phenomenon. For most materials, the index of refraction at X-ray energies is less than one. This opens the possibility of total external reflection where an electromagnetic incident on a surface can experience a reflectivity of 1.00 (transmissivity of 0.00).<sup>277</sup> This only happens at low angles of incidence and occurs at different angles for different materials. The resulting data takes the form of a number of fringes as a function of the angle and can be fit with a model of the sample.<sup>34</sup> A few important notes about the fitting of XRR data bear mentioning: 1) when fitting the model to the data what is actually being optimized is the scattering length density as a function of the depth from the surface of the sample, 2) the roughness value that is commonly shown as a fit parameter is used to blend the transition between the values of scattering length density, 3) XRR fitting parameters are heavily intertwined and should be fit iteratively allowing as many parameters as possible to vary. This combination of factors can lead to unintuitive results such as the roughness value being greater than the thickness of a very thin layer (e.g. the native oxide on silicon). However, this result cannot be immediately dismissed because diffusion of atoms (or shared species) between layers can require blending over a range of depths larger than the layer thickness.

In this dissertation, XRR is used sparingly due to its limitations on the thickness and surface roughness of films. X-ray reflectivity is limited to characterization of smooth films on smooth substrates with stack thickness of less than 200 nm. Most of the films shown in this dissertation are 300-500 nm in thickness but XRR was used for initial characterization of the deposition rates of LLTaO as a function of the PLD parameters. Measurements of XRR were performed using the Rigaku Smartlab diffractometers.

#### **3.4.4 Atomic Force Microscopy**

Atomic force microscopy (AFM) probes the surface of a sample by tracking the movement of a silicon cantilever with an extremely fine tip. Motion of the tip is controlled using piezoelectric elements for extremely fine positional control. At its limits, AFM is even capable of atomic resolution.<sup>35</sup> There are three main modes available to AFM instruments: topographic measurement, force measurement, and manipulation. Of interest to this dissertation are the topographic and force measurement modes. In both cases, the movement of the cantilever is tracked by reflecting a laser from the top of the cantilever and tracking the motion of the beam on a photodiode. This information can be directly translated to the relative surface height at each point in topography mode and can be converted to force information by applying the Young's modulus of the cantilever to the deformation of the tip. Topographic measurement can be carried out in "contact" mode, where the tip is dragged along the surface and allowed to physically track the height of the sample, or in "tapping" mode, where the tip is excited using a known drive frequency and deviations from the expected position generated by tip/sample interactions are tracked.

The tip used in AFM measurements can also be made to act as part of a circuit by applying a bias between it and the stage that holds the sample. Implementation of this capability allows for expanded capability for indirect measurements of a number of phenomena (e.g. piezoelectric response). In the context of this dissertation, a technique called electrochemical strain microscopy is attempted, where an excitation signal is applied to the tip and the resulting strain in the sample is measured. In ion conducting materials, this can be correlated with spatially resolved ion conductivity.<sup>36–39</sup> Specifically, the capabilities of the Oak Ridge National Laboratory (ORNL) Center for Nanophase Materials Science (CNMS) were used under a user proposal to perform band excitation ESM, allowing for measurement across a large frequency band simultaneously.<sup>40, 41</sup>

Atomic force microscopy that is presented in this dissertation was captured across several Asylum Instruments Cypher AFMs. Topographic images were largely captured using the Ihlefeld group's Cypher AFM using tapping mode imaging. Two other Cypher AFM instruments, with identical capabilities, were used for band excitation ESM at ORNL CNMS. Band excitation ESM and related topographic images were captures in contact mode to allow for sufficient electrical contact between the sample and the tip.

#### **3.4.5 Scanning Electron Microscopy**

Scanning electron microscopy (SEM) applies an electron beam with accelerating voltages in the range of 3-20 kV, that is steered by a set of electromagnetic coils to apply the beam at each pixel for measurement. Depending on the angle of incidence, the accelerating voltage, detector used, and the beam current, different volumes of the sample can be probed, with depths ranging from a few nanometers to several microns of material.<sup>42</sup> Two primary modes of imaging are used in this dissertation: secondary electron imaging using an Everhart-Thornley detector or ion conversion and electron detector and backscatter electron imaging using a circular backscatter detector. Secondary electron imaging is generally more sensitive to topographic contrast because secondary electrons are generated by ionizing interactions with the beam electrons. They tend to have relatively low energy and are reabsorbed if they are generated at depths greater than a few nanometers. Backscatter electrons are more sensitive to the bulk and particularly the average atomic weight of a sample region because they are the result of elastic collisions between the beam electrons and the sample atoms where the beam electrons rebound towards the detector (concentric

to the pole piece). Backscatter electrons have significantly higher energy, allowing deeper probing of the sample in exchange for the loss of spatial resolution due to overlapping interaction volumes that are larger than the beam spot on the surface of the sample. Combination of these two imaging techniques can provide qualitative understanding of the surface topology of samples and the spatial distribution of heavy and light elements in a sample. Furthermore, different orientations of the sample crystal structure can generate contrast between grains which aids in distinguishing grain boundaries on samples that have been polished to a high quality.

More exact information about the spatial distribution of elements can be gathered using an energy dispersive X-ray spectrometer (EDS). As described in the case of X-ray generating sources for XRD in Section 3.4.2, the electrons associated with each element contained in the sample can be excited and decay back to ground state, releasing an X-ray with a characteristic energy.<sup>43, 44</sup> As each pixel is scanned, the detector can separate the generated X-rays into an energetic spectrum, allowing for determination of the elements contained in the interaction volume associated with that pixel. Combination of this data allows for false coloration of SEM micrographs and mapping of approximate stoichiometry with spatial resolution. Notably, EDS is not a quantitative technique without the use of well calibrated standards and cannot be used to detect light elements such as lithium.

Exact crystal orientation information can also be determined using a technique called electron backscatter diffraction (EBSD). Due to the particle-wave duality of electrons, they can diffract from the crystal structure of the sample in the same way that X-rays can. The generated patterns can be captured using a detector and analyzed to give very precise information about the crystal orientation of the sample. Again, the scanning nature of SEM allows for this determination to be carried out at each pixel in the image, giving high spatial resolution information on the sample crystal orientation, grain boundary locations, and misorientation from one grain to another within the sample.

Finally, the simultaneous use of SEM and a focused ion beam (FIB, gallium source) can both mill away material with resolution similar to the imaging resolution of the SEM and deposit material in exact locations. Milling of the sample is carried out by the relatively heavy and high energy gallium ions in the beam ablating sample material. Deposition is carried out by injecting a gaseous precursor near the beam site that can be "cracked" by the electron or ion beam energy. Cracking refers to breaking a ligand away from the material that is to be deposited, resulting in the ligand being pulled from the chamber via the vacuum system and the deposited material being left on the surface of the sample. Again, this process can be carried out at resolutions similar to the imaging resolution and can be directed at very specific locations on the sample surface.

Scanning electron micrographs displayed in this dissertation are collected across three instruments. A ThermoFisher Phenom Desktop SEM was used to collect images and EDS data at relatively low magnifications for use in Chapter 4 and other low magnification work with polycrystalline samples. Higher magnification images, EDS data, and EBSD maps are generated by both the FEI Helios Dual Beam FIB and the FEI Quanta 650 SEM with Oxford EDS and EBSD detectors. All focused ion beam milling and deposition operations were completed using the FEI Helios Dual Beam FIB. Ion milling with the gallium source in the Helios Dual Beam FIB was used for the generation of transmission electron microscopy (TEM) foils and for the measurement of thickness without greater sample damage. Focused ion beam platinum deposition was used to generate fiducial markers for the alignment of electrodes with grain boundaries.

#### 3.4.6 Characterization of Lithium Content

Lithium is an important part of the materials studied in this dissertation but presents difficulties when one attempts to quantify its presence in a material. X-ray scattering based characterization techniques are generally not sensitive to the presence or location of lithium within the crystal structure as a result of its small X-ray scattering cross section. Similarly, lithium produces characteristic X-rays with extremely low energy that tend to not be detectable in techniques that detect characteristic X-rays (EDS, X-ray fluorescence). Techniques that tend to work well for the detection of lithium are based on mass spectroscopy, optical spectroscopy, and electron energy loss spectroscopy. For instance, inductively coupled plasma spectroscopy has been used to determine the composition of a number of lithium ion conductors, including lanthanum lithium titanate, which is very closely related to LLTaO.<sup>45-48</sup> However, it was found that a wide range of digestion techniques failed to break down LLTaO, including but not limited to digestion in a number of acids (HNO<sub>3</sub>, HCl, HF) and the dissolution of LLTaO fluxed with a boron based glass. Electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) are nominally sensitive to lithium, but it was found that in LLTaO there is a lanthanum- or tantalum-generated plasmon peak that lies at the same energy level as the only observable lithium peak. This prevents quantitative analysis of the lithium content with these techniques although the

plasmon peak could be fit out to give a reasonable, qualitative analysis of the relative lithium content in a sample.

Two techniques are used successfully in this dissertation to directly characterize the lithium content in this dissertation: time of flight secondary ion mass spectrometry (TOF-SIMS) and nuclear reaction analysis (NRA). In TOF-SIMS, material is sputtered from the sample surface, using a cesium beam and the resulting stream of secondary ions are characterized by mass spectrometry. This gives spatially and depth resolved compositional data at a maximum lateral resolution of about 300 nm that can be compared directly across samples of the same material. Generating quantitative material via TOF-SIMS requires a standard sample that can be referenced and is of similar material composition to the samples being measured. Nuclear reaction analysis (NRA) impinges a high energy ion beam on the sample and monitors the products of nuclear reactions to determine the composition. In the case of lithium, the reaction

$${}^{7}_{3}\text{Li} + {}^{1}_{4}p \Rightarrow {}^{4}_{2}\alpha + {}^{4}_{2}\alpha \tag{3.4}$$

is used, where  $\alpha$  represents an ionized helium nucleus and p represents a proton from the accelerator. This technique is not sensitive to the crystal structure of the material and is more sensitive to light elements than to heavy elements, giving good information about the lithium content and allowing the use of a non-isostructural standard.

TOF-SIMS data presented in this dissertation was collected at the North Carolina State University Analytical Instrumentation Facility (AIF) by Dr. Chuanzhen Zhou. A TOF-SIMS V instrument (ION TOF, Inc. Chestnut Ridge, NY) with a 10 keV Cs<sup>+</sup>, 23 nA beam was used to create a  $120 \times 120 \ \mu\text{m}^2$  milled area where the middle  $50 \times 50 \ \mu\text{m}^2$  area was analyzed using 0.35 pA Bi<sub>3</sub><sup>+</sup> primary ion beam. NRA data presented was collected at the State University of New York Albany ion beamline by Dr. William Lanford and Kevin Wynne. TEM data, including EELS was collected at ORNL by Dr. Kory Burns.

# Chapter 4: Effects of Burial Powder Configuration on the Microstructure, Composition, and Ion Conductivity of Perovskite Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> Ion Conductors

The majority of the contents of this chapter are published in the Journal of the American Ceramic Society as cited below. Text and figures have been adapted to match the styling of this document and embed supplementary information where appropriate. Additional sections regarding motivation and preliminary work are included prior to the beginning of the published work.

**Brummel IA**, Wynne K, Lanford WA, Ihlefeld JF. Effects of burial powder configuration on the microstructure, composition, and ion conductivity of perovskite Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> ion conductors. *J. Am. Ceram. Soc.* 2023;106(1):241–250. DOI: <u>10.1111/jace.18730</u>

# 4.1 Motivation

This chapter covers the development of processing methods and conditions for the generation of dense, single phase LLTaO ceramics. Ceramics with these qualities are required for use as PLD targets when working in the field of epitaxial deposition of LLTaO. Preliminary measurements are presented to give an outline of the initial data gathered to support the decisions made in the following, published work.

# **4.2 Preliminary Studies**

The samples presented in this study are produced using the combustion synthesis method described in Section 3.3 and in Section 4.5, below. While the sample set presented here were  $\geq$  90% of the theoretical density, most samples produced using this method were found to only increase in density from the green state to sintered densities in the range of 60-70% of the theoretical density. Initially, it appeared that increasing the lithium excess in the precursor mixture

led to increased density in the final pellets. In a bid to make use of this, several samples were prepared as described up to the point of pressing the pellets. At this point an additional 100 at.% lithium was added to the calcined mixture as a fluxing agent and pellets were sintered at two different temperatures. It was found that, at 1500°C, fluxing the LLTaO with Li<sub>2</sub>CO<sub>3</sub> led to increased density but at 1600°C, the fluxing procedure actually reduced density. In both cases, it can be seen that the fluxing procedure resulting in greater intensity of secondary phase reflections present at ~28°  $2\theta$  in Figure 4.1.



Figure 4.1: XRD patterns generated from a matrix of pellets with a fluxed and a no flux condition and sintered at either 1500°C or 1600°C. It can be seen that fluxing of the samples leads to increased secondary reflection intensity (~28° in  $2\theta$ ).

The fluxing experiments revealed that although the densification process was to some degree dependent on the lithium present, the dependence was not straight forward. Observation of the powder stock under SEM revealed that particle morphology and size are highly dependent on the amount of lithium in the system. This dependence is illustrated in Figure 4.2, where it can be seen that combustion synthesis material with 20% excess lithium content has significantly larger particle sizes than materials prepared with 10% or 30% excess lithium. While the presence of

lithium can apparently generate a fluxing effect in this material system, in the case of combustion synthesis methods, the increased mass transport may be limited to the exterior of particles. In conjunction with relatively static/stable tantalum oxide grain interiors this may have led to large amounts of trapped porosity in the final ceramics. Low density is expected to generate many bouldering events during pulsed laser deposition from these targets, thus standard solid state processing was investigated after the conclusion of this study.



Figure 4.2: Representative micrographs from combustion synthesis prepared powder batched with (A) 10% excess lithium, (B) 20% excess lithium, and (C) 30% excess lithium. All scale bars correspond to a width of 10  $\mu$ m and all micrographs were taken using the same instrument and magnification.

The phase purity of the LLTaO powder produced with both the combustion synthesis method and the powder processing method was investigated. As shown in Figure 4.3, for the

powder processing method, repeated calcining steps eventually resulted in single phase powders, but at the cost of significant time investment. It was found that a single calcine step in conjunction with a reactive sintering step as described above resulted in good phase purity of LLTaO and densities at or above 90% of theoretical. The phase progression for typical polycrystalline LLTaO sample after reactive sintering is shown in Figure 4.4.



Figure 4.3: Progression of phase conversion as a function of the number of calcining steps. The "0 Calcine Steps" pattern was measured from the mixed precursors prior to any application of high temperature processing. Partial conversion to LLTaO begins after three calcine steps, while greater than five calcining steps resulted in nearly phase pure LLTaO, without residual precursor reflections. Major LLTaO are marked with diamonds, major precursor reflections are marked with triangles, and impurity phase reflections are marked with stars.



Figure 4.4: Typical progression of phase formation using reactive sintering after a single calcine step. LLTaO phase reflections are marked with diamonds and impurity phases are marked with stars. All unmarked reflections present in the calcined powder pattern are residual precursors that were not converted to LLTaO during calcination.

# **4.3 Publication Abstract**

A combustion synthesis methodology for the preparation of perovskite  $Li_{3x}La_{1/3-x}TaO_3$ lithium-ion conductors with *x*=0.033 is presented. Bulk ceramic specimens were sintered under combinations of burial powder and cover crucibles to provide different lithium vapor overpressure conditions. A maximum total lithium ion conductivity of  $6 \times 10^{-6}$  S/cm at room temperature was found for the pellet covered by a crucible whose lip was sealed using parent powder (moderate overpressure), with agreement to the maximum in the intergranular ion conductivity. Intragranular conductivity was maximized at the low overpressure condition. The trend in ion conductivity was found to correspond to the lithium content in the samples through a combination of nuclear reaction analysis and energy dispersive X-ray spectroscopy phase constitution measurements. The mechanism impacting ion conductivity was determined to be changes in the amount of LaTaO<sub>4</sub> secondary phase as driven by the processing conditions during sintering.

## 4.4 Introduction

Solid-state, ion conducting ceramics provide a promising avenue for advancing energy storage technology. For lithium ion batteries specifically, solid-state electrolytes offer several potential benefits over liquid electrolytes, including increased energy density and improved safety.<sup>1</sup> Solid-state electrolytes can also offer improved mechanical stability in comparison to liquid electrolyte constructions, conferring enhanced resistance to dendrite formation.<sup>2, 3</sup> In addition, solid-state electrolytes can exhibit electrochemical stability over a broad voltage window, allowing for construction of batteries with high energy electrodes as well as reducing the likelihood of a mechanical failure leading to a violent reaction upon exposure to the atmosphere.<sup>4</sup> Currently, most commercially available solid-state batteries are based on lithium phosphorous oxynitride (LiPON) due to its stability at a wide range of voltages, high lithium ion transference number, and ease of preparation.<sup>5, 6</sup> While LiPON exhibits many of the desirable qualities for a solid-state electrolyte, its ion conductivity is modest (10<sup>-6</sup> S/cm),<sup>6</sup> and it is typically only prepared in thin film form. This limits the use of these batteries in high power applications because they cannot support the current densities required for fast charging or high power output, both of which are critical to industries such as the growing electric vehicle segment. Many studies have sought to discover a suitable replacement for LiPON in high power, solid-state battery applications and while materials have been identified that exceed the ion conductivity of LiPON, many are not yet suitable for deployment in commercial applications due to challenges with processing and integration into battery packages.<sup>7–10</sup>

Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> (LLTaO) shares the *A*-site deficient perovskite structure of the well-known lithium ion conducting system Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub>.<sup>11–13</sup> LLTaO exhibits lithium ion conductivity that falls between that of LiPON and the closely related titanate, but due to the valence-stable tantalum ion on the *B*-site, should not be as susceptible to reactions with high energy electrodes such as lithium metal and may be better suited for secondary battery applications.<sup>11</sup> However, the LLTaO system has also shown a dependence of conductivity on the lithium content in the system.<sup>13</sup> Lithium and lithium oxide have high vapor pressures at elevated temperatures, such as those used to sinter polycrystalline ceramic materials.<sup>14</sup> In other systems containing volatile cations, it is common to adjust the sintering atmosphere through the use of burial powder of the same composition to prevent losses of the volatile cation from the ceramic body.<sup>15–21</sup> Specifically in lithium containing garnets, it has been shown that the powder bed composition can lead to an

improvement in the density of the sintered body as well as modifying the ion conductivity. This effect was attributed to changes in the composition of the resulting sintered body due to cations available in the powder bed.<sup>22</sup> In this work, a combustion synthesis method for the production of LLTaO powders is presented and the effects of the sintering environment, specifically the burial powder configuration, on the final ceramic body are elucidated. It is shown that the sintering configuration did not have a direct relation to the measured lithium content of the sample, however, minor changes in the lithium content and phase constitution were evident, resulting in changes to the ion conductivity of the samples. Lithium losses during sintering were found to be considerably lower in all samples than predicted based on the vapor pressure of lithium-containing species over lithium oxide, with the overall composition of all samples remaining near the batched composition.

#### **4.5 Experimental Procedures**

Polycrystalline, bulk ceramic samples of  $Li_{3x}La_{1/3-x}TaO_3$ , where x=0.033, were prepared by a combustion synthesis approach.<sup>23</sup> Solutions of 0.4 M LiNO<sub>3</sub> (99.999%, Alfa Aesar) in ethanol and 1.9 M lanthanum acetate (99.9%, Alfa Aesar) in propionic acid were prepared from powder precursors. Ta<sub>2</sub>O<sub>5</sub> powder (99.9%, H.C. Starck) was suspended in ethanol by stirring at room temperature; during mixing, a stoichiometric amount of the lanthanum containing solution and a 20 at.% excess of the lithium containing solution were added to the Ta<sub>2</sub>O<sub>5</sub> suspension. The precursors were allowed to mix at room temperature overnight. Ethanol was then driven out of the solution by continuing to mix on a hotplate set at 80 °C. The solution was dried further at 130 °C in a drying oven. The resulting mass was ground using a mortar and pestle before calcining at 1050 °C for 8 hours. Calcined powders were ground in a mortar and pestle before being uniaxially pressed at 175 MPa in a 12.7 mm diameter die without binder to form pellets with a green mass of approximately 1.7 g. Resultant pellets had green densities between 49-50% of the theoretical value. Pellets were then loaded into the furnace for sintering according to the diagrams shown in Figure 4.5, where the burial powder configuration was altered in an effort to provide varying levels of lithium overpressure within the sintering vessel. Five sintering configurations were used in this study: the "none overpressure condition" consisting of the pellet set directly on the setter with no aids to lithium vapor pressure as shown in Figure 4.5(A); the "low overpressure condition," where the pellet was placed under a cover crucible with no burial powder, as shown in Figure 4.5(B); the "moderate overpressure" condition, where the pellet was placed under a cover crucible that was

sealed by a ring of burial powder (note that there is no contact between the pellet and burial powder) as shown in Figure 4.5(C); the "high overpressure condition," which used a cover crucible configured as in the moderate condition, but with an additional pile of burial powder adjacent to the pellet, as shown in Figure 4.5(D); and the "very high overpressure condition," which used a cover crucible as in the moderate condition, but with the pellet buried within a mound of burial powder, as shown in Figure 4.5(E). All burial powder used was of the same nominal composition as the pellets, including lithium excesses. Additionally, the amount of burial powder used for the sealing rings in all configurations was measured to be within 5% by mass for each condition. The high and very high overpressure conditions used the same amount of additional powder within the crucible. All samples were sintered at 1500 °C for 12 hours in a box furnace in a static air atmosphere. Density of the sintered samples was measured geometrically. The circular faces of the pellet were ground to create flat surfaces onto which 50 nm thick palladium electrodes were sputtered. X-ray diffraction patterns were collected using a Panalytical Empyrean diffractometer, using Cu-Ka radiation in Bragg-Brentano geometry with a GaliPIX detector in scanning line mode. (Malvern Panalytical, Malvern, UK). Impedance spectra were measured between 2 MHz and 20 Hz with an oscillator of 500 mV using an Agilent E4980A LCR meter (Agilent, Santa Clara, CA). A Sun EC1A environmental chamber (Sun Electronic Systems, Titusville, FL) and a custom pellet test fixture were used to perform measurements between 25 and 300 °C. Complex plane impedance spectra were fit using EC-Lab fitting software (Bio-Logic S.A.S., Claix, France) for calculation of conductivity values. Activation energies were calculated using an Arrhenius-type analysis for an activated process.<sup>24, 25</sup> Plan view scanning electron microscopy was performed using an FEI Quanta 650 scanning electron microscope (SEM) (Thermo Fisher Scientific, Waltham, MA, USA) with accelerating voltage of 20 kV in backscatter imaging mode. Grain size measurements were performed using the Hilliard method from ASTM E112.<sup>26</sup> Energy dispersive X-ray spectroscopy (EDS) composition maps were captured on a Thermo Fisher Scientific Phenom XLG2 SEM (Thermo Fisher Scientific, Waltham, MA, USA) system with an accelerating voltage of 20 kV and phase fraction analyses were performed following the methods in ASTM E562.<sup>27</sup> Lithium content was determined by nuclear reaction analysis (NRA) performed at the State University of New York at Albany ion beam line, using the  ${}^{7}\text{Li}(p,\alpha)\alpha$  nuclear reaction. Samples were irradiated with 50 µC of 1.2 MeV protons, resulting in alpha particles that were detected on an Si detector at 168° to the beamline. Quantified lithium to tantalum ratios were determined using a SAW-grade Li<sub>0.946</sub>TaO<sub>2.97</sub> single crystal (MTI Corporation) as a standard.



Figure 4.5: Diagram of the differing sintering conditions. The boxes outlining each condition diagram serve as a key to the colors used to represent data for each condition throughout the manuscript. (A) The none overpressure condition consisting of the pellet set directly on the setter with no aids to lithium vapor pressure. (B) The low overpressure condition, where the pellet was placed under a cover crucible with no burial powder. (C) The moderate overpressure condition, where the pellet was placed under a cover crucible that was sealed by a ring of burial powder (note that there is no contact between the pellet and burial powder). (D) The high overpressure condition, which used a cover crucible configured as in the moderate condition, but with an additional pile of burial powder adjacent to the pellet. (E) The very high overpressure condition which used a cover crucible as in the moderate condition, but with the pellet buried within a mound of burial powder.

### 4.6 Results and Discussion



Figure 4.6: Comparison of XRD patterns for each sintering condition. Sintering condition is noted in color-matched font above each pattern. Bar markers along the abscissa indicate peak positions and relative intensities for of reference patterns of for the A-site deficient perovskite with x=0LLTaO(ICSD Collection Code 20281)<sup>1</sup> and orthorhombic LaTaO4 (ICSD Collection Code 238801).<sup>2</sup>

Figure 4.6 shows the XRD patterns of each pellet after sintering under their respective overpressure conditions. Reference patterns are shown as red and blue bar markers along the abscissa for the *A*-site deficient perovskite with x=0 (ICSD Collection Code 20281)<sup>1</sup> and orthorhombic LaTaO<sub>4</sub> secondary phase (ICSD Collection Code 238801),<sup>2</sup> respectively. The majority of peaks in the pattern are well matched with the tetragonal phase of LLTaO, reported to exist below a lithium content of x=0.075 by Mizumoto and Hayashi.<sup>3</sup> The tetragonal LLTaO phase is made up of a supercell of two pseudocubic perovskite cells that exhibit ordering of the lanthanum atoms on alternating (100) planes. Two impurity phase peaks are present between 25 and 30° in 2 $\theta$  that are well indexed to the high intensity peaks the of the orthorhombic LaTaO<sub>4</sub> phase. The magnitude of the reference pattern bar markers serves to indicate the expected relative intensity of

each reflection. Comparison to the observed patterns reveals no preferred texture in the samples. Notably, the LLTaO peak at  $32^{\circ}$  in  $2\theta$  appears to be of greater intensity than expected, but this is due to the superposition of the (110) and (102) peaks within the resolution of the diffractometer. Comparison between the patterns of differing sintering conditions reveals no major changes in crystal structure or texture. Furthermore, the ratio of the LLTaO (100) and (001) peak intensities are approximately constant, indicating that the level of *A*-site ordering is not changing with sintering condition. Similarly, a comparison of the relative intensities for LaTaO<sub>4</sub> to the LLTaO shows a constant ratio, within sensitivity limits, for all sintering conditions.



Figure 4.7: Representative backscatter scanning electron micrographs taken from polished cross sections of the (A) none, (B) low, (C) moderate, (D) high, and (E) very high overpressure condition pellets. (F) Plot of the measured average grain size as a function of sintering overpressure condition. Error bars indicate 95% confidence intervals.

Cross-sectional scanning electron backscatter micrographs of pellets derived from each overpressure condition are shown in Figure 4.7(A)-(E). Contrast in these micrographs derives from electron channeling effects and differential backscatter yields of different crystal orientations in the material. The micrographs shown in Figure 4.7 are provided at a higher magnification than those used in characterization efforts. Representative micrographs at the magnification used in characterization are provided in Figure 4.8. In all samples, there are apparent voids throughout the
material, which appear to be residual porosity. Porosity was calculated from the micrographs by thresholding the void areas, resulting in values ranging from 2-4% by area. This value is consistent with geometrically derived density of the pellets, after accounting for error in the geometric measurement and potential implicit bias toward imaging areas with less porosity. Geometric density values ranged from 93% to 95% of the theoretical value with no clear trend with sintering condition. In all samples, there are visible twins in some grains, which is consistent with the observation of tetragonal ordering peaks observed in the XRD patterns. Qualitative examination of the SEM micrographs shows that most grains are equiaxed. The microstructure also appears to have a bimodal or multimodal grain size distribution; however, this was not quantitatively studied. Average grain size was found to be  $1.76 \pm 0.07$ ,  $1.77 \pm 0.08$ ,  $1.73 \pm 0.08$ ,  $1.59 \pm 0.05$ , and  $1.96 \pm 0.10 \,\mu\text{m}$  for the none, low, moderate, high, and very high overpressure conditions, respectively. These values are plotted against the sintering condition in Figure 4.7(F), where the error bars represent the 95% confidence interval for the measurements. The average grain size is nearly constant for the three lowest overpressure sintering conditions. While the high and very high overpressure conditions do fall slightly outside the 95% confidence interval of the other points, they do not form a trend that corresponds directly with the sintering condition or with the ion conductivity results shown in Figure 4.9.



Figure 4.8: Representative, low-magnification backscatter scanning electron micrographs taken from polished cross sections of the (A) none, (B) low, (C) moderate, (D) high, and (E) very high overpressure condition pellets.



Figure 4.9: (A) Room temperature complex plane impedance spectra for each overpressure condition. Experimental data (without geometric correction) is represented as open points with the fit plotted as a line of the same color. The equivalent circuit used for fitting is illustrated in the upper left of the panel and is color coded to indicate which part of the spectra is represented by each element. (B) Extracted room temperature ion conductivity values from the impedance spectra, separated by the microstructural feature leading to the response.

Ion conductivity was determined using impedance spectroscopy (IS), which measures frequency-dependent response of a material under alternating current (AC) fields. Figure 4.9(A) shows representative complex plane impedance spectra from each overpressure condition at 25 °C. Each spectrum is composed of two leading arcs followed by a final spike. Impedance data were then fit using the equivalent circuit illustrated in Figure 4.9(A), where a ZARC element (resistor in parallel with a constant phase element) is used to model each of the arcs that appear in the spectrum and a final constant phase element represents the blocking palladium electrode spike. The resulting fits are plotted as solid lines of the same color as the experimental data, and good agreement of the fit to the measured data is achieved. Because the grain and grain boundary responses are clearly separable in the impedance spectra, each response can be treated individually. Using the fitted values for the resistor and constant phase elements, an ideal capacitance value can be calculated for each response using the equation for the time constant,  $\tau_i = (R_i Q_i)^{1/a} = R_i C_i$ , where  $\tau_i$  is the time constant for the ZARC *i*,  $R_i$  is the resistance of the ZARC,  $Q_i$  is the constant phase element value, a is the constant phase element exponent, and  $C_i$  is the ideal capacitance to be extracted.<sup>4</sup> Comparison of the resulting capacitance reveals that  $R_1$  is associated with the grain response, while  $R_2$  is associated with the grain boundary response.<sup>5</sup> Then, the grain resistance is  $R_1$ , the grain boundary resistance is  $R_2$  and the total resistance is  $R_1+R_2$ . The ion conductivity was calculated by  $\sigma_i = L/(R_i * A)$ , where  $\sigma_i$  is the conductivity of the response associated with ZARC *i*, L perpendicular length between the electrodes, A is the area of the electrodes, and  $R_i$  is the fitted resistance for ZARC *i*. The results of this calculation are shown in Figure 4.9(B), with Table 4.1 showing the fitted values and error for each spectrum at room temperature. Examination of the ion conductivity trend reveals a maximum in the overall ion conductivity at the moderate overpressure condition, corresponding to the maximum conductivity in the grain boundary response. However, the grain response shows a maximum under the low overpressure condition indicating that the grain boundary response dominates the overall ion conductivity, as can be expected based on prior observations.44,45,293



Figure 4.10: (A) Representative impedance spectra from the moderate overpressure sample at temperatures ranging from 25 °C to 55 °C. (B) Arrhenius plot of the dependence of lithium ion conductivity on temperature for the moderate overpressure sample. Activation energy for individual responses was extracted from the linear fit to the data and noted in the upper right of the plot. (C) Summary of the activation energy values measured for each overpressure condition. Error bars depict the 95% confidence interval determined from the error of the linear regression for each data point and are present for all data points but are smaller than the marker in some cases.

	ZARC1 - Grain			ZARC2 - Grain Boundary			Electrode Spike		Fit Error
Condition	<i>R</i> 1	<b>Q</b> 1	<i>a</i> 1	<i>R</i> 2	Q2	<i>a</i> 2	<i>Q</i> 3	a3	$\chi^2/ Z $
	Ohm	<b>F</b> • <b>s</b> <sup>(1-a)</sup>		Ohm	<b>F</b> • <b>s</b> <sup>(1-a)</sup>		F-s <sup>(1-a)</sup>		
None	18,714	1.08×10 <sup>-10</sup>	0.92	58,775	2.91×10 <sup>-8</sup>	0.84	4.62×10 <sup>-7</sup>	0.88	1.87×10 <sup>-3</sup>
Low	15,52	1.01×10 <sup>-10</sup>	0.92	35,088	3.03×10 <sup>-8</sup>	0.85	1.08×10 <sup>-6</sup>	0.89	1.19×10 <sup>-2</sup>
Moderate	15,582	1.03×10 <sup>-10</sup>	0.92	31,839	3.00×10 <sup>-8</sup>	0.85	9.44×10 <sup>-7</sup>	0.84	1.19×10 <sup>-3</sup>
High	15,880	1.01×10 <sup>-10</sup>	0.92	34,876	3.15×10 <sup>-8</sup>	0.85	7.97×10 <sup>-7</sup>	0.99	1.62×10 <sup>-3</sup>
Very High	20,549	9.73×10 <sup>-11</sup>	0.92	49,221	2.68×10 <sup>-8</sup>	0.85	3.47×10 <sup>-7</sup>	0.87	1.98×10 <sup>-3</sup>

Table 4.1: Fitted Values of Circuit Elements and Fit Error

Activation energy was determined by measuring the impedance response at temperatures ranging from 25 to 300 °C. An example of the impedance spectra measured from the moderate overpressure sample at several different temperatures is shown in Figure 4.10(A). An Arrhenius plot of the resulting temperature dependent ion conductivity for the moderate overpressure sample is shown in Figure 4.10(B) for each of the grain, grain boundary, and overall responses.

Temperature dependent impedance spectra and Arrhenius plots for activation energy are shown for the none overpressure, low overpressure, high overpressure, and very high overpressure are shown in Figure 4.11, Figure 4.12, Figure 4.13, and Figure 4.14, respectively. The Arrhenius-type relation used is shown below:

$$\sigma T = \sigma_0 e^{\frac{-E_a}{kT}} \rightarrow \ln(\sigma T) = -\frac{E_a}{k} * \frac{1}{T} + \ln(\sigma_0)$$
(4.1)

where  $\sigma$  is the ion conductivity, *T* is the absolute measurement temperature,  $\sigma_0$  is a prefactor,  $E_a$  is the activation energy, and *k* is the Boltzmann constant. Fitting the ion conductivities versus inverse temperature enables calculation of the activation energies of lithium ion conduction. A summary of the activation energies for each sample is shown as a function of sintering overpressure in Figure 4.10(C). It is observed that the grain boundary conduction activation energy is the highest, followed by the overall and grain responses. These results match well with previous literature as well as theoretical predictions on the mechanisms of lithium ion conductivity, where the grain boundary is resistive due to one of several effects, the grain response is facile due to the high crystallinity and many equivalent sites in the *A*-site defective perovskite lattice, and finally the overall response represents some value intermediate to the other responses because it is a combination of both responses over the volume of the sample.<sup>23, 293, 294</sup> Further comparison of these results to the ion conductivity trends that were observed at room temperature does not reveal a clear correlation between the activation energy and the ion conduction in these samples, indicating that the local environment for lithium ion conduction is similar between all samples.



Figure 4.11: Summary of the activation energy data collected for the none overpressure condition. (A) Impedance spectra plotted in the complex plane for temperatures between 25 °C and 55 °C. Experimental data is represented by open circles and calculated fits by lines of the same color as the corresponding data. (B) Arrhenius plot of the temperature dependent ion conductivity of the none overpressure sample. Activation energy for individual responses is extracted from the linear fit to the data and noted in the upper right of the plot.



Figure 4.12: Summary of the activation energy data collected for the low overpressure condition. (A) Impedance spectra plotted in the complex plane for temperatures between 25 °C and 55 °C. Experimental data is represented by open circles and calculated fits by lines of the same color as the corresponding data. (B) Arrhenius plot of the temperature dependent ion conductivity of the low overpressure sample. Activation energy for individual responses is extracted from the linear fit to the data and noted in the upper right of the plot.



Figure 4.13: Summary of the activation energy data collected for the high overpressure condition. (A) Impedance spectra plotted in the complex plane for temperatures between 25 °C and 55 °C. Experimental data is represented by open circles and calculated fits by lines of the same color as the corresponding data. (B) Arrhenius plot of the temperature dependent ion conductivity of the high overpressure sample. Activation energy for individual responses is extracted from the linear fit to the data and noted in the upper right of the plot.



Figure 4.14: Summary of the activation energy data collected for the very high overpressure condition. (A) Impedance spectra plotted in the complex plane for temperatures between 25 °C and 55 °C. Experimental data is represented by open circles and calculated fits by lines of the same color as the corresponding data. (B) Arrhenius plot of the temperature dependent ion conductivity of the very high overpressure sample. Activation energy for individual responses is extracted from the linear fit to the data and noted in the upper right of the plot.



Figure 4.15: Lithium to tantalum ratios determined by nuclear reaction analysis. Error bars represent the statistical counting error calculated for each sample and are approximately equal to 5% for all samples.

To further investigate the origin of the change in ion conductivity with sintering condition of LLTaO, nuclear reaction analysis was performed on each sample to quantitatively measure the lithium to tantalum ratio. NRA quantifies the abundance of each element by measuring the byproducts of the interaction of high energy particles with the nuclei of the atoms in the test material. In the case of lithium, the reaction employed takes the form shown in the following equation:

$${}^{7}_{3}\text{Li} + {}^{1}_{1}p \Rightarrow {}^{4}_{2}\alpha + {}^{4}_{2}\alpha \tag{4.2}$$

By measuring the number of alpha particles ( $\alpha$ ) that are produced by a known proton (p) flux, lithium nuclei can be counted indirectly. The results of the NRA analysis are shown in Figure 4.15, where the lithium to tantalum ratio is plotted against the sintering overpressure condition. The values determined for each sample follow a trend inverted from the overall ion conductivity, however the scale of the error bars on these values prevent drawing meaningful

conclusions from the NRA data alone. Of note, the Li:Ta ratio in all samples is arrayed around 0.12, which is the original batch ratio of Li:Ta when including the lithium excess. This indicates that the vapor phase losses of lithium during sintering are significantly lower than expected based on the vapor pressure of lithium-containing species over lithium oxide.<sup>11</sup> The apparent low lithium vapor pressure over LLTaO could also explain the small variation in sample composition with changes in sintering condition. Assuming that lithium only resides in the perovskite phase, which is reasonable given that no lithium-containing secondary phases were observed, the lithium to tantalum ratio measured implies an increase in the value of *x*. Increasing the value of *x* indicates that less lanthanum can exist in the perovskite phase to satisfy electroneutrality, which leads to the conclusion that the batched composition effectively has an excess of lanthanum. This is consistent with the identification of LaTaO<sub>4</sub> in the XRD patterns shown in Figure 4.6, because a lanthanum-rich phase would need to form to accommodate its excess.



Figure 4.16: Representative EDS maps composed of the superimposed lanthanum and tantalum signals, where tantalum is represented in blue, and lanthanum is represented in green. Atomic ratios determined from EDS indicate that lanthanum rich areas correspond to the LaTaO<sub>4</sub> secondary phase, and tantalum rich areas correspond to LLTaO. Maps are taken from the (A) none, (B) low, (C) moderate, (D) high, (E) very high overpressure samples. The scale bar in all images represents  $10 \ \mu$ m.



Figure 4.17: Backscatter electron images of the same fields used to collect the EDS maps in Fig. S5. Images are taken from the (A) none, (B) low, (C) moderate, (D) high, (E) very high overpressure samples. The scale bar in all images represents  $10 \ \mu$ m.

Studies of the closely related lithium lanthanum titanate have reported secondary phases and compositional deviation at the grain boundary, including Li<sub>2</sub>CO<sub>3</sub> and a Ti-O layer that was observed via TEM studies.<sup>7, 12</sup> However, the appearance of the LaTaO<sub>4</sub> secondary phase in XRD indicates that the excess lithium in the samples in this study is being accommodated within the LLTaO lattice, resulting in expelling other cations to maintain charge balance and due to the valence stability of tantalum, the reduction mechanism that is observed in the titanate is unlikely to occur in these samples. To investigate the location and prevalence of the secondary phase, energy dispersive X-ray spectroscopy was performed on the same samples that were used for grain size measurements. The lanthanum and tantalum signals were superimposed to create maps that represent LaTaO<sub>4</sub> where the lanthanum concentration is enhanced and LLTaO where the tantalum concentration is high. Representative, combined EDS maps from each sintering condition are shown in Figure 4.16. Comparison of the EDS maps with backscatter imaging of the same region did not indicate that LaTaO<sub>4</sub> grains were differently sized from LLTaO grains and that the secondary phase was not obviously delineated by intensity contrast in backscatter imaging mode. Backscatter electron images are shown in Figure 4.17 for the same fields that are represented as EDS maps in Figure 4.16. This suggests that the LLTaO phase is present as discrete, discontinuous grains within the microstructure. The procedures from ASTM E562 were then applied to these

maps in order to determine the volumetric phase fraction of LaTaO<sub>4</sub> in the samples. The results of this phase fraction analysis are shown in Figure 4.18. This plot illustrates a bowl-like trend that aligns well with the lithium to tantalum ratios that were found in Figure 4.15, and matches well with the trend of the overall ion conductivity found in Figure 4.9, when inverted. These data points are much better differentiated than the Li:Ta ratios, which lends confidence to the absolute values of the lithium content measured by NRA because, as discussed above, larger amounts of the LaTaO<sub>4</sub> secondary phase can be expected for larger excesses of lithium. Finally, the phase fraction analysis indicates that the samples contain between 12% and 16% LaTaO<sub>4</sub>, which appears to be more than was observed in XRD based on the peak intensity ratios (Figure 4.6). There are several potential explanations for this discrepancy: 1) The X-ray beam used in diffraction has a penetration depth of between 3.8 and 4.4  $\mu$ m<sup>277, 285</sup> on the exterior surface of the pellet, the most likely region of depleted lithium in the samples. Spatially resolved lithium quantification was not possible through NRA, so it is possible that a layer of reduced lithium content formed on the exterior of the pellet, reducing the phase fraction of LaTaO<sub>4</sub> in that volume and resulting in the relatively low level of XRD intensity for the secondary phase. 2) The analysis of phase fraction makes an assumption that the micrographs represent a 2D slice of the material, however the electron interaction volume in LLTaO at 20 kV and the large dose used for EDS extends 1.8 µm into the sample, as calculated using a Monte-Carlo simulation from the NIST DTSA-II software package.<sup>15,</sup> <sup>16</sup> This is approximately the average diameter of a grain, however most grains on a polished surface are partially removed and will not extend their full diameter into the plane of the image. This indicates that the EDS maps may represent a thicker slice of the material than assumed, leading to overcounting of the presence of LaTaO<sub>4</sub> in the material. 3) A final option, although unlikely based on the thermal budget of these samples, is that the LaTaO<sub>4</sub> within the sample is not fully crystallized leading to reduced signal in the XRD patterns. This suggests that the changing ion conductivity in LLTaO with sintering configuration is primarily driven by the minor changes in amount of lithium vapor evolution during the high temperature sintering step. The change in lithium concentration then drives the formation of LaTaO<sub>4</sub> secondary phase particles that act as a resistive element in the material, reducing the overall ion conductivity. Specifically, the secondary LaTaO<sub>4</sub> phase is unlikely to be capable of transporting lithium, therefore, a lithium ion approaching the boundary between an LLTaO and an LaTaO<sub>4</sub> grain would need to be transported around the LaTaO<sub>4</sub> grain through the resistive boundary. Conversely, in the case where a lithium ion

encounters a LLTaO-LLTaO grain boundary, it would be transported into the next grain, across the grain boundary. This would manifest in the IS spectra as an increase in the impedance of the grain boundary response. This also explains the relatively constant activation energy of the samples, because the conditions for lithium ion conduction in the LLTaO lattice are not changing significantly from sample to sample. This would indicate that the composition within the LLTaO grains in the samples is similar for all overpressure conditions, as the composition of LLTaO can have a strong effect on the ion conductivity that is observed.<sup>17</sup> A recent work on Li<sub>0.33</sub>La<sub>0.56</sub>TiO<sub>3</sub> has shown a similar effect wherein the composition of the major phase was constant with changing amounts of secondary phase, indicating a change in overall composition.<sup>18</sup>



Figure 4.18: Phase fraction of LaTaO<sub>4</sub> as a function of the sintering overpressure condition as determined from cross sectional EDS maps. Error bars represent the 95% confidence interval from the analysis.

#### 4.7 Conclusions

In summary, it has been shown that minor variations in the lithium concentration in LLTaO can lead to minor changes in the ion conductivity. The mechanism for this appears to be the changes in lithium content leading to increased formation of a secondary phase that hinders the overall lithium ion conduction response by effectively increasing the length of grain boundary through which a lithium ion must transport. This is supported by the grain boundary response acting as the dominant contribution to the total ion conductivity, as well as its inverse correlation

with the Li:Ta ratio and the phase fraction of LaTaO4. Further, this data indicates that the high vapor pressure of lithium that is known to exist for lithium metal and its oxides does not strongly affect LLTaO, as shown by the lithium to tantalum ratios, determined by NRA, remaining very near the batching composition including excess that was added to accommodate predicted lithium losses. It is likely that the apparent low vapor pressure of lithium over LLTaO also contributed to the observation of only small changes in lithium concentration with sintering condition. Conversely, it is unclear how variations in the sintering configuration affected the lithium content in each sample, implying that control over the lithium content would need to be studied and is likely furnace- and sintering environment-specific. Finally, the activation energy appears to have a weak dependence on the lithium content, as it remains constant with minor variations in the Li:Ta ratio. It is proposed that this is due to the local lithium environment in the bulk and grain boundaries remaining nearly constant due to charge compensation through the formation of a secondary phase.

# 4.8 Acknowledgments

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# Chapter 5: The Effects of Oxygen Content of Background Gas During Pulse Laser Deposition

The contents of this chapter are published in the Journal of Vacuum Science & Technology A, as cited below. Text and figures have been adapted to match the styling of this document and embed supplementary figures where appropriate.

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#### **5.1 Motivation**

The results in this chapter/publication are centered on the transfer of lithium from the PLD target to the substrate during deposition. Control of the lithium content in the epitaxial films is important to the final conductivity of those films as shown by Mizumoto and Hayashi in their work on bulk LLTaO.<sup>1, 2</sup> To this end, understanding how PLD parameters affect the transfer of lithium between the target and substrate is an important area of understanding. The specific condition investigated here is the composition of the background gas as this is an area that has not been investigated thoroughly in the literature.

# **5.2 Abstract**

Lithium lanthanum tantalate (Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub>, x = 0.075) thin films are grown via pulsed laser deposition using background gas atmospheres with varying partial pressures of oxygen and argon. The background gas composition was varied from 100% to 6.6% oxygen with the pressure fixed at 150 mTorr. The maximum ion conductivity of  $1.5 \times 10^{-6}$  S/cm was found for the film deposited in 100% oxygen. The ion conductivity of the films was found to decrease with reduced oxygen content from 100% to 16.6% O<sub>2</sub> in the background gas. The 6.6% oxygen background condition produced ion conductivity that approached that of the 100% oxygen condition film. The lithium transfer from the target to the film was found to decrease monotonically with decreasing oxygen content in the background gas but did not account for all changes in the ion conductivity. The activation energy of ion conduction was measured and found to correlate well with the measured ion conductivity trends. Analysis of X-ray diffraction results revealed that the films also exhibited a change in the lattice parameter that directly correlated with the ion conduction activation energy, indicating that a primary factor for determining the conductivity of these films is the changing size of the ion conduction bottleneck, which controls the activation energy of ion conduction.

#### **5.3 Introduction**

Solid state ion conductors are a promising component toward improving the safety and energy density of lithium ion battery technology. Electrolytes composed of these materials may enable the use of higher energy electrode materials because they exhibit wide practical electrochemical stability windows as a result of the formation of solid electrolyte interlayers that passivate the electrode-electrolyte contact.<sup>300-302</sup> The mechanical and thermal stability of solid state lithium ion conductors can also confer benefits in the form of safety, by reducing the likelihood of dendrite formation or thermal runaway events.<sup>6</sup> Finally, solid state ion conductors, particularly those that are oxides, are rarely highly reactive to air or other chemicals, eliminating the explosive failure mode of liquid electrolyte lithium ion batteries that can cause property damage or the loss of lives.<sup>7-9</sup> Solid state electrolytes commonly comprise a single, dense layer in order to serve as both a separator and the ion conduction medium in a battery. This calls importance to understanding the fundamental properties of the materials. For instance, understanding the anisotropy of ion conduction could be important for layers with a textured microstructure. To best understand the fundamental mechanisms of ion conduction in solid electrolyte materials, measurements of single-crystalline materials would be desirable. In many cases, however, single crystalline specimens of materials of interest are not available commercially, are challenging to prepare in sizes amenable to characterization, or they are prohibitively expensive. Epitaxial depositions of these materials can fill these gaps by enabling the measurement of single crystalline materials prepared via commonly available vapor deposition techniques, such as pulsed laser deposition (PLD).

Much of the historical PLD literature cites the technique as providing stoichiometric transfer of materials from the target to the substrate.<sup>10</sup> While this appears approximately true when

working with materials that are composed of atoms with similar atomic masses,<sup>11–13</sup> there has been more recent work that shows with large variation in cation mass, the composition in the film can deviate from that of the target by up to 70%.<sup>14–16</sup> Other experiments have revealed that lithium transfer from the target to the substrate is significantly less than unity, requiring accommodation to generate films with the desired composition.<sup>17</sup> Several aspects of the PLD parameter space have been investigated for their effects on the transfer ratios of different cations, revealing that there is a complicated interplay of factors that determines the final film composition.<sup>13, 15, 16, 18, 19</sup> While the total background gas pressure has been investigated for composition control, the effect of varied background gas composition on cation transfer during PLD is a notable knowledge gap.

In this work, the *A*-site deficient perovskite,  $Li_{3x}La_{1/3-x}TaO_3$  (LLTaO) is used as a model system for studying single crystalline ion conductivity behavior as a function of the variation of the background gas composition during epitaxial PLD. LLTaO is chosen as a model system because it shares the *A*-site deficient perovskite structure of the well-studied lithium ion conducting system  $Li_{3x}La_{2/3-x}TiO_3$ . However, for some compositions of LLTaO (e.g.  $x \ge 0.075$ ) the material adopts a cubic symmetry, eliminating the need to account for the effects of twin boundaries when measuring epitaxial film properties.<sup>2, 20, 21</sup> Additionally, LLTaO has a lattice parameter of ~3.94 Å, which makes it amenable to epitaxial growth on widely available cubic SrTiO<sub>3</sub> substrates with less than 1.5% lattice mismatch strain.<sup>22, 23</sup> While LLTaO exhibits lower lithium ion conductivity than that of the closely related titanate, due to the valence-stable tantalum ion on the *B*-site, it should not be as susceptible to reactions with high energy electrodes such as lithium metal and may be better suited for secondary battery applications.<sup>20</sup>

#### **5.4 Experimental Procedures**

Epitaxial thin films with the nominal composition of  $Li_{3x}La_{1/3-x}TaO_3$ , where x = 0.075, were fabricated on single crystalline (001)-oriented SrTiO<sub>3</sub> substrates (MTI Corporation, Richmond, CA, USA) using pulsed laser deposition (PLD). Depositions were conducted within a custom high-vacuum system using a target carousel and substrate heater from NBM Design (Bel Air, MD, USA), where substrates were attached to the heater platen using conductive silver paint (Ted Pella, Redding, CA, USA). All films were deposited at a substrate temperature of 700 °C ± 10 °C as measured by a Fluke Endurance E2RL 2-color pyrometer (Everett, WA, USA) with a target-to-substrate distance of 68 mm. The total background pressure for each film growth was kept constant

at 150 mTorr as measured with an MKS Instruments 627F capacitance manometer gauge (Andover, MA, USA), with varying partial pressure of oxygen and argon determined by the relative gas flow set using mass flow controllers (Alicat Scientific, Tucson, AZ, USA). Oxygen content was varied to generate  $pO_2$  conditions of 100%, 50%, 16.6%, and 6.6%. Gas pressure and temperature were allowed to stabilize for 40 minutes prior to commencing deposition. The laser excitation voltage of the Lambda Physik COMPex 205 excimer laser (248 nm wavelength) was kept constant for each deposition and was set such that the fluence at the target surface was  $\sim$ 1.4 J/cm<sup>2</sup>. Prior to deposition, the targets were exposed to 1800 laser pulses at 10 Hz to clean the target surface then 18200 pulses at 10 Hz were used to deposit the film. Targets were rastered and rotated such that the point of laser focus was not allowed to dwell in a single area to allow even usage of the target surface for deposition. Targets were fabricated using a solid state synthesis method. Precursors of Li<sub>2</sub>CO<sub>3</sub> (99+%, Arcos Organics), La<sub>2</sub>O<sub>3</sub> (99.9%, Alfa Aesar), and Ta<sub>2</sub>O<sub>5</sub> (99.9%, TANiOBIS GmbH) were combined in stoichiometric amounts, plus 20 at.% excess lithium to account for losses during high temperature calcining and sintering treatments and in the plasma during deposition. The target synthesis procedure is detailed in previous work.<sup>24</sup> All targets were generated from the same parent batch of precursors and were sintered in a single furnace run. After initial characterization, the films were annealed at 950 °C for 30 minutes in flowing oxygen in a tube furnace to promote crystallinity and LLTaO phase formation.

The crystal structure of the films in an out-of-plane  $(2\theta - \omega)$  geometry was characterized by X-ray diffraction (XRD) using a Panalytical Empyrean diffractometer, using Cu-K $\alpha$  radiation (Malvern Panalytical, Malvern, UK). The epitaxial relationship ( $\phi$ -scans) between the film and substrate was characterized using a Rigaku Smartlab diffractometer with Cu-K $\alpha$  radiation (Rigaku Corporation, Akishima-shi, Tokyo, Japan). Film cross sections were prepared by milling a trench in the film using a focused ion beam (FIB) with a gallium ion source in a Helios UC G4 Dual Beam FIB (Thermo Fisher Scientific, Waltham, MA, USA). Scanning electron microscopy (SEM) of the cross sections was then performed using beam conditions of 5 keV, 0.20 nA at an incident angle of 56° with tilt correction and dynamic focus within the same instrument. Characterization of the lithium content in the films was carried out with secondary ion mass spectroscopy (SIMS) by the Analytical Instrumentation Facility (AIF) at North Carolina State University using a TOF SIMS V instrument (ION TOF, Inc. Chestnut Ridge, NY). 10 keV Cs<sup>+</sup> with 23 nA current was used to create a 120 µm × 120 µm milled area and the middle 50 µm by 50 µm area was analyzed using

0.35 pA Bi<sub>3</sub><sup>+</sup> primary ion beam. Depth profile data was measured, and the relative lithium content was determined by using the average counts for each species in the steady-state region of the depth profiles. Platinum electrodes were deposited by DC magnetron sputtering through a custom shadow mask to produce bar-shaped electrodes with nominal dimension of  $3 \times 0.75$  mm and nominal spacing of 0.75 mm along the conduction path. Actual electrode dimensions were measured by image analysis of optical micrographs using a stage micrometer for scale. Impedance spectroscopy data was collected between 10 MHz and 50 mHz with a 2.5 V oscillator, using a Solartron 1260A frequency response analyzer with a Solartron 1296A dielectric interface to allow for measurement of high impedance samples (Solartron Metrology, Bognor Regis, West Sussex, UK). Impedance spectroscopy measurements were carried out in an Instec vacuum probe station with a heating stage (model HP621HVF, Instec Inc., Boulder, CO, USA) where typical vacuum levels of  $1 \times 10^{-4}$  Torr were achieved during measurement. Impedance spectra were fit using EC-Lab software (Bio-Logic S.A.S., Claix, France) for extraction of conductivity and activation energy values.

# 5.5 Results and Discussion

Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> exhibits both a cubic and a tetragonal polymorph depending on the value of *x*, where the tetragonal phase is made up of a supercell of two pseudocubic perovskite cells that exhibit ordering of the lanthanum atoms on alternating (001), planes (where the subscript *t* denotes tetragonal symmetry).<sup>1</sup> The out-of-plane XRD patterns are shown for the as-deposited films in Figure 5.1(A), with smaller  $2\theta$  range views of the peaks associated with {001}<sub>p</sub> reflections shown in Figure 5.1(B-E) (where the *p* subscript denotes pseudo-cubic symmetry). From these patterns, it is evident that all films showed some crystallinity in their as-deposited state. The 100%, 50%, and 16.6% oxygen background films exhibit peaks that can be readily indexed to the cubic LLTaO phase and the substrate, which are indicated by the diamond and star markers, respectively. Careful observation of the spacing between the film and substrate peaks in Figure 5.1(B-C) reveals that there is a slight decrease in the lattice parameter of the LLTaO phase with decreased oxygen partial pressure. These patterns also display two peaks that can be indexed to the (001)<sub>t</sub> and (003)<sub>t</sub> peaks of the tetragonal phase, as indicated by triangular markers. The tetragonal peaks are of low intensity but increase in relative intensity slightly as the oxygen partial pressure in the background

gas is reduced. The intensity ratio for the  $(001)_t$  to  $(001)_p$  peaks was found to be 0.33%, 0.49%, and 0.70% for the 100%, 50%, and 16.6% oxygen background samples, respectively. This is markedly lower than the calculated intensity ratio of 23% for the tetragonal structure, indicating a very low level of ordering in the as-deposited films. The 6.6% oxygen background film exhibits peaks on the high  $2\theta$  side of the STO substrate peaks, indicating that a significant deviation from the expected LLTaO lattice parameter exists. The peaks are also broader and of lower intensity than those observed for the films deposited with higher oxygen content background gas mixtures indicating reduced crystallinity. While the peaks in the 6.6% oxygen background film follow a trend that could be consistent with a perovskite of the same space group as the cubic LLTaO, but with a significantly smaller lattice parameter, there are not enough peaks present to positively identify this phase.



Figure 5.1 Normalized X-ray diffraction patterns generated from a  $2\theta$ - $\omega$  geometry to identify the phases present in the as deposited films. The full  $2\theta$  range is shown in panel (A), with detail views of the regions surrounding the (B) SrTiO<sub>3</sub> (001), (C) SrTiO<sub>3</sub> (002), (D) SrTiO<sub>3</sub> (003), and (E) SrTiO<sub>3</sub> (004) peaks. Substrate peaks are marked with a star, psuedocubic films peaks are marked by diamonds, and tetragonal film peaks are marked by triangles.

Most of the trends that were present in the as-deposited films persist after annealing at 950 °C. Figure 5.2 shows an identical set of measurements to Figure 5.1, taken after the films had been annealed. The most notable change is the complete conversion of the film peaks observed in the 6.6% oxygen background film from the unidentified phase to the LLTaO phase. The loss of definition of the K $\alpha_1$  and K $\alpha_2$  peaks for the 6.6% oxygen background film in Figure 5.2(B)

indicates that the film has a poorer crystal quality than that of the films deposited with higher oxygen partial pressures. The (001)<sub>t</sub> to (001)<sub>p</sub> intensity ratio remained constant after annealing for the 100%, 50%, and 16.6% oxygen background films. With the conversion of the 6.6% oxygen background film to the LLTaO phase, the (001)<sub>t</sub> to (001)<sub>p</sub> intensity ratio can now be measured and was found to be 6.6%. This indicates that films deposited with lower oxygen contents have increased cation ordering leading to the formation of the tetragonal phase. Based on the results of Mizumoto and Hayashi, where they found that the tetragonal phase of LLTaO formed for x < 0.075,<sup>1</sup> this trend points toward a reduction in lithium transfer from the target to the films with decreased oxygen partial pressure. Finally, the trend of decreased lattice parameter with decreasing oxygen background film exhibits a lattice parameter that is similar to the 100% oxygen background film. The planar spacing was calculated from each of the (002), (003), and (004) planes with displacement correction based on the STO peak positions. The lattice parameters were found to be 3.933 Å, 3.930 Å, 3.922 Å, and 3.937 Å for the 100%, 50%, 16.6%, and 6.6% oxygen background films, respectively.

Figure 5.3 shows the XRD scans of the (103) planes in the  $\phi$ -axis to illustrate the epitaxial relationship between the substrate and film. Measurements were performed at  $\chi = 18.435^{\circ}$ , with  $2\theta = 77.28^{\circ}$  for the (103) substrate peaks and  $2\theta = 76.55^{\circ}$  for the (103) film peaks. The scans show strong agreement of the substrate and film peak positions in  $\phi$ . In combination with the data shown in Figure 5.2, this indicates cube-on-cube epitaxy of the LLTaO film on the STO substrate. The peaks in Figure 5.3 also display splitting that generally agrees between the film and substrate peaks, indicating that the starting substrates had some degree of mosaicity, which was templated into the growth of the films.



Figure 5.2: Normalized X-ray diffraction patterns generated from a  $2\theta$ - $\omega$  geometry to identify the phases present in the annealed films. The full  $2\theta$  range is shown in panel (A), with detail views of the regions surrounding the (B) SrTiO<sub>3</sub> (001), (C) SrTiO<sub>3</sub> (002), (D) SrTiO<sub>3</sub> (003), and (E) SrTiO<sub>3</sub> (004) peaks. Substrate peaks are marked with a star, psuedocubic films peaks are marked by diamonds, and tetragonal film peaks are marked by triangles.



Figure 5.3:  $\phi$ -scans of the LLTaO (103) and STO (103) peaks illustrating cube-on-cube epitaxy. Multiple peaks are present in some scans as a result of mosaicity in the substrates, which was templated into the film.

Representative scanning secondary electron microscopy cross sections produced by milling a channel in the films with a gallium ion beam are shown in Figure 5.4. During milling the film surface was protected using two layers of platinum, the first deposited using the electron beam and the second deposited using the ion beam. The thickness of the platinum protection layers varies from sample to sample due to charging during the deposition process leading to the beam position being outside of the intended area. After milling, the channels were approximately 25  $\mu$ m in width. The thickness of the films was sampled at equal intervals for a total of 20 points on each film. Thickness was determined to be  $362 \pm 9$  nm,  $375 \pm 3$  nm,  $359 \pm 5$ nm, and  $409 \pm 4$  nm, where the reported error is the 95% confidence interval, for the 100%, 50%, 16.6%, and 6.6% oxygen films, respectively. Qualitatively, all films appear dense with very few boulders visible. Notably, the surface of the 100% oxygen film appears significantly rougher than those of the other films which may indicate faceted growth on the surface.



Figure 5.4: Representative scanning electron micrographs of the (A) 100%, (B) 50%, (C) 16.6%, and (D) 6.6% oxygen background films after annealing. Cross sections were exposed using gallium source ion milling to cut a channel through the film and into the substrate. Films were protected using a platinum top layer that was deposited first with the electron beam then brought to thickness using ion beam deposition. A key for the visible layers is shown in panel (A).

Depth profile data from each film was collected using TOF-SIMS, then the average number of counts in the steady state composition region was used to calculate the ratio between the constituent atoms, as described in Figure 5.5. The average ratio of CsLi<sup>+</sup> to CsTa<sup>+</sup> counts shown in Figure 5.6 as a function of the oxygen content of the background gas. The CsLi<sup>+</sup> to CsTa<sup>+</sup> complexes were selected for measurement to suppress the contribution of matrix effects to the measurement.<sup>318</sup> Because there is no available standard for this material, the raw ratio of counts is presented for comparison of the amount of lithium between films. Note that this does not represent

the quantitative ratio of lithium to tantalum in the films but provides a relative measure that enables comparisons between process conditions. The lithium content decreased monotonically with decreasing oxygen content in the background gas, although the compositional difference between the 16.6% and 6.6% oxygen films was smaller than the differences found between other processing conditions. For all films, the lithium to tantalum ratio was lower than that found in a ceramic target that had not been ablated for deposition (upper solid horizontal line in the figure), with the 16.6% and 6.6% films exhibiting a lithium content lower than that of an ablated target (post-deposition, lower solid horizontal line). This indicates that while the targets are depleted of lithium during deposition, there are further losses during the transport of material from the target to the substrate, which is consistent with the formation of the tetragonal phase observed via XRD. At the relatively high deposition pressures used in this study, the mean free path of any atom in the plume is expected to be on the order of 10s of microns, which is three orders of magnitude smaller than the target to substrate distance of 68 mm. This implies that any atom that is transported from the target to the film can be expected to undergo multiple collisions with other atoms/ions in the plume or the background gas and the plume should take on diffusive characteristics.<sup>26</sup> See Chapter 6 for calculations of the mean free path of each constituent atom. While the increased radius of argon reduces the expected mean free path, this change is on the order of a few microns. The more likely explanation for a significant decrease in the lithium transfer with decreasing oxygen (increasing argon) background is a result of the atomic mass of argon being more than double that of oxygen resulting in preferential scattering of light elements by the background gas.<sup>26</sup>



Figure 5.5: TOF-SIMS depth profiles measured for (A) an ablated target, (B) a pristine target, (C) 100% oxygen background, (D) 50% oxygen background, (E) 16.6% oxygen background, (F) 6.6% oxygen background films. The dashed, vertical lines indicate the region of each depth profile that was considered "steady state" for the purposes of determining average counts value for each of the Cs*X* complexes. The average value of the CsLi<sup>+</sup> counts was normalized by the average value of the CsTa<sup>+</sup> counts to determine the ratios presented in Figure 5.6.



Figure 5.6: Average lithium to tantalum ratio determined from TOF-SIMS depth profile measurements as a function of background oxygen during deposition. The oxygen background percentage is plotted on a log scale. Solid, horizontal lines represent the lithium to tantalum ratio found in targets prior to deposition and after the target was ablated during deposition. The dashed line between points is a guide to the eye.

An in-plane geometry, with parallel bar electrodes, was used to measure the impedance response of the LLTaO films, as represented in Figure 5.7(B). Representative, complex plane impedance spectra, collected at 150 °C, are shown in Figure 5.7(A) for each film. The data were fit using the model equivalent circuit illustrated in Figure 5.7(B). The circuit contains a series arrangement of one ZARC element (resistor and constant phase element in parallel) and one constant phase element representing the electrolyte and blocking electrode response, respectively. Ion conductivity was derived using Equation (5.1):

$$\sigma_f = \frac{s}{RtL} \tag{5.1}$$

where *s* is the electrode spacing, *t* is the film thickness, *L* is the electrode length, and *R* is the resistance of the ZARC in the equivalent circuit fit. Figure 5.7(C) shows the extracted conductivity values of the films at room temperature. Comparison of the trend in conductivity values reveals that the reduction in lithium transfer with reduced oxygen content in the processing atmosphere cannot explain the entirety of the trend in conductivity. Conductivity is generally represented by Equation (5.2):

$$\sigma = nZ\mu \tag{5.2}$$

where *n* is the number of charge carriers, *Z* is the electrical charge of a carrier, and  $\mu$  represents the mobility of the charge carrier. This can then be summed over all available charge carriers to give a strong approximation of the total conductivity of a material. Importantly, this implies that conductivity should be directly proportional to the number of charge carriers (lithium ion concentration) if all other elements are assumed equal. Because the conductivity of the samples deviates heavily from this assumption and the ionic charge of lithium is fixed, it can be surmised that the mobility of lithium ions is not constant with changes in the makeup of the background gas during film deposition.



Figure 5.7: (A) Complex plane impedance spectra measured at 150 °C for each film. Measured data are represented as open circles with the fit plotted as a solid line. Note that data density has been reduced to increase the legibility of the plot. (B) Schematic representations of the equivalent circuit used in fitting (top) and the electrode configuration used for in-plane impedance spectroscopy measurements (bottom) (C) Room temperature conductivity plotted as a function of the log of the oxygen content in the background gas.

The diffusion coefficient can be calculated as shown in Equation (5.3):

$$D = D_0 e^{-E_a/kT} \tag{5.3}$$

can be combined with the Einstein relationship to reveal that the activation energy is related to the mobility of lithium in an ion conducting material as follows:

$$\mu = \frac{D}{kT} \longrightarrow \mu = \frac{D_0 e^{-E_a/kT}}{kT}$$
(5.4)

where  $\mu$  is the mobility, *D* is the diffusion coefficient,  $D_0$  is an exponential pre-factor,  $E_a$  is the activation energy discussed above, *k* is Boltzmann's constant, and *T* is the absolute temperature. Incorporation of the Nernst-Einstein relationship allows for the development of an Arrhenius-type relationship between conductivity and activation energy via Equation (5.5):

$$\sigma T = \sigma_0 e^{-E_a/kT} \rightarrow \ln(\sigma T) = -\frac{E_a}{k} * \frac{1}{T} + \ln(\sigma_0)$$
(5.5)

where  $\sigma$  is the ion conductivity and  $\sigma_0$  is a material-dependent pre-factor. Thus, the activation energy can be calculated in a straightforward manner from the slope of a linear regression between  $\sigma T$  and  $T^{-1}$  and can provide insight into conducting species mobility.<sup>27, 28</sup> Impedance spectroscopy was measured at a range of temperatures from 25 to 300 °C to allow the extraction of the activation energy for ion conduction. Representative complex plane impedance spectra measured on the 100% oxygen background film are shown in Figure 5.8(A) to illustrate the change in impedance with increasing temperature. The analysis of conductivity, described above, was carried out at each temperature, yielding the Arrhenius-type plot shown in Figure 5.8(B). The activation energy was determined to be 0.41, 0.45, 0.49, and 0.43 eV for the 100%, 50%, 16.6%, and 6.6% oxygen background films, respectively. Publications investigating the bulk properties of LLTaO have shown similar values for the bulk activation energy.<sup>2, 21, 29</sup>

The qualitative trend seen for the activation energy in Figure 5.8(C) closely matches with the inverse of the conductivity. The ion conductivity was observed to change by more than an order of magnitude as the background oxygen content was varied, while the CsLi<sup>+</sup>:CsTa<sup>+</sup> ratio only changed by a factor of ~2. Additionally, the films exhibiting the highest ion conductivity (100% and 6.6%  $O_2$ ) represent both the maximum and minimum values of the CsLi<sup>+</sup>:CsTa<sup>+</sup> ratio. This

implies that the lithium ion mobility, as represented by measurement of the activation energy, is the dominant factor in determining the conductivity. This is further evidenced by comparing the pre-factor ( $\sigma_0$ ) values from the Arrhenius analysis, which had a maximum difference of ~7.5% from one film to another, ruling out large changes in other parts of the ion conduction process. The activation energy for ion conduction is commonly correlated with the structural bottleneck, which must be the correct size to minimize the energy necessary for the conducting ion to move from one position to another.<sup>21, 28, 30</sup> The analysis of diffraction peak positions from Figure 5.2 indicates that the activation energy for lithium conduction in LLTaO is inversely correlated to the lattice parameter, with the 100% and 6.6% oxygen background films having larger lattice parameters than the other films and therefore having lower activation energy and higher ion conductivity. A similar result has been observed for bulk LLTaO where a decrease in the lattice parameter caused a significant increase in the activation energy.<sup>23</sup>



Figure 5.8: (A) Representative complex plane impedance spectra measured at 100 °C, 150 °C, and 200 °C from the 100% oxygen background film. The equivalent circuit used to fit the data is shown to the left of the legend. Measured data are represented as open circles with the fit plotted as a solid line. Note that data density has been reduced to increase the legibility of the plot. (B) Arrhenius-type plot showing the dependence of conductivity on temperature. Activation energy of ion conduction values, extracted from the linear regression (dashed lines) are shown in the top right. (C) Activation energy of ion conduction as a function of the oxygen content of the background gas. Error bars represent the error of the linear regression fit.

#### **5.6 Conclusions**

It has been shown that the partial pressure of oxygen in the background gas during PLD has a direct effect on the transfer ratio of lithium from the target to the deposited film. The amount of lithium transferred decreased monotonically with decreasing oxygen content in the background gas. It is suggested that the change in transfer ratio was driven by the replacement of oxygen in the background gas with more massive argon, which preferentially scattered the lithium in the plasma. It was also found that decreasing the oxygen content of the background gas altered the crystal structure of the films, reducing the lattice parameter for films that formed crystalline LLTaO in the as-deposited state and inhibiting the formation of LLTaO, prior to annealing, for the film prepared with 6.6% oxygen background gas. Conductivity was found to decrease with decreasing oxygen content for 100%, 50%, and 16.6% oxygen background conditions, however the conductivity increased sharply for the 6.6% oxygen background condition. The activation energy was found to vary with the inverse of the lattice parameter as a result of changes in the bottleneck size for lithium ion conduction. Changes in activation energy were ultimately determined to be the majority factor in determining the final conductivity of the films. This study provides insight into the effect of processing conditions on the structural, chemical, and ion conducting properties of lithium ion conductors and provides a platform for studying the intrinsic ion conduction properties of these materials.

#### 5.7 Acknowledgements

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# Chapter 6: Measuring the Ion Conductivity Across Single Grain Boundaries Using Bicrystal Substrates

# 6.1 Motivation

The work presented in this chapter is being prepared for submission to the open literature and summarizes efforts to measure the single grain boundary impedance in LLTaO thin films. This is accomplished by epitaxially depositing LLTaO on (previously) commercially available bicrystals and generating electrodes that allow for the measurement of the grain boundary region with impedance spectroscopy measurement. To our knowledge this is among the first quantitative measurements of the impedance of single grain boundaries in a lithium ion conducting material.

#### 6.2 Abstract

A measurement strategy to enable the quantitative measurement of the impedance of single grain boundaries is presented.  $Li_{3x}La_{1/3-x}TaO_3$  with x = 0.075 was grown epitaxially on (001)oriented bicrystal SrTiO<sub>3</sub> with tilt-type misorientations of 24°, 45°, and 6°. The resulting films were verified to have grown with a cube-on-cube epitaxial relationship to the substrates and to be phase pure by XRD. Topographic SEM of the grain boundary regions further confirmed the change in orientation across the film as the faceting directions were measured to be offset by the misorientation angle of the substrate. Additionally, the 24°- and 45°-tilt samples exhibited similar surface morphology, while the 6°-tilt sample was observed to have significantly different surface morphology. The composition of the films was characterized by TOF-SIMS and revealed that the 6°-tilt sample had a larger ratio of counts of O<sup>+</sup> and CsLa<sup>+</sup> to CsTa<sup>+</sup> and a decrease in the CsLi<sup>+</sup>:CsTa<sup>+</sup> ratio compared to the other films, indicating there may have been differences in the surface of the bicrystal leading to differences in the resulting film. Impedance spectroscopy was measured across the grain boundary and in the bulk region of each film, revealing that the 45°-tilt sample exhibited grain boundary conductivity approximately two orders of magnitude less than in the other samples, although the activation energy measured was similar for all samples. Electrochemical strain microscopy and Kelvin probe force microscopy in the grain boundary region did not show significant contrast, indicating a lack of space charge behavior at the boundary. The impedance spectroscopy and scanning probe microscopy results suggest that the tilt-type
boundaries measured here do not inherently have a strong influence on the impedance of the grain boundary due to the alignment of (001) type planes across the grain boundary. In this case, some combination of the severity of the 45°-tilt misorientation and the poorer crystal quality of that substrate led to an imperfect boundary during the epitaxial growth of LLTaO on that substrate. In total, the results suggest that the large grain boundary resistance that is observed in sintered bodies might be primarily attributed to twist- and mixed-type grain boundaries.

## **6.3 Introduction**

In recent decades, the solid state lithium ion battery has become a point of much interest to the research community.<sup>1-4</sup> Since their inception, lithium ion batteries have become omnipresent in modern life, particularly with the advancement of mobile computing technologies such as smart phones and laptop computers.<sup>4, 5</sup> Over time, the quality and capability of lithium ion batteries has increased and the massive demand has led to economies of scale driving the prices per kilowatt hour to historic lows and are predicted to continue dropping in the coming years.<sup>6, 7</sup> With these advancements, new battery applications are becoming increasingly common, including grid scale storage and electric vehicles.<sup>8-11</sup> Both of these applications involve the storage of very large amounts of energy relative to the requirements of more traditional lithium ion battery applications, such as mobile devices, which demands more scrutiny in the realms of safety and energy density. Traditional liquid electrolyte lithium ion batteries use organic electrolytes, which are commonly highly reactive when exposed to the atmosphere and can lead to fires that are exceedingly difficult and dangerous to extinguish.<sup>12,13</sup> This risk is exacerbated in both automotive and grid scale storage due to the potential for physical damage during impacts and the sheer volume of energy stored, respectively. Solid state lithium ion batteries represent a potential solution to these problems by offering paths toward the advancement of both safety and energy density. In the context of safety, oxide solid state lithium ion electrolytes tend to be non-reactive when exposed to air in addition to being more tolerant of heating than liquid electrolytes, providing protection against thermal failure events.<sup>257, 333–335</sup> Solid state lithium ion batteries also have significant advantages for energy density compared to liquid electrolyte batteries. Firstly, the reduced thickness required from a solid state electrolyte compared to a liquid electrolyte and separator in addition to reduced packaging requirements effectively increase the energy density of solid state lithium ion batteries by reducing the amount of inactive materials in a battery cell.<sup>18, 19</sup> Additionally, some success toward the

integration of high energy anodes, such as lithium metal, through the application of interphase layers at the interface between the electrolyte and the anode has been found.<sup>338, 339</sup>

While some solid state battery technologies have matured to the point where they have entered the market, a key challenge to widespread adoption and the expansion of materials systems has been the relatively low total ion conductivity of the solid state electrolytes at room temperature.<sup>22, 23</sup> A wide range of lithium ion conducting ceramics have been discovered that exhibit ion conductivity that is comparable or better than that of liquid electrolyte within bulk, crystalline regions, however, these materials in a polycrystalline form usually possess grain boundary ion conductivity as much as several orders of magnitude less than in the bulk at room temperature.<sup>17, 23, 342–344</sup> Crucially, most of the studies observing this behavior are working with bulk materials and, as such, are measuring the aggregate of many grain boundaries (100s to 1000s depending on grain and sample sizes) that may have any number of orientations. Because the grain boundary is a region of great disruption to the chemical, structural, and electrical properties of any given crystal, it is reasonable to expect that differently misoriented grains would generate different conditions for ion conduction and lead to some boundaries having much larger impedance than others. In fact, the dependence of ion conductivity as a function of grain boundary misorientation was indirectly observed in sodium ion conductors starting in the 1970s<sup>29-32</sup> and has subsequently been observed in lithium ion conducting thin films.<sup>33–36</sup> Additionally, computational results have shown that the difference in ion conductivity across the boundaries separating differently oriented grains can be expected to be significant.<sup>37-42</sup> Some experimental work has been performed on single grain boundaries using electrochemical strain microscopy (ESM) to generate understanding of the impedance as a function of misorientation, but this technique can only provide coarse, qualitative understanding of the ion conductivity behavior.<sup>43, 44</sup> ESM, in conjunction with transmission electron microscopy (TEM), was also used to identify the reduction of titanium, from Ti<sup>4+</sup> to Ti<sup>3+</sup>, at the grain boundaries as the driving factor for the reduction in grain boundary ionic conductivity in Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub>.<sup>44, 45</sup> This leaves the state-of-the-art understanding of grain boundary ion conduction with a dearth of quantitative knowledge about ion conductivity as a function of misorientation.

This study presents a method for the quantitative characterization of single grain boundary ion conductivity using impedance spectroscopy via the epitaxial growth of electrolyte materials on bicrystalline substrates. The solid electrolyte  $Li_{3x}La_{1/3-x}TaO_3$  (LLTaO) is used to study this

phenomenon because it is isostructural with the well-studied  $Li_{3x}La_{2/3-x}TaO_3$  *A*-site deficient perovskite lithium ion conductor, but can be coerced to adopt a cubic perovskite structure, where the lanthanum disorders and distributes evenly across all (001)-type planes, for values of  $x \ge 0.075$ .<sup>47, 48</sup> The tantalum ion that occupies the *B*-site in LLTaO is also highly stable against changes in valence, unlike titanium. These properties make LLTaO an ideal candidate to enable the measurement of ion conductivity as a function of misorientation without the convolution of results by twin boundaries or chemical changes at the grain boundary.

### **6.4 Experimental Methods**

Polycrystalline Li<sub>3x</sub>La<sub>1/3-x</sub>TaO<sub>3</sub> targets were synthesized from Li<sub>2</sub>CO<sub>3</sub> 99+%, Arcos Organics), La<sub>2</sub>O<sub>3</sub> (99.9%, Alfa Aesar) and Ta<sub>2</sub>O<sub>5</sub> (99.9%, TANiOBIS GmbH) precursors. A nominal composition of x = 0.075 was used for batching with an additional 20 at.% lithium added to the stoichiometric amounts to account for losses of lithium during high temperature processing and pulsed laser deposition (PLD). Binder was added via a milling step to the powder, then it was compacted uniaxially in a 31.75 mm diameter pressing die to green densities in the range of 55-60% of the theoretical value. Pellets were then sintered in air for 12 hours at 1500 °C, resulting in pellets with a sintered density greater than 90% of the theoretical value. The solid state synthesis methods are described in more detail in previous work.<sup>49</sup> Because it has been seen that laser ablation of LLTaO results in preferential removal of lithium from the target, each deposition was performed using a different target, pressed from the same batch of powder and sintered simultaneously with the others. Targets were placed in the PLD chamber prior to deposition and held in vacuum for 24 hours, resulting in a chamber base pressure  $\leq 4 \times 10^{-7}$  Torr.

Epitaxial LLTaO films were deposited onto bicrystalline SrTiO<sub>3</sub> (STO) substrates with 24°, 45°, and 6° tilt boundaries and (001)-orientation (MTI Corporation, Richmond, CA, USA) via PLD. Depositions were conducted within a custom high-vacuum system using a target carousel and substrate heater from NBM Design (Bel Air, MD, USA), where substrates were attached to the heater platen using conductive silver paint (Ted Pella, Redding, CA, USA). All films were deposited at a substrate temperature of 720 °C  $\pm$  10 °C as measured by a Fluke Endurance E2RL 2-color pyrometer (Everett, WA, USA) with a target-to-substrate distance of 68 mm. The background pressure for each film growth was held constant at 150 mTorr as measured with a

capacitance manometer gauge (MKS Instruments 627F, Andover, MA, USA) at a flow rate of 12 sccm  $O_2$ , controlled using mass flow controllers (Alicat Scientific, Tucson, AZ, USA). Background gas pressure and substrate temperature were allowed to settle for 1 hour prior to the start of deposition to prevent fluctuations during the deposition period. Laser pulses (248 nm wavelength, 20 ns) were generated using a Lambda Physik COMPex 205 excimer within constant voltage mode. The excitation energy was set such that the energy fluence at the surface of the target was ~1.43 J/cm<sup>2</sup> and the repetition rate was 10 Hz. The substrate was first covered with a shutter while the target was exposed to 1800 pulses of the laser to clean the target surface, then the shutter was opened and the films were deposited with a total of 18,200 pulses. During deposition, the targets were rotated about their own axis and raster motion was performed by rotating about the target surface. The films were amorphous as-deposited, thus, after deposition, the samples were annealed in static air at 950 °C for 1 hour to crystallize.

The crystal structure of the films was characterized by X-ray diffraction (XRD). For outof-plane  $(2\theta - \omega)$  scans, a Panalytical Empyrean diffractometer (Malvern Panalytical, Malvern, UK) with a Cu K $\alpha$  radiation source was used. For other  $\phi$ -scans and reciprocal space mapping a Rigaku Smartlab diffractometer (Rigaku Corporation, Akishima-shi, Tokyo, Japan) with a Cu Ka radiation source and a Ge-220 two bounce monochromator were employed. Topographic scanning electron microscopy (SEM) and focused ion beam (FIB) milling and fiducial depositions were performed in a Helios UC G4 Dual Beam FIB (Thermo Fisher Scientific, Waltham, MA, USA) with a gallium ion source. Topographic imaging used beam conditions of 5 kV accelerating voltage and 0.20 nA beam current. Trenches were milled through the film in order to enable the measurement of film thickness and platinum fiducials were deposited on the film surface to mark the bicrystal boundary region as it was not easily observed in optical microscopy. AZ-nLOF 2020 photoresist is then spun onto the film surface. Using the fiducials deposited in the FIB, bar electrodes were photolithographically patterned using a MicroWriter ML3 laser writer (Durham Magneto Optics, Durham, North Carolina) equipped with a 385 nm light source. Platinum electrodes were then deposited by DC magnetron sputtering to a thickness of ~35 nm before the photolithographic resist was lifted off by ultrasonic cleaning in acetone. The electrode marking, patterning, and deposition process is represented schematically in Figure 6.1(A)-(C). Figure 6.1(D) shows the nominal dimensions and layout of the electrodes used for electrical characterization. Actual electrode

dimensions were measured by optical image analysis of micrographs with a stage micrometer. Impedance spectroscopy (IS) data was collected between 10 MHz and 500 µHz with a 1 V oscillator, using a Solartron 1260A frequency response analyzer with a Solartron 1296A dielectric interface to allow for measurement of high impedance samples (Solartron Metrology, Bognor Regis, West Sussex, UK). Impedance spectroscopy measurements were carried out in an Instec vacuum probe station with a heating stage (model HP621HVF, Instec Inc., Boulder, CO, USA) where typical vacuum levels of  $1 \times 10^{-4}$  Torr were achieved during measurement. Impedance spectra were fit using EC-Lab software (Bio-Logic S.A.S., Claix, France) for extraction of conductivity and activation energy values. Fitting was performed on points with frequencies above 1 Hz due to inductive effects observed in the measurement setup. Measurements for the "bulk region" and "grain boundary region" were carried out sequentially, by exchanging leads at the Solartron 1296 dielectric interface, allowing the probe contacts to remain stationary throughout the measurement cycle. Atomic force microscopy (AFM) was performed using several Asylum Research Cypher AFM instruments (Oxford Instruments Asylum Research, Santa Barbara, CA) located at both the University of Virginia and the Oak Ridge National Laboratory (ORNL) Center for Nanophase Materials Sciences (CNMS). Band excitation electrochemical strain microscopy (ESM) was performed using the custom implementations developed by scientists at the ORNL CNMS user facility. Band excitation ESM parameters were 3 V oscillator, 5 V bias, and a 150 kHz band centered on 365 kHz. Relative film compositions were characterized by time-of-flight secondary ion mass spectroscopy (TOF-SIMS) by the Analytical Instrumentation Facility (AIF) at North Carolina State University using a TOF SIMS V instrument (ION TOF, Inc. Chestnut Ridge, NY). 10 keV Cs<sup>+</sup> with 23 nA current was used to create a 120  $\mu$ m × 120  $\mu$ m milled area and the middle 50  $\mu$ m by 50  $\mu$ m area was analyzed using 0.35 pA Bi<sub>3</sub><sup>+</sup> primary ion beam. Depth profile data was measured, and the relative lithium content was determined by using the average counts for each species in the steady-state region of the depth profiles.



Figure 6.1: Schematic diagrams illustrating the process for orienting the bar electrodes to be parallel to the bicrystal boundary. (A) After deposition and annealing the sample was loaded into the FIB and platinum fiducial markers were deposited in four spots surrounding the grain boundary with a gallium ion beam. (B) After fiducial markers were deposited photoresist was spun onto the film surface and the electrode layout exposed via a laser writer. (C) Platinum electrodes were sputtered through the photoresist mask to a thickness of ~35 nm with the sputter gun oriented normal to the sample surface. Finally, the photoresist was lifted off the surface to leave the electrodes behind by ultrasonic cleaning in acetone. (D) The final configuration of the bar electrodes on the sample surface. Nominally, the electrodes are  $3.5 \times 0.75$  mm with 200 µm spacing. The grain boundary is located between the center two electrodes (as represented by the dotted line).

#### 6.5 Results and Discussion

The lattice expected lattice mismatch between LLTaO  $(a_0 \approx 3.92 \text{ Å})^{50}$  and the SrTiO<sub>3</sub> substrates  $(a_0 = 3.905 \text{ Å})^{51}$  is less than 1%, which implies that generating heteroepitaxial growth between these materials would be straightforward. Additionally, LLTaO and STO share a common perovskite structure. For compositions where  $x \le 0.075$ , LLTaO takes on a tetragonal structure, where the unit cell is formed by a doubling in the *c*-axis direction. The reduced symmetry comes about due to ordering of lanthanum onto alternating (001)-type pseudocubic planes.<sup>52</sup> The nominal composition of the targets used to deposit these films exceeded the threshold where the LLTaO would be expected to form a cubic structure as the increased lithium forces disordering of the lanthanum. The out-of-plane XRD patterns shown in Figure 6.2(A) illustrate the loss of lithium during the deposition process through the appearance of faint reflections characteristic of the tetragonal LLTaO phase at  $2\theta \approx 12^{\circ}$  (marked with a triangle). This reflection is far less intense than would be expected for a fully ordered structure, indicating that there are likely small domains of ordered lanthanum-rich and lanthanum-poor planes in the film. An artifact reflection is also present at  $2\theta \approx 42^\circ$ , which is the result of errant generation of W L $\alpha$  in the diffractometer source, is marked with a dagger. Beyond these, only reflections associated with the STO {001} and LLTaO {001}<sub>cubic</sub> planes are visible. These are present in the form of pairs of peaks at  $2\theta \approx 22^\circ$ ,  $46^\circ$ , and  $73^\circ$  with the LLTaO reflections falling at slightly lower angles due to their larger lattice parameter. The LLTaO and STO peaks are marked with diamonds and stars, respectively. In Figure 6.2(B),  $\phi$ -axis scans on the LLTaO and STO (013) reflections are shown. For single-crystal, cubic materials such as STO, only four reflections would be expected in this scan. However, eight are observed here as a result of the bicrystal boundary in the substrate. All patterns exhibit a reflection at  $\phi = 0$ , followed by the bicrystal reflection at  $\phi$  equal to the bicrystal misorientation angle. This pattern is then repeated every 90°, resulting in eight total reflections. Comparison of the film patterns, shown on the top of the plot, with the substrate patterns, shown on the bottom, reveals good matching of the lower intensity film peak positions to the substrate peak positions, indicating cube-on-cube epitaxy of LLTaO on STO on both sides of the bicrystal boundary. The films were further characterized by reciprocal space mapping (RSM) centered on the STO (002) reflection. The collected RSM maps are shown in Figure 6.3(A)-(C), with the STO (002) reflections highlighted in red, dashed ellipses. Notably, all bicrystals exhibit splitting of the STO (002) peak which indicates that the misorientation is not purely tilt type which would manifest as a single STO (002) reflection

because the (002) planes on either side of the boundary would be parallel for a purely tilt type misorientation. The misalignment varies from sample to sample, with the 6°-tilt bicrystal exhibiting the largest magnitude of splitting in  $\omega$  at about 1°. The other samples have approximately 0.5° splitting in  $\omega$ , with the 24°-tilt bicrystal showing a splitting into three peaks, which might indicate mosaicity on one size of the boundary. The LLTaO (002) reflections are highlighted by yellow ellipses, where it can be seen that the 24°-tilt and 45°-tilt samples exhibit a much broader spread of orientations relative to the 6°-tilt sample, as shown by the diffuse diffraction ring surrounding the primary LLTaO (002) reflection. The intensity of the STO (002) reflections are mimicked by those of LLTaO (002) in all cases, again indicating epitaxy on both sides of the bicrystal. Rocking curves were extracted from the RSM maps to give more insight to the out of plane misorientation observed and are plotted in Figure 6.3(D)-(F). The 24°-tilt sample only appears to exhibit one reflection when a rocking curve is extracted due to the extremely sharp nature of the left-most STO (002) reflections resulting in them not being included in the slice. Otherwise, the splitting observed in the RSM maps is confirmed by the rocking curves. Average full width half max values for each the  $24^{\circ}$ -tilt,  $45^{\circ}$ -tilt, and  $6^{\circ}$ -tilt films were measured at  $0.23^{\circ}$ , 0.20°, and 0.05°, respectively. For the 24°-tilt, 45°-tilt, and 6°-tilt substrates, average full width half max values were measured as 0.02°, 0.12°, and 0.04°, respectively. Based on the significantly larger full width half max value, the 45°-tilt bicrystal appears to have poorer crystal quality than the other substrates. This is largely generated by only one of the peaks observed in the rocking curve, indicating that one side of the bicrystal has more deviations from the (001) out-of-plane orientation than the other.



Figure 6.2: (A) Normalized,  $2\theta$ - $\omega$  XRD patterns for each of the 24°-, 45°-, and 6°-tilt bicrystal films for use in phase identification. All patterns show epitaxially matched LLTaO and STO reflections marked with diamonds and stars, respectively. Additionally, the patterns contain a low intensity reflection that is characteristic of the tetragonal LLTaO structure, marked with a triangle, and a W L $\alpha$  generated STO (002) reflection, marked with a dagger. (B)  $\phi$  scans of the LLTaO (013) (top set) and STO (013) reflection (bottom set). While low intensity, the LLTaO (013) reflections match well with those of STO (013) in  $\phi$  indicating cube-on-cube epitaxy.



Figure 6.3: Reciprocal space maps of the region surrounding the STO (002) reflection for the annealed (A) 24°-tilt, (B) 45°-tilt, and (C) 6°-tilt bicrystal films. Splitting of the STO (002) peaks (red dashed ellipses) indicates the bicrystals are misoriented in- and out-of-plane. Similar splitting is observed for the LLTaO (002) peaks (yellow dashed ellipses). Epitaxy on the 6°-tilt appears to be of higher quality than in the films with larger misorientations. Rocking curves were extracted from the reciprocal space maps for the STO (002) and LLTaO (002) reflections for the (D) 24°-tilt, (E) 45°-tilt, and (F) 6°-tilt bicrystal films. In all three cases, there is good matching between the film and substrate reflections in terms of shape and position. The (D) 24°-tilt and (E) 45°-tilt bicrystal films exhibit broad shoulders (corresponding to the yellow dotted ellipse on reciprocal space map) indicating a distribution of orientations of the LLTaO (002) peaks.

Film topography was characterized by secondary electron SEM. Images of the grain boundary regions for each film are shown in Figure 6.4. In the left-hand column, a set of images at low magnification is shown to illustrate the typical topography of each film. It is immediately apparent that the surfaces of the 24°-tilt and 45°-tilt samples are similar, with cubic, faceted pillars

growing out from the surface. The region immediately surrounding the boundary in these films appears less densely populated with the faceted outgrowths. On the other hand, the 6°-tilt sample has a different surface morphology, dominated by similarly faceted, crater-like features. The boundary line is the most obvious for the 6°-tilt sample owing to the nearly continuous line of these crater-like features along the boundary. Measuring the angle between the faces of the faceted features readily reveals supplement of the bicrystal angle for each sample, as marked in the righthand column of images. The difference in surface morphology of the samples follows the same trend that was observed in XRD measurements, with the 6°-tilt sample exhibiting notably different structure from the other two samples. Representative FIB cut cross sections, used for determining the thickness of the films, are shown in Figure 6.5. In each image, four layers are present, from top to bottom they are ion beam deposited platinum, electron beam deposited platinum, the LLTaO film, and the STO substrate. The platinum is deposited prior to initiating the FIB milling process to protect the film surface and prevent excessive gallium contamination in the foil. Examination of the top surface of the LLTaO film layer corroborates the outgrowth faceting observed in the 24°-tilt and 45°-tilt samples as well as the cratering observed in the 6°-tilt sample in Figure 6.4. From the cross-sectional images, the average thickness of the films was measured to be 247 nm, 257 nm, and 268 nm for the 24°-tilt, 45°-tilt, and 6°-tilt samples, respectively. The grain boundary in each substrate can be observed near the scale bar in each micrograph as a white line that travels perpendicular to the face of the substrate, however, the same contrast is not as obvious in the films. Electron diffraction through the film was performed and found that the location of the zone axis moved suddenly as the beam was scanned over the grain boundary region indicating a relatively sharp transition from one orientation to another at the boundary in the film.



Figure 6.4: Topographic secondary electron SEM of the grain boundary regions in each film. The micrographs in the right-hand column ((B), (D), and (F)) are regions in the center of the corresponding image in the left-hand column ((A), (C), and (E)) at six times higher magnification. The films grown on (A)-(B) 24°-tilt and (C)-(D) 45°-tilt bicrystals exhibit faceted, upward growth on the surface. In the high magnification images, the change in orientation across the grain boundary is visible in the orientation of the facets forming a "V" near the center of the image. The film grown on the (E)-(F) 6°-tilt bicrystal exhibits a different surface morphology with most facets taking the form of craters. The grain boundary is visible as a near-continuous line of faceted craters near the center of the image.



Figure 6.5: Representative cross section cut from the grain boundary region of the (A)  $24^{\circ}$ -tilt, (B)  $45^{\circ}$ -tilt, and (C)  $6^{\circ}$ -tilt samples. The four layers present are labeled to the left, and the black area at the top of each micrograph is off the sample. The average thickness of the films was measured to be 247 nm, 257 nm, and 268 nm for the  $24^{\circ}$ -tilt,  $45^{\circ}$ -tilt, and  $6^{\circ}$ -tilt samples, respectively.

TOF-SIMS was used to characterize the relative content of the cations in the films by taking the average composition of the film over the steady state region of a depth profiling scan, as shown in Figure 6.6. Figure 6.7(A) and (B) show the measured ratio of counts for the cesium-lithium complex and the cesium-lanthanum complex to the cesium-tantalum complex, respectively. The  $CsM^+$  to  $CsTa^+$  complexes were selected for measurement to suppress the contribution of matrix effects to the measurement.<sup>318</sup> While these ratios do not correspond directly to the stoichiometric ratios of the cations, it can be seen that samples with larger  $CsLi^+:CsTa^+$  ratios have correspondingly lower ratios of  $CsLa^+:CsTa^+$ , as would be dictated by the charge balance in the formula  $Li_{3x}La_{1/3-x}TaO_3$  (as *x* increases, the amount of lanthanum decreases). The time the films spent at high temperature during processing in air implies that the LLTaO should be fully oxidized, which could imply that there is less tantalum present in the 6°-tilt sample than in the others. However, there is no evidence of secondary phases in the XRD patterns or SEM that would indicate large deviations from the expected stoichiometry. The reason for this apparent discrepancy between the film compositions is unclear at this time, as the films were grown under identical conditions, using the same batch of targets, in the same chamber, and within the same day. It is speculated that this could be due to differences in the surfaces of the bicrystal substrates, which could also account for the differences in surface morphology observed in SEM. Unfortunately, TOF-SIMS standards for LLTaO do not exist, precluding a more substantial evaluation of the exact film compositions.



Figure 6.6: TOF-SIMS depth profiles measured for films deposited on (A) the 24°-tilt bicrystal, (B) the 45°-tilt bicrystal, and (C) the 6°-tilt bicrystal. The dashed, vertical lines indicate the region of each depth profile that was considered "steady state" for the purposes of determining average counts value for each of the Cs*X* complexes and oxygen ions. The average value of the CsLi<sup>+</sup>, CsLa<sup>+</sup>, and O<sup>+</sup> counts was normalized by the average value of the CsTa<sup>+</sup> counts to determine the ratios presented in Figure 6.7.



Figure 6.7: Qualitative comparison of the composition of each film as determined by TOF-SIMS depth profiling. The ratio of the counts for the (A)  $CsLi^+$ , (B)  $CsLa^+$ , and (C)  $O^+$  channels to the  $CsTa^+$  counts. These ratios do not correspond directly to the atomic ratios in the sample but are valid for comparison from sample to sample.

Impedance spectroscopy was performed using the electrode configuration shown in Figure 6.1(D), where the following will refer to measurements between electrode 1 and 2 as the "bulk region" and measurements between electrode 2 and 3 as the "GB region." The complex plane impedance data, measured at 350 °C in the bulk region are plotted in Figure 6.8(A). The results in the bulk region were fit using a single ZARC with a leading resistor, as indicated in the plot area. In all cases it was found that the leading resistor was best fit with a zero value. The data are truncated to a frequency of 1 Hz due to artifacts generated during the measurement, thus removing the ability to fit using a blocking electrode as the sample configuration would imply. Figure 6.8(B) shows the corresponding data set, as measured in the grain boundary (GB) region. For measurements in the GB region, the equivalent circuit was expanded to include a second ZARC to represent the grain boundary contribution to ion conductivity. Because the two semicircles that are expected to be present in this data are not easily separable, fitting was carried out by first fitting the bulk arc and then transferring those parameters into a new fit with a second ZARC. The second ZARC was then used to minimize the error that existed in the fit after fitting was completed with a single ZARC equivalent circuit. In all cases the value of  $\chi^2/|Z|$  reported by EC-lab was improved by approximately 30% compared to the single ZARC fit. The extracted conductivity values from the bulk and grain boundary regions at 250 °C are shown in Figure 6.8(C)

and (D), respectively. Here, it can be seen that the ion conductivity of the bulk region for all three films is similar, with the 6°-tilt sample having the highest conductivity at 250 °C by a slight margin. Because the bulk region was fit with a single ZARC, only the bulk conductivity is displayed as the total conductivity would be identical. Conversely, the two ZARC fit applied to the grain boundary region allows for the separation of different ion conductivity contributions. The grain boundary conductivity is calculated here as the "apparent" grain boundary conductivity, by using the same geometry values as were used in the bulk calculation, because the physical geometry of the grain boundary is not currently known. Furthermore, there is some debate on whether it is appropriate in this case to use the "electrical" or the "structural" geometry of the grain boundary.<sup>54</sup> Thus, the apparent grain boundary conductivity is calculated here and the assumption made that the geometry of the extents of the grain boundaries is similar between films. In these films, the conductivity of the grain boundaries in the 24°-tilt and 6°-tilt samples is roughly two orders of magnitude greater than the grain boundary conductivity in the 45°-tilt sample. The Arrhenius-type analyses used for extracting the activation energy of the different ion conductivity mechanisms are shown in Figure 6.9(A)-(D). Comparison of the activation energy of bulk ion conductivity in the bulk and grain boundary regions reveals that these numbers are the same, within error. This lends credibility to the fitting method although the two arcs in the grain boundary region could not be easily distinguished. In Figure 6.9(C) it is shown that the activation energy of the conduction is similar between samples, with the conductivity of the 45°-tilt sample having significantly lower conductivity across the measured temperature range, indicating that the energetic barrier in the low conductivity, 45°-tilt boundary is not significantly higher than in the other configurations studied. This observation could be due to a reduction in the number of sites available to mobile lithium ions without significant modification of their chemical/coordination environment due to the structure of the boundary.



Figure 6.8: Impedance spectroscopy data plotted in the complex impedance plane for the (A) bulk region of the film and (B) the grain boundary region of the film. The data were truncated to a minimum frequency of 1 Hz to aid in the legibility of the plot and remove the artifact contributions from the measurement setup. Measured data points are shown as open circles and the fit is plotted as a solid line of the same color as the corresponding data. Data were fit using the equivalent circuit models shown in their respective panels. The extracted conductivity values at 250 °C are shown for the (C) bulk region and (D) grain boundary region from each film. Bulk conductivity is represented in circular points, boundary conductivity by square points, and total conductivity by triangular points. Note that in the bulk region, only one value is shown because the bulk and total conductivity are equivalent in this region.



Figure 6.9: Arrhenius type analyses for extracting the activation energy of the (A) bulk conductivity in the bulk region, (B) the bulk conductivity in the grain boundary region, (C) the grain boundary conductivity in the grain boundary region, and (D) the total conductivity in the grain boundary region. Bulk conductivity is represented in circular points, boundary conductivity by square points, and total conductivity by triangular points.

Finally, electrochemical strain microscopy (ESM) and Kelvin probe force microscopy (KPFM) were measured in the grain boundary region of the films. Typical results from ESM scans are shown in Figure 6.10. Comparison of the topographic scans (top row) with the ESM amplitude (middle row) and resonant frequency (bottom row) maps quickly indicates that there is little

information being generated electrically because a large majority of the observable signal in the ESM amplitude and frequency maps is identical to the topographic maps. It is somewhat expected to observe crosstalk between the topography and the ESM results due to their closely related techniques, therefore analysis of these data must be based on signals that do not appear in all maps. The only instance of contrast in the ESM amplitude maps appears very faintly as a darker, vertical line in the map of the 45°-tilt grain boundary shown in Figure 6.10(E) and highlighted with white arrows. This corresponds well to the lower ion conductivity of the 45°-tilt grain boundary, observed in impedance spectroscopy measurements. KPFM measurements are not pictured here due to the complete lack of contrast observed. The lack of KPFM contrast does indicate that there is effectively no surface charging nor different surface charging behavior across the grain boundary, implying that there is not a significant space charge zone present in these grain boundary configurations for LLTaO. Combining the lack of evidence for a space charge region around the grain boundary via KPFM and ESM and the similar activation energy of ion conduction across all the boundaries, it appears that, for these samples, the primary driver for impedance at the grain boundaries is structural.

It bears mention that in all plots, the order that the films are referred to is specifically 24°-tilt, 45°-tilt, and then 6°-tilt because there is no inherent reason to expect that the ion conductivity should follow a monotonic trend with changes in the misorientation angle. Just as in the grain boundary energy, 55–59 it is expected that there could be multiple minima in the impedance of the grain boundary, especially in structurally constrained cases, as a result of some orientations exhibiting overlapping lattice points and planes.<sup>60</sup> The most well-known formulation of this idea is the concept of coincident site lattices (CSL), where, at certain angles points in two disparate lattices overlap forming a new unit cell. This is illustrated in Figure 6.11(A) and (B). In the case of the misorientation angles investigated here, for the 45°-tilt and 6°-tilt, the closest low  $\Sigma$ -value CSL angles are 36.87° ( $\Sigma$ 5) and 16.26° ( $\Sigma$ 25), which are both more than 7° different than the misorientation measured by XRD. The 24°-tilt misorientation is similar to the 22.62° ( $\Sigma$ 13) CSL configuration but is still more than 1° off the misorientation measured by XRD, which would have been readily resolved in the XRD scans. Importantly, when considering any CSL in a cubic system for a single axis rotation, such as a tilt-type boundary, the (001)-type planes are always aligned. Lithium in LLTaO moves through the lattice by hopping from one vacant A-site to another. This means that a purely tilt boundary, without the generation of a space-charge layer, would effectively

leave conduction pathways open from one grain to another. This is illustrated by the alignment of the (001)-type planes in Figure 6.11(C). While this configuration would be expected to apply to all samples studied here, it is suggested that the severe misorientation of the 45°-tilt boundary and the poorer crystalline quality of the bicrystal generated an imperfect boundary during the epitaxial growth of the film. This would account for the observed increased impedance as well as the minor decrease in the ESM amplitude near the 45°-tilt grain boundary.



Figure 6.10: Representative AFM height maps, captured in contact mode of the (A)  $24^{\circ}$ -tilt, (B)  $45^{\circ}$ -tilt, and (C)  $6^{\circ}$ -tilt bicrystal films. The ESM amplitude and the tracked resonant frequency are plotted for the same fields in (D)-(F) and (G)-(I) respectively. All contrast observed in the ESM amplitude and resonant frequency maps is apparently derived from topographic interference as can be seen by comparison to the height maps.



Figure 6.11: Illustration of the relationship between two cubic lattices in coincident site lattice relationships. (A) Plan view illustration of the  $\Sigma 5$  CSL boundary and the newly formed CSL cell, which has edge lengths of  $\sqrt{5}a$ . Only the basal planes are shown as the crystals are identical in the [001] (out of plane) direction. Thus, the volume of the CSL cell is five times that of the primitive unit cell, resulting in the designation  $\Sigma 5$ . (B) Schematic illustration of the special ordering that may occur in the grain boundary between two crystals that form a CSL in plan view. It can be seen that at certain intervals points align, resulting in a special grain boundary with some level of periodicity. (C) Schematic representation of a tilt boundary in a cubic system, where it can be seen all (001)-type planes are aligned, which would leave conduction pathways for lithium ions in LLTaO open through the grain boundary region.

## **6.6 Conclusions**

A method for the measurement of the impedance of single grain boundary structures via the epitaxial growth of LLTaO on STO bicrystals has been presented. Bicrystals with 24°-, 45°-, and 6°-tilt misorientations were used as substrates for the cube-on-cube growth of LLTaO as evidenced by a variety of X-ray diffraction measurements. Furthermore, the morphology of the faceted elements on the surface of the films adhered well to the expected misorientation across the boundary. Impedance spectroscopy measurements of the grain boundary and bulk regions were performed with the grain boundary region not producing readily separable semicircles for the grain and grain boundary response. After fitting the bulk response, the fit was adjusted using a second ZARC to improve the fit, resulting in well-formed Arrhenius-type regressions that showed the activation energy of ion conduction across the grain boundary was similar in each film, but the 45°-tilt sample exhibited significantly lower ion conductivity than either the 24°- or 6°-tilt samples. Electrochemical strain microscopy was performed on the grain boundary regions of each film, but only observed faint contrast in the ESM amplitude for the 45°-tilt sample. Kelvin probe force microscopy was also performed in the same area and showed no evidence of surface charges that would imply the existence of a space charge region in these films. Together, the lack of measured effects in the 24°- and 6°-tilt samples indicates that the alignment of (001)-type planes across tilt boundaries results in smaller-than-expected disruptions to the ion conduction pathways in LLTaO. With the above evidence, the increased impedance observed in the 45°-tilt sample was attributed to some combination of the severe structural disruption and poor crystal quality of the bicrystal substrate resulting in a malformed interface in that film. Prior work on polycrystalline, sintered LLTaO indicated that the activation energy of ion conduction across the grain boundary could be expected to be 20-40% higher than that of the bulk.<sup>49</sup> However, the tilt boundaries studied here exhibited similar activation energy values for ion conduction across the grain boundary vs. the bulk, indicating that twist-type boundaries would be the primary contributors to the increased impedance that is commonly observed as the grain boundary response in sintered bodies.

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# Chapter 7: Generation of Strontium Titanate Substrates with Large Grains for Use in Combinatorial Substrate Epitaxy

## 7.1 Motivation

The work presented in this chapter encapsulates efforts to generate a procedure for synthesizing undoped strontium titanate (STO, SrTiO<sub>3</sub>) with large enough grains to allow for combinatorial substrate epitaxy growths and subsequent characterization of the ion conductivity across single grain boundaries. The initial goal was set as an average grain size larger than 100  $\mu$ m to allow space for the deposition of fiducial markers using FIB and subsequent deposition of photolithographically defined electrodes.

## 7.2 Introduction

Strontium titanate is extremely widely studied due to its position as a "prototypical" perovskite and wide application space.<sup>1-4</sup> In the context of this dissertation, STO is an attractive material specifically because the lattice parameter is very similar to LLTaO.<sup>5</sup> Additionally, strontium titanate in an undoped state is highly insulating making it an ideal candidate for the epitaxial deposition and subsequent electrical characterization of LLTaO. In the previous chapters, commercially available wafers were used in both single- and bicrystalline forms to generate epitaxial films of LLTaO to enable the measurement of ion conductivity with controlled grain boundary contributions. As an extension of this technique, combinatorial substrate epitaxy was proposed to allow for the measurement of grain boundary configurations that are not available for purchase commercially. Combinatorial substrate epitaxy (CSE) is a technique pioneered in the Rohrer group at Carnegie Mellon University wherein epitaxial growth is carried out on a polycrystalline substrate.<sup>6-9</sup> A schematic representation of a combinatorial substrate epitaxy film is shown in Figure 7.1. In this growth mode, the grains of the substrate are templated directly into the film, generating a microstructure that can be characterized ahead of time using the bare substrate, as well as allowing for control of the grain sizes without needing to alter processing conditions to enhance the grain growth behavior of the material of interest.



Figure 7.1: Schematic illustration of the ideal CSE film, where each grain orientation from the substrate is templated directly into the microstructure of the film, resulting in the ability to measure many grain boundary orientations and theoretically do so in a statistical distribution more representative of a real material than by using bicrystals. Electrodes as depicted could be generated using photolithographic techniques after marking areas of interest using FIB to generate fiducials.

For the purposes of performing in-plane impedance spectroscopy on CSE films, it is worth revisiting the equation used for derivation of ion conductivity when using bar electrodes on the surface of the film, rearranged for the resistance value that will be measured:

$$R = \frac{s}{\sigma_f tL} \tag{7.1}$$

where s is the electrode spacing, t is the film thickness, L is the electrode length, and R is the resistance of the ZARC determined by equivalent circuit fitting. From the geometric constraints presented here it becomes obvious that increasing the length of the electrodes and reducing the spacing between them is the best way to reduce the magnitude of the measured impedance values. For this, large grains are desirable in the substrate material to generate larger areas for the deposition of electrodes. Furthermore, large grains are generally expected to have larger line

lengths containing a single misorientation relationship, which would reduce the convolution of results from the measured volume overlapping multiple misorientations.

Notably, STO exhibits an anomaly in grain growth rate trends above 1300 °C, where the rate of grain growth actually decreases with increasing temperatures. This has been observed several times,<sup>10–14</sup> even in the presence of non-stoichiometry which has been observed to increase grain growth rates in structurally-similar, but compositionally diverse, perovskite materials.<sup>15</sup> Most doping studies of STO show that the doping atoms generate conditions where bimodal growth dominates during sintering leading to a mixture of very large and very small grains which would be suboptimal for use as a CSE substrate.<sup>16–18</sup> Studies using electric fields have indicated that increased grain growth rates may be a result of point defect redistribution.<sup>19</sup> It has also been found that the atmosphere during heat treatment can strongly influence the grain growth kinetics of STO as a result of changes in grain boundary wetting behavior.<sup>20, 21</sup>

Of these options, the most accessible was the use of a reducing atmosphere for the grain growth of STO. The primary issue with reduction treatment of STO is that strongly reducing conditions result in STO with significant electronic conductivity,<sup>3, 22, 23</sup> which would be expected to influence the measurement of ion conductivity of LLTaO films. Similarly, introduction of dopants or other impurities to STO can result in electrical conductivity with the same ramifications.<sup>24, 25</sup> With these results and challenges under consideration, it was determined that a reduction-oxidation process was the most likely to produce large-grained, insulating STO for use as CSE substrates.

## 7.3 Initial Powder and Bulk Synthesis

Initial attempts toward the production of large-grained STO used individual precursors for each cation. Powders were produced using standard solid state synthesis procedures. The precursors were combined in stoichiometric ratios then milled in ethanol overnight using a roller mill. The resulting slurry was then dried for at least 12 hours in a drying oven at 80 °C. The powder was then calcined at 1050 °C for 6 hours in an effort to react precursors into STO. After calcination, the powder was combined with 2 wt.% polyethylene glycol binder before ball milling overnight in ethanol. The calcine/binder mixture was then dried at 80 °C for at least 12 hours. Pellets were formed using uniaxial pressure of 175 MPa on a 12.7 mm diameter die resulting in pellets with green densities between 55 and 60% of the theoretical density. Pellets were then sintered using a

profile derived from the procedures used in work on the development of CSE.<sup>7</sup> Binder burnout took place at 600 °C for 4 hours followed by an initial sintering step at 1360 °C for 12 hours to allow the sample to densify followed by secondary sintering step at 1470 °C for 6 hours.

In all cases, strontium cations were provided by strontium carbonate but both rutile and anatase titanium oxide were investigated as potential sources of titanium. While these have the same chemical formula, it was assumed that different powder stocks may have different morphologies or impurities that could change the sintering behavior of STO produced with each precursor. This was borne out to some degree as significant differences were observed in the phase purity after calcination for powders produced with anatase and rutile titanium oxide. However, after sintering, it was found that both precursors resulted in equally phase pure STO as can be seen in the XRD patterns in Figure 7.2. On the other hand, it was observed that the samples batched from rutile titanium oxide obtained higher final densities with up to 84% of theoretical being observed (compared to a maximum of 72% of theoretical for samples batched from anatase).



Figure 7.2: Comparison of the phase purity of STO produced with anatase and rutile titanium oxide powder stocks. It can be seen that the sample produced with anatase titanium oxide was phase pure after calcination, while the sample produced with rutile titanium oxide required more extensive thermal processing to become phase pure. The blue bar markers at the bottom of the page represent the expected pattern for STO.<sup>26</sup>

Owing to the low density achieved by using precursor synthesis methods, commercially produced STO powders were obtained from Alfa Aesar (now Fisher Chemical) and Nanografi. Two grades of powder were ordered from Nanografi with quoted particle sizes of 3 um and 300-500 nm, which are denoted micron and nano in the following, respectively. The powder stock obtained from Alfa Aesar was quoted at an average particle size of 50-150 nm and will be referred to as 50-150 powder. Pellets from each of these powder stocks were generated using the process developed for in-house synthesized STO, starting from the post-calcine/binder addition milling step. After sintering, the microstructures generated using the commercial powder stocks were characterized for density and grain size. Density was determined from the mass and dimensions of the pellets (assumed to be cylindrical) and was confirmed by a thresholding analysis run on SEM

micrographs. Grain size was determined using the Hilliard method as defined in ASTM E112-13.<sup>27</sup> Representative micrographs from the Nanografi nano, Alfa Aesar 50-150 nm, and Nanografi micron powders are shown in Figure 7.3 (A), (B), and (C), respectively. In Figure 7.3(D) the grain size and density of the pellets is shown. It can be seen that the Alfa Aesar powder resulted in both the highest density and the largest average grain size. While it was hypothesized that this powder would result in the greatest density due to the small size of the particles, it was not expected to generate the largest grain size after being co-processed with powder stocks with a larger starting particle size. In total this indicates that the grain growth rate was higher than the other powders.



Figure 7.3: Representative, secondary electron micrographs taken from pellets formed using the (A) Nanografi nano, (B) Alfa Aesar 50-150 nm, and (C) Nanografi micron powder stocks. (D) Measured density (circles, left y-axis) of the pellets presented as the percentage of the theoretical maximum density of STO and average grain size as determined by the Hilliard method (squares, right y-axis).

The wide range of sintering behavior can be relatively readily explained by the morphology of the starting powder stocks. Figure 7.4 shows micrographs collected by sprinkling the powder stocks over carbon tape then tapping away any excess powder that did not stick. Figure 7.4(A) shows the as-delivered Nanografi nano powder, which not only contains many particles that are more than 1 µm in diameter, but also contains a number of needle-like structures. It can be expected that these high-aspect-ratio structures would act as a hindrance to the flow of the powder in the mold, reducing both the green and final density of the pellets as observed. In Figure 7.4(B) the particle size distribution of the Alfa Aesar 50-150 nm powder is shown to be relatively monodisperse with significantly smaller particle size than either of the other powder stocks. The nature of this powder allowed for good flow of the powder inside the pressing die which led to larger green and sintered density of the pressed pellets. Finally, the Nanografi micron powder, shown in Figure 7.4(C), exhibits what appears to be multimodal distribution of particle sizes ranging from  $\sim 0.5 \,\mu\text{m}$  to  $\sim 3 \,\mu\text{m}$ . In many cases, the larger particles appear to be hard agglomerates which do not flow well when pressed, again resulting in low green density and commensurately low sintered densities as is clearly demonstrated by the large pore networks visible in Figure 7.3(C).



Figure 7.4: Morphology of commercial powders as-delivered. (A) Nanografi nano powder which contains needle-like particles as well as larger-than-advertised particles. (B) Alfa Aesar 50-150 nm powder which exhibits a relatively monodisperse particle size distribution with a small mean diameter. (C) Nanografi micron powder which has a wide variety of particle sizes present, with the larger particles appearing to be hard agglomerates which are not expected to flow well during uniaxial pellet pressing processes.

## 7.4 Attempted Methods for Grain Growth

## 7.4.1 Maintaining Stoichiometry

While the density of the pellets produced using the Alfa Aesar 50-150 nm powder was of a value desired for CSE, the grain size measured for all samples was significantly lower than the stated goal of  $\geq 100 \ \mu\text{m}$ . This necessitated changes to the procedures laid out above, to encourage the growth of much larger grains. As discussed above, moving STO away from stoichiometric ratios can lead to the development of electrical conductivity, therefore the first two methods

pursued were modifications of the particle morphology via combination of the powder stocks to produce a bimodal distribution and extremely extended anneals. Bimodal powders often exhibit larger final grain sizes as a result of the elevated total surface/interface energy present in smaller particles. This results in the larger grains consuming smaller grains as described in Ostwald Ripening with diffusion as the rate limiting process.<sup>28</sup> Secondarily, the mixture of powder sizes results in more favorable packing geometries when assuming spherical particles because the small particles can fill gaps between the larger particles resulting in larger green densities for pressed pellets. Bimodal powders were prepared by mixing different proportions of the nano powder and either in-house synthesized STO or micron powder. These mixtures will be referred to as the percentage (by weight) of the powder that was not the nano powder stock. Mixtures containing 60% in-house synthesized STO, 60% micron, and 40% micron powder mixtures were tested in this procedure. Representative micrographs from the sintered pellets are shown in Figure 7.5(A)-(C) with the measured values of density and average grain size plotted in Figure 7.5(D). It can be seen that, when compared to the pellets generated from only micron or only in-house synthesized powders, the density has improved but the grain size has not increased appreciably. This indicates that while the nano powder was able to fill the gaps created by the larger powder stocks and potentially aid in the flowability of the mixed powder stocks, the expected behavior of larger grains consuming pockets of smaller particles during sintering was not present. This has been observed in some cases, where the smaller particles are consumed, but tend to only grow to the point of matching the larger particles present in the initial mixture.<sup>29</sup>



Figure 7.5: Representative, secondary electron micrographs taken from pellets formed using the (A) 60% in-house, (B) 60% micron, and (C) 40% micron bimodal powder stocks. (D) Measured density (circles, left y-axis) of the pellets presented as the percentage of the theoretical maximum density of STO and average grain size as determined by the Hilliard method (squares, right y-axis).

The second method employed for the growth of STO grains was to simply anneal the pellets at high temperatures for significantly longer times than in the initial sintering. While the grain growth rate anomaly that is observed in STO was likely to preclude this as a useful strategy, long annealing was attempted because grain growth curve curves tend to show large increases in size over some short period then reach an asymptotic value of grain size that cannot be increased significantly without a time investment of geological scale.<sup>30</sup> It was hypothesized that the initial sintering procedure had not reached the asymptote, therefore, further annealing might reveal both the asymptotic grain size and generate larger grains than in pellets that only experienced the initial sintering procedure. A longer annealing period also promised the advantage of not inducing non-stoichiometry and the consequent conductivity to the STO. Figure 7.6(A), (B), and (C) show micrographs from the same pellets as in Figure 7.3(A), (B), and (C), respectively. From these micrographs, it is apparent that the density of the pellet produced with Nanografi micron powder

has significantly increased in density with extended sintering. The density observed for the Nanografi nano and Alfa Aesar 50-150 nm pellets remained approximately the same with extended annealing. In all cases, the grain size increased, with the largest average grain size being ~9.5  $\mu$ m for the micron pellet; the grain size of the nano and 50-150 pellets approximately doubled after extended annealing. Furthermore, it can be seen that both the nano and micron pellets have larger grain sizes than the 50-150 nm pellet, indicating that the initially rapid growth observed in the 50-150 nm samples may be a result of the fact that it achieves high density more readily. Traditionally, sintering is broken into three stages: 1) rapid transport and growth of necks between particles for initial densification, 2) removal of pores via their diffusion out of the lattice, ending in isolated pores in the microstructure, and 3) pores may continue to shrink and grains may grow depending on the details of the materials system.<sup>28</sup> In general, step 2) takes the majority of the time in sintering, but it may be that the initial sintering procedures did not move the nano and micron pellets past step 1), leading to a lack of grain growth opportunities without extended annealing.



Figure 7.6: Representative, secondary electron micrographs taken from pellets formed using the (A) Nanografi nano, (B) Alfa Aesar 50-150 nm, and (C) Nanografi micron powder stocks after 180 hours of high temperature annealing. (D) Observed density (circles, left y-axis), measured by thresholding the pores in a number of micrographs from each of the pellets presented as the areal percentage of dense material and average grain size as determined by the Hilliard method (squares, right y-axis).

#### 7.4.2 Modifying Stoichiometry

Given the limited success toward achieving grain sizes in the range of hundreds of microns, two strategies were attempted with modification of the stoichiometry: 1) addition of titanium or borates to the stoichiometric STO and 2) reduction sintering of the STO. The addition of titanium has been shown to encourage the growth of large grains in similar structures such as BaTiO<sub>3</sub><sup>31, 32</sup> and some work on STO has shown the presence of titanium rich phases wetting the grain boundaries and leading to enhanced grain growth.<sup>21</sup> Excess titanium was added to the powder along with the binder prior to milling to allow it to mix thoroughly. It was quickly determined that pushing the STO away from stoichiometry using the processing conditions discussed previously reduced the sintered density of the parts in addition to providing little change in the measured grain

sizes and introducing the potential for undesirable electronic behavior with secondary phases at grain boundaries. Representative micrographs from pellets produced using the 50-150 nm powder with 0.25 at.%, 0.5 at.%, 0.75 at.%, and 1.0 at.% excess titanium oxide are shown in Figure 7.7 (A), (B), (C), and (D), respectively.



Figure 7.7: Representative micrographs from pellets generated using the Alfa Aesar 50-150 nm powder with an excess of (A) 0.25 at.%, (B) 0.5 at.%, (C) 0.75 at.%, and (D) 1.0 at.% excess titanium. All samples showed significant porosity with similar grain sizes to the unmodified commercial powders after initial sintering.

Finally, reduction annealing was investigated as a catalyst for enhanced grain growth in STO. While the reduction of STO results in electrically conductive material, optical property investigations indicate that the generation of conductive defects in the STO is reversible on reoxidation.<sup>23, 33</sup> This would make reduction and reoxidation a good candidate for the purposes of CSE on strontium titanate if it produces the large average grain sizes desired. As mentioned above,
the liquid, titanium-rich phase that has been observed in reduction sintered STO would be expected to act as a fast transport medium during sintering.<sup>21, 34</sup> Additionally, it has been shown in several ceramic systems, including STO, that the grain average grain size in a sample tends to increase as the partial pressure of oxygen during sintering decreases.<sup>35–37</sup> Pellets were first sintered in air as described above to achieve high density because it was found that sintering in a reducing atmosphere did not lead to sufficient densification, likely as a result of the increased mass transport leading to high levels of trapped porosity.<sup>28</sup> Reduction annealing was carried out in a tube furnace with a 50 mm diameter, alumina tube for 180 hours at 1470 °C using pellets generated from the 50-150 nm powder. Pellets were contained in a thick bed of uncompacted 50-150 nm powder to separate them from the alumina crucible. The reducing atmosphere was generated by flowing ~105 sccm of forming gas (3% hydrogen, argon balance) throughout the annealing process including heating and cooling steps. This process resulted in dark grey to black STO pellets with grain facets on the surface that were visible without magnification. Successful reoxidation conditions were found to require slow heating and cooling of the samples to prevent cracking at both the grain boundary regions and through the grain interiors. The most success was found using ramp rates of less than 1 °C/min in static air in a tube furnace. Another strategy that was found to mitigate cracking was the use of thick pellets (3-5 mm height) as cracks were found to be confined mostly to the surface of the sample and could be ground away during polishing. Reoxidation annealing was performed at 950 °C for varying amounts of time, dependent on the condition of the samples. In some cases, the STO re-oxidizes fully (as determined by the change in color) within 5 hours at temperature, while other samples required more than 48 hours for the reoxidation front to move through the entire sample. It is most likely that these discrepancies are related to both the grain size and the defect structure of the STO, wherein oxygen is more readily conducted along the grain boundary channels in STO leading to different rates of oxygen transport through the sample depending on the specific grain boundary area. As an additional guard against reactions taking place during the reoxidation process, the pellets were held on a platinum foil to separate them from the fused silica furnace hardware. Separating the STO from the furniture consistently prevented observed issues with discoloration of the STO upon reoxidation in contact with the fused silica. Figure 7.8(A) shows the resultant microstructure after reduction annealing and Figure 7.8(B) shows the same pellet after undergoing reoxidation with a ramp rate of 1 °C/min. For illustration of the cracking discussed above, shown in Figure 7.8(C) is a sample that was

processed in tandem with that shown in Figure 7.8(A) and (B), but which underwent reoxidation using ramp rates of 5 °C/min. From the micrographs presented in Figure 7.8 it is apparent that the grain size has increased dramatically and appears to have exceeded the 100  $\mu$ m threshold set as the goal of this experiment. Unfortunately, the maximum field width of the SEM used to capture these images does not allow a large enough field to perform a statistical characterization of the grain size but from what measurements could be captured the grains were observed with diameters in the range of 250-600  $\mu$ m.



Figure 7.8: Representative micrographs taken from pellets produced with the 50-150 nm powder (A) after the reduction annealing process, (B) after reoxidation using a ramp rate of 1 °C/min, and (C) after reoxidation using a ramp rate of 5 °C/min. Note that the scale in these micrographs has increased by an order of magnitude compared to all previous micrographs presented in this chapter, with the apparent grain size increasing by closer to two orders of magnitude.

#### 7.5 Surface Preparation for Epitaxial Deposition

The final consideration prior to the use of these polycrystalline STO samples as CSE substrates is preparation of the surface to allow for epitaxial growth. Manual polishing of the

pellets to a finish of 0.05 µm using colloidal silica was found to provide a good surface finish for the purposes of EBSD as shown on a sample without reduction annealing in Figure 7.9(A). Additionally, a final ion polishing step was employed as a way to remove the final layer of material damaged by the polishing process and provide as close as possible to a deformation-induced defect-free surface. An etch-anneal procedure is commonly used with STO to generate wellterminated surfaces with atomic terraces.<sup>38</sup> However, this process relies on the formation of strontium hydroxide and its eventual etching to result in nearly ideal surfaces. It was found that this process only works reliably on single crystals because the polished surface of a polycrystal can expose multiple strontium ({001}-type) planes at the surface depending on each grain's orientation. This leads to preferential etching at the edges of these planes and results in a rough, inconsistent surface as illustrated in the atomic force microscopy topography scan in Figure 7.9(B). Traditional polishing media were found to generate up to 300 nm in relief between grains as shown in Figure 7.9(C) and was optically apparent after polishing. This process was adjusted to make use of diamond lapping films in conjunction with the Allied Multiprep wedge polishing system, which reduced the grain-to-grain relief significantly.



Figure 7.9: (A) Example of EBSD generated inverse pole figure representation of the grain orientations in polished STO, prior to reduction annealing. Colors are mapped to the axis normal to the plane of the image/sample surface. (B) AFM scan of the surface generated by etching procedures on polycrystalline STO. (C) AFM scan over the grain boundary after polishing with traditional media, showing the relief between grains.

#### 7.6 Conclusions

The work presented in this chapter provides a method for the generation of dense, largegrained STO without the addition of dopants or use of non-stoichiometric compositions. The reduction-oxidation process allows for the growth of grains on the order of several hundred microns across while still resulting in STO without significant electrical conductivity. It was found that reoxidation was possible without compromising the structure of the pellets by using slow heating and cooling rates in addition to the use of thick samples that could be ground to the point of removing cracks on the surface. Traditional polishing media was shown to generate large enough relief between STO grains in the polycrystal that thin films may not be continuous across the grain boundary. Additionally, this sharp step in the topography could be expected to introduce defects to an epitaxial film. At this stage, the process for the generation of polycrystalline STO substrates for CSE will require finalizing the polishing procedure prior to use for depositions. However, the challenge of grain growth has been sufficiently addressed for use in the measurement of single grain boundaries of CSE films.

# Chapter 8: Temperature and Processing Effects on Lithium Ion Conductivity of Solution-Deposited Lithium Zirconium Phosphate (LiZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub>) Thin Films

The contents of this chapter are published in the Journal of the American Ceramic Society as cited below. Text and figures have been adapted to match the styling of this document and embed supplementary figures where appropriate.

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#### 8.1 Motivation

This chapter represents an effort to continue the production of scientific work during the pandemic lockdown to prevent the spread of SARS-CoV-2 (the cause of COVID-19). The data contained herein was gathered by Daniel Drury during his time as a cooperative student intern at Sandia National Laboratories, under the advisement of Jon Ihlefeld. The primary goal of this work was to identify successful processing conditions for the production of lithium zirconium phosphate thin films via chemical solution deposition for use in thin film solid state lithium-ion batteries. Ian Brummel conducted all data analysis beyond collection of the raw data (XRD, SEM, and ion conductivity) and generated the conclusions presented about the process-structure-property relations in this material system and wrote the manuscript.

#### 8.2 Abstract

Lithium zirconium phosphate (LiZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub>) thin films have been prepared on platinized silicon substrates via a chemical solution deposition (CSD) approach. Films that were subject to a single high temperature anneal were found to crystallize at temperatures above 725 °C. Crystallization was observed in films annealed after each deposited layer at 700 °C and above. In

both cases, grain size was found to increase with annealing temperature. Ion conductivity was found to increase with annealing temperature in singly annealed films, and was found to initially increase then decrease with increasing annealing temperature in per-layer annealed films. A maximum ion conductivity of  $1.8 \times 10^{-6}$  S/cm was observed for the singly annealed 775 °C condition. These results are consistent with an increasing influence of cross-plane, internal interface resistance and vapor phase carrier loss in the per-layer annealed samples.

#### **8.3 Introduction**

Ion conducting thin films are of great interest for mobile, low profile, and deployable energy storage applications. Solid-state electrolytes hold potential for significant gains in terms of minimizing packaging requirements and improvements to battery safety when compared to the liquid electrolytes that are widely used today.<sup>1</sup> For example, solid-state electrolytes may exhibit increased resistance to dendrite formation<sup>2</sup> and many have large windows of electrochemical stability, allowing for the application of higher voltage cathode materials.<sup>3</sup> To date, amorphous lithium phosphorous oxynitride (LiPON) has been the most widely used solid-state electrolyte in lithium-ion battery applications owing to its stability over large voltage ranges, low electronic conductivity (~10<sup>-6</sup> S/cm at room temperature), which can lead to a significant internal resistance in LiPON-based batteries.<sup>3</sup> This high internal resistance makes LiPON-based solid-state batteries poorly suited for applications requiring high output power. For this reason, efforts have been devoted to discovering suitable, high lithium-ion conductivity, solid-state materials to replace LiPON in thin film batteries.<sup>5–7</sup> In general, the application of these newly discovered materials has been hindered by difficulties in processing and stability.

Lithium zirconium phosphate (LZP) can exhibit a crystal structure that is closely related to NaSICon (sodium super ionic conductor), with the conducting ion being lithium instead of sodium.<sup>5</sup> It has been shown that NaSICon-structured LZP exhibits a phase change from a low ion conductivity, triclinic phase to a fast ion conducting, rhombohedral phase at slightly elevated temperatures (25-60 °C).<sup>6,7</sup> The temperature of this phase transition has been shown to depend on the processing temperature as well as the composition of the material.<sup>5,8</sup> The triclinic phase has been shown to have an ion conductivity of ~10<sup>-9</sup> S/cm at room temperature,<sup>5</sup> whereas the

rhombohedral phase can exhibit ion conductivities of up to  $8 \times 10^{-6}$  at  $150 \,^{\circ}$ C.<sup>9</sup> The NaSICon framework of LZP is highly adaptable to the substitution of other elements, which allows properties to be altered through doping.<sup>394–396</sup> For example, lanthanum doping can increase the ion conductivity of Li<sub>1.1</sub>Zr<sub>1.9</sub>La<sub>0.1</sub>P<sub>3</sub>O<sub>12</sub> to  $7.2 \times 10^{-5}$  S/cm at room temperature,<sup>13</sup> which is approaching that of well-known ion conductors such as perovskite lithium lanthanum titanate and garnet lithium lanthanum tantalate.<sup>182, 398</sup> Understanding the processing behavior of the end-member LiZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub> will provide a foundation for further exploration of this materials space. In this study, a method is presented for the preparation of LZP thin films employing a chemical solution deposition technique. All resultant films are stable in the rhombohedral phase at room temperature. It will be shown that varying the high temperature processing conditions has a significant effect on the final ion conductivity. An unexpected reduction in ion conductivity with increasing thermal budget for films subject to preparation via multiple high temperature annealing steps is attributed to lithium vapor losses during processing.

#### **8.4 Experimental Procedures**

Chemical solutions were prepared using an alkoxide-based chemistry similar to previous work on NaSICon films,<sup>35, 38</sup> with the sodium precursor substituted by lithium isopropoxide. Stoichiometric amounts of zirconium (IV) butoxide (80 wt.% solution in 1-butanol, Sigma-Aldrich), dibutyl phosphate (≥97%, Sigma-Aldrich), and lithium isopropoxide (95%, Sigma-Alrich) with a 2 mol. % lithium excess were batched within an argon atmosphere glovebox with an anhydrous 1-butanol solvent. The synthesis procedure started with massing zirconium butoxide into a vial to which 1-butanol was added. The solution was stirred for several minutes after which dibutyl phosphate was added followed by stirring for 30 minutes to 1 hour. Finally, lithium isopropoxide was massed and added to the solution and stirred for 30 minutes to 1 hour. The final molarity of the solution was 0.15 M, as referenced to a complete LZP formula unit. The resulting solution was transparent and slightly yellow. Metallized substrates with lithium ion blocking contacts were prepared by RF magnetron sputtering of ZnO and platinum onto commercially acquired, thermally oxidized silicon wafers (SiliconQuest International, Santa Clara, CA) in a Kurt J. Lesker Lab 18 deposition system.<sup>18</sup> The resultant substrate stack was composed of 100 nm Pt/40 nm ZnO/400 nm SiO<sub>2</sub>/Si and the wafer was cleaved into sections for preparation of LZP samples. For spin casting, solutions were dispensed onto the platinized silicon coupon

(15 mm × 15 mm squares) through a 0.2  $\mu$ m filter then spun at 3000 RPM for 30 seconds. Immediately following spin casting, samples were pyrolyzed on a 300 °C hotplate for 5 minutes and allowed to cool to room temperature for 1 minute. Two different annealing procedures were studied in this work: 1) a high temperature anneal after every deposited and pyrolyzed layer (per-layer annealed) and 2) a single high temperature anneal after multiple layers were deposited and pyrolyzed (singly annealed). The high temperature annealing was carried out at 700 °C, 725 °C, 750 °C, and 775 °C for 10 minutes in a preheated tube furnace that was open to air. For the singly annealed samples, the spin casting and pyrolysis process was repeated to create a sample with three total layers prior to high temperature annealing. For per-layer annealed samples, after each pyrolysis step, the sample was exposed to high temperature annealing and this was completed for three total layers. The resulting films, for both annealing processes, were 300 ± 20 nm thick and thicknesses for each sample were verified by cross-sectional electron microscopy.

After film processing was complete, 100 nm thick lithium-ion-blocking platinum top electrodes were sputtered through a shadow mask to create the metal-electrolyte-metal devices used to characterize the ion conductivity of the material. The electrode pads were approximately  $400 \times 400 \,\mu\text{m}$  squares and actual areas were calculated from optical micrographs using image analysis software (ImageJ, National Institutes of Health).<sup>19</sup> Room temperature impedance spectroscopy was performed from 20 Hz to 1 MHz with an oscillator of 30 mV to determine ion conduction behavior of the samples using a HP 4284A precision LCR meter (Keysight Technologies, Santa Rosa, CA). For temperature dependent measurements, the samples were mounted to 1" square alumina coupons (Superstrate, CoorsTek, Golden, CO) to serve as a stabilizing thermal mass. Gold wires (0.001" diameter) were bonded between the platinum contacts and larger gauge (20 AWG) contact wires affixed to the alumina coupons using silver epoxy (Epo-Tek H20E), which were then connected to an electrical feedthrough within a Delta Design 9023 environmental chamber (Cohu, Inc. Coway, CA). Temperature dependent impedance spectroscopy was measured in 12.5 °C steps between 37.5 °C and 75 °C using an HP 4192A LF (Keysight Technologies, Santa Rosa, CA) impedance analyzer over a frequency range of 20 Hz to 1 MHz with an oscillator of 30 mV. Complex plane impedance spectra were fit using the EC-Lab software suite (Bio-Logic S.A.S., Claix, France). X-ray diffraction (XRD) patterns were obtained using Cu Ka radiation with a Bruker Phaser X2 (Bruker, Madison, WI) instrument between 10° to

 $80^{\circ}$  in  $2\theta$ . Manual phase identification and qualitative texture analysis were performed. Plan-view and cross-section imaging were carried out using a Zeiss Supra 55VP (Jena, Germany) scanning electron microscope (SEM) in an in-lens imaging mode with a 5 kV accelerating voltage. Average grain sizes were measured using a lineal intercept method, with circular intercept procedures as set out in the ASTM standard E112-13.<sup>20</sup> Plan-view, backscatter electron micrographs used for analysis of the degree of dewetting were collected using a 15 kV accelerating voltage to ensure that the interaction volume included the layers below the LZP films.

#### 8.5 Results and Discussion

Figure 8.1(A) and Figure 8.1(B) show the XRD patterns from films crystallized at 700 °C, 725 °C, 750 °C, and 775 °C using a singular anneal for all layers and an anneal per deposited layer, respectively. Marker bars have been inserted along the abscissa representing the characteristic reflections of LZP<sup>21</sup> and an impurity tetragonal ZrO<sub>2</sub> phase,<sup>22</sup> in red and blue, respectively. The LZP reflections are well indexed to the rhombohedral phase that has been reported to exist above room temperature, with high ionic conductivity.<sup>5, 11, 21</sup> Additional impurity phases and substrate reflections are labeled above the patterns by name, while LZP peaks are labeled with their indices. Figure 8.1(A) shows that singly annealed samples did not exhibit crystallinity for annealing temperatures below 750 °C. There are visible LZP reflections for all per-layer annealing conditions, but low intensity in the 700 °C pattern indicates a limited degree of crystallinity. For a given annealing temperature, it is evident that samples exposed to the greater thermal budget of per-layer annealing (Figure 8.2(B)) show a greater degree of crystallinity than the singly annealed counterparts. This can be deduced from the increasing intensity and sharpness of LZP peaks in the pattern. It should be noted that the reduced crystallinity of the singly annealed samples leads to limited intensities of LZP peaks, even in the samples annealed at 775 °C, compared to the perlayer annealed samples.

Comparison of LZP peak intensities reveals a preferred (110) texture under both annealing procedures. In the LZP powder pattern, shown with red bar markers, the (014) reflection at 19.8° should be approximately 40% more intense than the (110) reflection at 20.1°.<sup>21</sup> Given the breadth of the peaks in the thin films, this should result in an asymmetric combined peak, with a lower intensity shoulder at high  $2\theta$  angles. The (110) texture is shown by the reversal of the asymmetry

of the combined (014)/(110) peak, where the low intensity shoulder is observed to the low  $2\theta$  side, indicating that the (110) reflection is more intense than the (014) reflection. Peak broadening due to fine crystallite sizes does not allow for clear separation of the (014) and (110) peaks, preventing more quantitative analysis of the texture. In the per-layer annealed samples, an additional (100) oriented texture with increasing annealing temperature is revealed as the (300) peak becomes more prominent. However, the (300) reflection is not apparent in the patterns of the singly annealed samples, suggesting that the (100)-oriented texture does not develop in singly annealed samples, regardless of annealing temperature. While many solution-deposited thin films commonly exhibit a degree of crystallographic texture, there is no apparent lattice match between the platinum (111) plane and the LZP (110) or LZP (100) planes, indicating that the observed textures are not likely to be driven by local epitaxy from the underlying substrate. Rather, the texture may be related to free energy minimization of specific growth directions. Both sample sets show evidence of a ZrO<sub>2</sub> impurity phase, which appears to increase with temperature and has been observed in prior thin film works on NaSICon.<sup>35, 38, 403</sup> Additionally, for the highest annealing temperature for both sample sets, a LiZnPO4 impurity phase can be identified, which will be discussed later.



Figure 8.1: X-ray diffraction patterns for (A) singly annealed films and (B) per-layer annealed films at temperatures of 700 °C, 725 °C, 750 °C, and 775 °C. Red and blue bar markers represent the powder diffraction patterns for rhombohedral LZP<sup>21</sup> and tetragonal ZrO2,<sup>22</sup> respectively.

Figure 8.2 shows plan view scanning electron micrographs of the films annealed at 725 °C, 750 °C, and 775 °C. Films annealed at 700 °C for both the single and per-layer processing conditions were excluded from microstructural analysis due to lack of evidence of crystallization in the singly annealed films and low crystallinity in the per-layer annealed films. The micrograph in Figure 8.2(A) from the 725 °C, single anneal sample also appeared amorphous by XRD and is representative of the 700 °C micrographs for both annealing conditions. In Figure 8.2(B-C) and Figure 8.2(D-F) increasing grain size of the films with increasing annealing temperature is apparent for singly and per-layer annealed samples, respectively. Lateral grain sizes are shown in Figure 8.3, where error bars represent the 95% confidence interval for the average grain size. A monotonic increase in grain size with annealing temperature was observed and grain sizes were slightly larger for samples that experienced per-layer anneals, compared with the samples that were annealed once for all deposited layers. A number of small, equiaxed grains of a high atomic number phase are evident as bright spots at the triple points and grain boundaries of the microstructure. These appear to increase in frequency with increasing annealing temperatures and are consistent

with the ZrO<sub>2</sub> impurity phase identified in the XRD patterns of Figure 8.1. Further, the morphology of the ZrO<sub>2</sub> secondary phase is consistent with prior work on NaSICon films.<sup>35, 38, 403</sup>



Figure 8.2: Plan-view, secondary electron SEM of singly annealed (A) 725 °C, (B) 750 °C, and (C) 775 °C and per-layer annealed (D) 725 °C, (E) 750 °C, and (F) 775 °C sample. The small, bright white inclusions (most prevalent in panel (F)) were identified as ZrO2 impurities as a result of non-stoichiometry. The gamma values and levels were adjusted using Adobe Photoshop to enhance image contrast.



Figure 8.3: Average grain sizes measured from plan-view SEM micrographs using a lineal intercept method. Error is reported as the 95% confidence interval of the average grain size.

Representative room temperature complex plane impedance responses for samples annealed at 750 °C are shown in Figure 8.4 to allow direct comparison of the different annealing procedures. Figure 8.5 and Figure 8.6 show representative room temperature impedance spectra for each annealing temperature for singly and per-layer annealed samples, respectively, to aid in understanding the effects of temperature on the impedance response of these films. The complexplane impedance spectra exhibit a combination of a single arc and a low-frequency spike in the imaginary impedance. This response is consistent with other ion conducting thin films, where the arc represents ion conduction through an electrolyte, and the spike represents the blocking response of the electrode,<sup>24</sup> as expected for platinum electrodes and a lithium ion conducting electrolyte. Data were fit using the equivalent circuit illustrated in Figure 8.4(A), which consists of a ZARC (resistor,  $R_1$  and constant phase element,  $Q_1$ , in parallel) and a constant phase element,  $Q_2$ , in series. A ZARC element is commonly used for fitting depressed semicircles in impedance spectra that do not exhibit ideal semicircular responses, as would be expected for a resistor and a capacitor in parallel (RC element).<sup>25</sup> Depression of the semicircular response of an RC element is due to non-ideality in the capacitive response of the material. Chemical and structural inhomogeneity produce non-single valued relaxation times, which alters the frequency response in the impedance spectrum.<sup>26</sup> In a real microstructure, the locations of material defects, porosity, and chemical gradients lead to the relaxation time having a spatial dependence, which is measured as the average of a distribution throughout the measurement volume and has an impedance modeled by:

$$Z_{\text{ZARC}} = \frac{R_1}{1 + Q_1(j\omega)^n} \tag{1}$$

where  $R_1$  is the resistance of the parallel branch,  $Q_1$  is the constant phase element value, j is the imaginary unit,  $\omega$  is the angular frequency, and *n* is the constant phase element exponent. A second ZARC in series with the first can be used to represent the separate grain and grain boundary responses in the fitting of bulk materials, but did not improve the quality of fit for these films.<sup>24</sup> High quality fits were produced for all samples that exhibited significant crystallinity, however measurement frequency limitations led to incomplete capture of the 700 °C material response at low frequencies. Samples that did not crystallize sufficiently were fit on the assumption that available data represented the ZARC response. Based on the value of the resistor in each fit, with the film thickness and electrode geometry, the conductivity of a given device was calculated. The room temperature conductivity as a function of annealing temperature is shown in Figure 8.7, with error bars calculated based on the 95% confidence interval of the average ion conductivity. Comparing the XRD patterns in Figure 1, the SEM micrographs in Figure 8.2, and the conductivity values in Figure 8.7 reveals that LZP with low crystallinity exhibits a low ion conductivity on the order of  $\sim 10^{-9}$  S/cm. With sufficient thermal budget during annealing to achieve crystallinity, ion conductivities on the order of 10<sup>-7</sup>-10<sup>-6</sup> S/cm are observed. This is much improved over the conductivity of the triclinic phase that is typically stable at room temperature (10<sup>-9</sup> S/cm),<sup>396</sup> and the ion conductivity found for fast ion conducting, rhombohedral LZP at 150 °C (8×10<sup>-6</sup> S/cm), taking into account the large difference in measurement temperature.<sup>9</sup> The ion conductivity of these films also matches some reports for bulk, aluminum doped LZP at room temperature (~2.5×10<sup>-6</sup> S/cm).<sup>395, 404</sup> There are two possible contributing factors to the increased ion conductivity of these films; first, the stabilization of the fast ion conducting rhombohedral phase and second, the measurement geometry limiting the number of grain boundary scattering events that are introduced to the conduction path, resulting in a value that approaches the intrinsic ion conductivity of the material.

Interestingly, the trends for singly annealed samples and per-layer annealed samples diverged with increasing annealing temperature. Singly annealed samples displayed an increasing trend in ion conductivity, consistent with the increasing grain size.<sup>35, 38, 394, 405</sup> Conversely, the per-layer samples that were exposed to multiple annealing steps show an increase of two orders of magnitude in ion conductivity between 700 °C and 725 °C, followed by a decrease in the ion conductivity with increasing annealing temperatures. This decrease in ion conductivity with increasing process temperature differs from results in previous studies of NaSICon films. In those studies, increased ionic conductivity was observed with increasing processing temperature, which was related to increased grain size and crystallinity, a trend that persisted across multiple compositional variants.<sup>35, 38</sup> From the divergent trends of grain size and ion conductivity in this study, it is clear that a different mechanism is contributing to and affecting the ion conductivity of LZP, compared to the sodium conducting counterparts.



Figure 8.4: Representative complex-plane impedance spectra for 750 °C (A) singly and (B) perlayer annealed LZP films with platinum contacts. The equivalent circuit model used to fit all data is shown in (A). Open circles represent measured data and solid lines represent the modeled response calculated from fits to the data.



Figure 8.5: Room temperature complex plane impedance spectra and accompanying fits for singly annealed samples processed at (A) 700 °C, (B) 725 °C, (C) 750 °C, and (D) 775 °C. On plots are truncated to remove noise generated by the measurement equipment, the insets show the full complex plane impedance. The equivalent circuit model used to fit all data is shown in (C). Open circles represent measured data and solid lines represent the modeled response calculated from fits to the data.



Figure 8.6: Room temperature complex plane impedance spectra and accompanying fits for perlayer annealed samples processed at (A) 700 °C, (B) 725 °C, (C) 750 °C, and (D) 775 °C. On plots are truncated to remove noise generated by the measurement equipment, the insets show the full complex plane impedance. The equivalent circuit model used to fit all data is shown in (C). Open circles represent measured data and solid lines represent the modeled response calculated from fits to the data.



Figure 8.7: Room temperature lithium ion conductivity as a function of the annealing temperature for singly and per-layer annealed samples. Ion conductivity was extracted from fits to the measured impedance data and averaged across three electrodes per data point. Error bars are reported as the 95% confidence interval for the average ion conductivity of a sample.

Dewetting of the platinum substrate layer from the silicon substrate, as observed previously for NaSICon thin films with increasing sodium and silicon content,<sup>38</sup> was considered as a potential contributor to the decreasing ion conductivity of the per-layer annealed samples. In the prior work, this dewetting was attributed to diffusion of sodium into the platinum electrode causing an increase in mass transport of the electrode material. Such dewetting would be anticipated to result in decreased electrode area, leading to erroneously low ion conductivity based on the assumed area of the device that is measured from the top electrode using optical micrographs. The dewetting was examined by backscatter electron imaging in the SEM using a 15 kV beam acceleration voltage as well as cross sectional micrographs of the films collected in an in-lens imaging mode. The high energy electron beam increases the interaction volume allowing the bottom electrode to be imaged with minimal influence of the overlying LZP film. Figure 8.8(A-C) shows backscattered electron images of the 725 °C, 750 °C, and 775 °C per-layer annealed samples, where dark, low atomic number regions can be distinguished against an otherwise uniformly bright field. The dark

contrast indicates areas of the electrode that have dewet from the silicon substrate, resulting in lower backscattered electron yield from the underlying SiO<sub>2</sub>/silicon substrate compared to the higher backscatter yield of the platinum that covers the rest of the field. Figure 8.8(D) shows the cross section of the 725 °C per-layer annealed sample, with obvious voids in the platinum electrode. Figure 8.9 contains an analogous set of images from the singly annealed sample set. Singly annealed samples exhibit qualitatively similar micrographs, with less dewetting compared to per-layer annealed samples, consistent with the dewetting being a function of thermal budget (i.e. the per-layer samples were exposed to the annealing temperature 3X the amount of time as the singly-annealed samples). The area of dewet electrode was quantitatively analyzed using thresholding with image analysis for each annealing condition.<sup>19</sup> Area loss was determined and applied to ion conductivity calculations. In all cases, application of the corrected electrode area increased the ion conductivity by less than 3.5%, with the unexpected, decreasing trend for the per-layer samples remaining qualitatively identical. Therefore, the dewetting effect cannot explain the unexpected decrease in ion conductivity with increased annealing temperature of the per-layer annealed samples. Note that this dewetting does explain the minority LiZnPO<sub>4</sub> phase observed in XRD for the highest process temperature used, whereby the dewetting of the platinum electrode exposed the underlying ZnO adhesion layer and allowed a region of the film to react. A similar result was observed in prior research on NaSICon films.<sup>38</sup> This reaction is only anticipated to occur within the vicinity of the dewet electrode and, therefore, is unlikely to be the origin of the reduced ionic conductivity with increasing temperature for the per-layer annealed samples.



Figure 8.8: Plan-view, backscattered electron SEM images of per-layer annealed (A) 725 °C, (B) 750 °C, and (C) 775 °C films. Darker areas show dewetting of the bottom electrode under the film. (D) Cross-sectional image of the per-layer annealed, 725 °C sample, with voids in the platinum bottom electrode as a result of dewetting.



Figure 8.9: Plan-view, backscattered electron SEM images of singly annealed (A) 725 °C, (B) 750 °C, and (C) 775 °C films. Darker areas show dewetting of the bottom electrode under the film. (D) Cross sectional image of the singly annealed, 725 °C sample, with a void in the platinum bottom electrode as a result of dewetting.

As a simple electrode geometry change could not explain the decreasing ionic conductivity with increasing processing temperature for the per-layer sample set, differences in the conduction resulting from activation energy changes were considered. Arrhenius plots of the temperature dependent ion conductivity behavior are shown in Figure 8.10(A) and Figure 8.10(B) for both the single anneal and per-layer anneal sample sets. The activation energy for each sample was extracted from the slope of the regression lines, and was found to vary between 0.55 and 0.56 eV for per-layer annealed samples, and was 0.49 eV for singly annealed samples. The activation energy for the uncrystallized, 725 °C single anneal sample was found to be significantly lower, at 0.25 eV. The activation energy of the singly annealed samples was similar to the 0.44 eV obtained

by Petit et al. and the 0.42 eV obtained by Sudreau et al. on bulk LZP samples, 5, 7 while the perlayer annealed samples exhibited larger activation energies. The increased activation energy in the per-layer annealed samples is believed to be a result of some form of internal boundaries in the film. While successive anneals were anticipated to result in self-templated columnar microstructures, as is possible in solution prepared films,<sup>29,30</sup> there could be some small degree of misorientation or disorder between the layers, resulting in a minor increase in the resistance to ion transport through the film. Unfortunately, electron microscopy of fracture cross sections did not provide clear resolution of the microstructures. Another possibility is local lithium concentration gradients where the free surfaces during annealing may have lithium deficiencies that form resistance to ionic conduction, and function similarly to the high resistance attributed to grain boundaries. Because the data was well fit to a single ZARC element, we were unable to clearly differentiate grain and grain boundary responses based on the shape of impedance spectra. However, the thickness normalized capacitance of the ZARC can be used to aid in differentiating intra- versus inter-granular conduction mechanisms. To determine the origin of the measured ion conductivity response, the ideal capacitance was calculated from the ZARC element of each impedance spectrum. The ideal capacitance can be obtained from a ZARC element by solving for  $C_{\text{ideal}}$  from the time constant relation:

$$\tau = R_1 C_{\text{ideal}} = (R_1 Q_1)^{1/n} \tag{2}$$

where  $\tau$  is the time constant for the impedance response represented by the ZARC,  $R_1$  is the resistance of the parallel branch,  $C_{ideal}$  is the ideal capacitance to be extracted,  $Q_1$  is the constant phase element value, and *n* is the constant phase element exponent. The fitting software provides  $R_1$ ,  $Q_1$ , and *n*, allowing for calculation of  $C_{ideal}$ . After area and thickness normalization, the capacitance was found to vary directly with temperature from ~2-18 pF/cm and ~5-75 pF/cm for the singly and per-layer annealed samples, respectively, with the low capacitance values being associated with low measurement temperatures and high values with increased measurement temperatures. Table 8.1: ZARC calculated capacitance values for singly and per-layer annealed LZP films measured at room temperature. Table 8.1 shows thickness and area normalized ideal capacitance values for each annealing condition and temperature. For most temperatures, the normalized capacitance of the single anneal samples is lower than that of the corresponding per-layer annealed samples. Previous work on similar, bulk materials found the grain boundary capacitance to be ~250 pF/cm, an order of magnitude larger than the values observed in these

films.<sup>31</sup> Work with other ion conducting materials indicates that normalized grain boundary capacitances tend to be several orders of magnitude greater than intragranular capacitance values.<sup>32</sup> While data for the intragranular capacitance of LZP are not readily available in the literature, the values observed in this study are at least an order of magnitude less than the reported grain boundary capacitance, indicating that the measured ZARC response is primarily derived from intragranular ion conductivity. However, the increased capacitance of the per-layer annealed samples relative to the singly annealed samples may suggest that there are minor grain-boundary-like features in the conduction pathway of these samples. This would be consistent with defects or, possibly, lithium-depleted regions between the annealed layers behaving similarly to low impedance grain boundaries in the microstructure.



Figure 8.10: Temperature dependent ion conductivity of (A) singly and (B) per-layer annealed LZP films as measured between 37.5 °C and 75 °C. Activation energies are calculated using the Arrhenius relation and the slope of the linear fits. Uncertainty is calculated from the standard error for the least squares fit of the linear slope.

Table 8.1: ZARC calculated capacitance values for singly and per-layer annealed LZP films measured at room temperature.

	ZARC Capacitance (pr/cm)				
	Single Anneal	Per-Layer Anneal			
700 °C	2.7	5.1			
725 °C	2.8	12.3			
750 °C	11.4	11.9			
775 °C	18.5	75.3			

ZARC Capacitance (pF/cm)

Based on the near constant activation energy values for a given annealing procedure, it is proposed that the decrease in ionic conductivity with increasing process temperature and lateral grain size is a function of lithium losses as a result of volatility at elevated temperatures. It is well documented that the vapor pressure of lithium species above Li2O is high at elevated temperatures.<sup>33</sup> Consideration of the large surface-area-to-volume ratio of the films during annealing suggests that the per-layer annealed films would have more opportunity to evolve lithium and lithium-oxide vapors during annealing steps. The lithium ion conducting behavior of the per-layer annealed samples is consistent with an initial increase in the ion conductivity due to the onset of crystallinity, followed by increasing loss in lithium with increasing temperature. Conversely, the singly annealed samples show lithium ion conductivity increasing monotonically with increasing annealing temperature and grain size, which is consistent with limited lithium ion loss due to the lower surface-area-to-volume ratio for the single annealing event in conjunction with increasing crystallinity with increasing annealing temperatures. This lithium loss hypothesis is supported by the micrographs in Figure 8.2, which show increasing ZrO<sub>2</sub> impurity content as the process temperature increases. Qualitatively, there appear to be more ZrO<sub>2</sub> impurities on the per-layer annealed samples than the singly annealed samples, which is suggestive of increased volatilization of other species, specifically lithium.

The possibility of defective cross-planar interfaces being present in the per-layer samples cannot be completely discounted as impacting the ion conduction. However, it would be anticipated that these cross-planar interfaces would be present in all per-layer annealed samples and that the structural quality of that interface should improve with increased process temperature as a result of increased mass transport. Improvement of the structural quality of the interface would be expected to lead to increasing ion conductivity through the interface, however, the opposite trend is observed. Therefore, while this may be one factor influencing decreased ion conductivity with increased processing temperature, it is expected to be a minority influence. Further, the difference in crystallographic texture in the per-layer samples compared to the singly annealed samples could also affect ion conductivity. Nevertheless, the XRD results clearly show that each set of films have similar intensities of (110) reflection and the crystallinity of the per-layer samples is higher than that of the singly annealed samples and that crystallinity increases with process temperature. Even with differences in texture, we would anticipate that the increased crystallinity would lead to improved ion conductivity. Furthermore, given that the activation energy differed between the singly annealed and per-layer annealed samples, it is unlikely that a simple decrease in active carriers can explain the decreased ion conductivity with increasing processing temperature. Rather, it seems more likely that lithium loss during per-layer annealing results in a local structural change that impacts the ability of lithium to transport across the film thickness and results in increased activation energy and decreasing total ion conductivity with increasing process temperature for the per-layer annealed samples.

#### **8.6 Conclusions**

In conclusion, this study has demonstrated the preparation of LiZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub> thin films as a candidate material for solid-state thin film lithium ion battery electrolytes. We investigated the effects of annealing procedures on the ion conductivity of the films. For films that were singly annealed after all deposition was completed, it was found that a higher temperature was required to initiate crystallization of the film. Singly annealed samples were found to have increased ion conductivity and grain size with increasing annealing temperatures, consistent with prior works on NaSICon films. The maximum ion conductivity for singly annealed films was found to be  $1.8 \times 10^{-6}$  S/cm at an annealing temperature of 775 °C, which is similar to bulk LZP at elevated temperatures or aluminum doped samples from the literature. For films that were annealed after each deposited layer, an initial increase in conductivity that coincides with extensive crystallization of the film was found, followed by a reduction in ion conductivity with increasing annealing

temperature. This is counter to the increasing grain size and crystallinity of the films. Dewetting of the platinum electrode with increasing processing temperature could not explain the reduction in ion conductivity. The reduction in the per-layer annealed samples' ion conductivity was attributed to a likely increased lithium vapor loss due to increased thermal budget and surface-area-to-volume ratio of per-layer annealed films during high temperature annealing that imparts an increased resistance to ion conduction across the thickness of the films. This work ultimately shows that LZP-based materials may be a viable electrolyte to replace LiPON and that the simplest processing method (single high temperature excursion) results in the highest ion conductivity. The fact that the ion conductivity of the thin films exceeded those of the bulk ceramics of the same compositions at the same temperatures suggests that with appropriate doping, even higher ion conductivities are possible.

#### 8.7 Acknowledgments

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## **Chapter 9: Conclusions**

The future implementation of solid state battery technology relies on the development and understanding of ion conduction in solid state electrolytes. A key challenge to further development of this technology has been the elevated impedance to ion conduction that is observed due to grain boundaries in polycrystalline materials. While it is widely understood that grain boundaries tend to decrease the total conductivity of solid state electrolytes, the techniques available for measurement of the electrical responses of grain boundaries are limited in their ability to distinguish the effects of different grain boundary configurations. Study of the individual behavior of individual grain boundaries is key to the development of low cost, polycrystalline ion conducting materials with sufficient ion conductivity for use in applications with large power demands. Through the development of new measurement techniques, this dissertation makes some of the first steps toward quantitatively identifying the behavior of different grain boundary configurations.

Toward this end, work was performed to understand the generation of lithium ion conducting materials. In polycrystalline form, it was determined that the ion conductivity of LLTaO is highly dependent on the lithium concentration, with increased lithium content in the sample causing a reduction in the total ion conductivity. This was determined to be driven by the formation of a LaTaO<sub>4</sub> secondary phase that is not expected to be ion conducting and, therefore, forces more of the conduction pathway into the low conductivity grain boundary regions/reduces the cross section available for ion conduction in LLTaO. This manifested as an apparent increase in the grain boundary impedance during impedance spectroscopy measurements and the presence of LaTaO<sub>4</sub> was confirmed via XRD and EDS.

Based on the sensitivity of LLTaO to the lithium content, a study was undertaken to determine the effect of PLD deposition parameters on the lithium transfer from the target to the substrate and the commensurate effects on the crystal structure, composition, and ion conductivity in epitaxial LLTaO films. It was determined that the background gas composition played an important role in the transfer of lithium from the target to the substrate, with a 100% oxygen atmosphere resulting in the maximum amount of lithium in the resultant film. However, it was also found that all investigated conditions resulted in a reduction of lithium in the deposited film compared to the concentration measured in the initial target. The background gas composition,

most likely as a result of the differing lithium transfer, was determined to alter the energetics of LLTaO formation, with the lowest oxygen content atmosphere resulting in an amorphous film asdeposited and poor crystallinity after annealing. The lithium concentration was ruled out as the sole factor affecting the ion conductivity of these films, with the measured lattice parameter being linked to changes in the activation energy and therefore the ion conductivity of the films.

Study of the parameter space for PLD was in service of the goal of quantitatively measuring the ion conductivity of single grain boundaries, enabled by the epitaxial growth of LLTaO on bicrystal STO substrates. These films, in conjunction with a combination of fiducial markers deposited by focused ion beam and photolithography allowed impedance spectroscopy to be performed on the grain boundary and bulk regions individually. This allowed for the determination that the activation energy observed in the tilt-type boundaries defined by the STO bicrystals were similar for all misorientations that were available. Using scanning probe microscopy techniques, the existence of a strong space charge region was ruled out in these samples. Together these results indicate that tilt-type boundaries do not generate an inherent impediment to ion conduction as a result of their well-aligned (001) planes across the grain boundary. It was found that only the 45°-tilt sample generated a significant impedance at the grain boundary, and it is suggested that this could be due to poor crystallinity of the substrate and the severity of the misorientation leading to defects in the epitaxial process that are not apparent to the characterization techniques employed.

To continue this work in the future, combinatorial substrate epitaxy is expected to be used to generate grain boundary configurations that are not available as bicrystals. The synthesis of STO ceramics was studied for the purposes of generating large-grained, dense, polycrystalline bodies to be used as substrates for combinatorial substrate epitaxy. It was found that air sintering followed by a reduction anneal for grain growth and then a reoxidation anneal was able to produce STO ceramics with a grain size on the order of several hundred microns. Additionally, this processing route does not require the introduction of off-stoichiometric compositions and does not appear to generate secondary phases at the grain boundary. Air sintering prior to the reduction annealing step was found to be necessary to achieve sufficient density for use in combinatorial substrate epitaxy.

Finally, a study of the relationship between processing, structure, and performance in LZP is presented. In this work it was found that there is a complex interplay of factors that result in the final ion conductivity of a thin film sample, with CSD films showing different behavior depending on the number of times they were annealed as a result of different levels of vapor phase lithium

losses during annealing and an increase in the crystalline quality of the films with increased annealing temperature.

In total, the work contained in this dissertation provides the first quantitative measurements of single grain boundaries in lithium ion conducting materials in addition to setting the groundwork for future study of the grain boundaries in LLTaO or other materials with similar crystal structures via the work on STO substrate synthesis. Understanding of the individual effects of different grain boundary configurations could facilitate the microstructural engineering of lithium ion conducting solid state electrolytes such that their total ion conductivity could be improved by orders of magnitude in polycrystalline form.

### **Chapter 10: Recommendations on Future Research**

#### **10.1 Improvement of LLTaO Conductivity and Surface Quality**

While the investigation of the singular grain boundaries presented in Chapter 6 resulted in what appears to be a relatively straightforward conclusion, a major blocker to the completion of that study was the inconsistent behavior of LLTaO depositions and the resulting performance. A key instance of this would be the difference in composition and surface morphology of the 6°-tilt sample compared to the others. Furthering the understanding of the deposition parameter space for LLTaO on STO, including sweeping characterization of the substrate crystallography and surfaces would be beneficial. Largely, the work in this dissertation was driven by the final result presented in Chapter 6, which led to several cases where the first deposition or synthesis condition that met the basic requirements of future measurements was "standardized" to provide more comparable results with future samples. Characterization of the effects of the substrate on the epitaxial films and a better understanding of the effects of lithium content in the targets and deposition parameters has the potential to increase the conductivity of the deposited films significantly. The primary goal of this work was not to improve the inherent ion conductivity of the LLTaO, but to understand specifically the grain boundary behavior. In hindsight, improvement of the ion conductivity and the surface quality of the epitaxially grown films would have likely enabled more straightforward understanding of the grain boundary behavior via allowing for the separation of the bulk and grain boundary arcs and may have enabled the measurement of smaller signals in ESM/KPFM around the grain boundaries by eliminating some of the topographic crosstalk that was observed.

#### **10.2** Combinatorial Substrate Epitaxy

Continued work on epitaxial deposition of LLTaO onto polycrystalline STO is key to further understanding and validation of the results included in this thesis. The combinatorial substrate epitaxy technique would enable the measurement of grain boundaries that are simply not available for purchase as bicrystals. While the development of bicrystal synthesis capabilities could be a solution to this problem, combinatorial substrate epitaxy offers a large number of benefits over the continued use of bicrystal substrates:

- Synthesis of a large grained STO pellet is considerably less expensive than the purchase of bicrystals, because enough powder for many pellets can be purchased for far less than a single bicrystal substrate.
- 2) The use of polycrystalline substrates opens the door to the measurement of a more representative selection of grain boundaries than the pure tilt-type misorientations that are available for purchase as bicrystals.
- In-house generation of substrates gives much more control to the researcher over the quality and preparation of the substrates, which appears to be important based on the results of this dissertation.
- 4) The use of combinatorial substrates does not preclude the use of multiple electrode sets to measure the bulk and grain boundary regions individually, as long as the grains of the substrate being utilized are of sufficient size (which is minimized by the development of the fiducial marking and photolithography techniques in this dissertation).
- 5) Following the disruptions to the supply chain caused by the COVID-19 pandemic, the market availability of STO bicrystals has become extremely sparse, driving up prices and reducing quality in the rare cases that they are available for purchase.
- 6) The continued development of combinatorial substrate epitaxy opens research to the use of other substrates that may not have ever been offered commercially bi- or single-crystal substrates but can be synthesized as polycrystalline bodies.

This dissertation has laid the groundwork for combinatorial substrate epitaxy depositions by producing a procedure for the generation of STO substrates. Additionally, some preliminary work toward this goal has been carried out, but was blocked due to surface roughness that prevented the identification of epitaxy via EBSD and the fact that the large-grained STO synthesis procedures had not been completed at the time.

#### **10.3 Expansion to Other Ion Conducting Systems**

The next major evolution in this work would be the expansion of the techniques discussed in this dissertation to the measurement of other ion conducting systems. It may be noted that the use of LLTaO is justified in all published parts of this dissertation, which was done because LLTaO is not widely considered to be a technologically relevant candidate for commercialization as a solid state electrolyte due to its lower ion conductivity compared to the isostructural titanate or even more conductive materials such as garnet structured lithium lanthanum tantalates. While LLTaO made for a strong choice as a model system for the studies herein, future research could be dramatically more impactful by working with materials that are leading candidates for the study of lithium ion conducting solid state electrolytes. Unfortunately, this may require the development of new substrate materials as well as study of the deposition parameter space for these new materials, which will prevent the expansion to new materials systems from being a trivial task. Additionally, the relatively low conductivity of LLTaO may have been a benefit in that resolving the different microstructural features through impedance spectroscopy, near room temperature can prove very difficult for materials with markedly higher ion conductivity values due to the small absolute difference in the relaxation times of the different responses.

Additionally, study of sodium ion conducting systems may be of interest because they are likely to be a future direction of research as a result of their inexpensive and abundant precursor materials. This is specifically true in the context of grid-scale and stationary energy storage applications because those applications do not suffer as much of a penalty for the reduction in energy density (kWh/kg) that results from the use of more massive sodium. This area of study has the added benefit, in the sphere of research, that the increased scattering cross section of sodium enables a number of experimental techniques (particularly for compositional measurements) that are not straightforward when attempting to characterize lithium-containing materials.

# **Chapter 11: Appendices**

# **Appendix I: Species Dependent Mean Free Path**

The mean free path can be estimated from:

$$\lambda = \frac{k \times T}{\sqrt{2} \times P \times \pi \times d_m^2} \tag{11.1}$$

where k is the Boltzmann constant, T is the temperature, P is the pressure, and  $d_m$  is the average diameter of the concerned species calculated as  $d_m^2 = (d_{gas} + d_{species})/2$ , using a weighted average of the argon and oxygen diameters based on the fraction of oxygen in the background gas:

$$d_{gas} = f_{Oxygen} * d_{Oxygen} + \left(1 - f_{Oxygen}\right) * d_{Argon}$$
(11.2)

Table 11.1: Estimated mean free path for each ablated species from the above equation. Mean free path values are reported for each background gas composition in units of meters.

		Mean Free Path (m)					
Species	Atomic Radius (m)	100% O <sub>2</sub>	50% O <sub>2</sub>	16.6% O <sub>2</sub>	6.6% O <sub>2</sub>	100% Ar	
Ar	7.100E-11	7.906E-06	7.282E-06	6.905E-06	6.798E-06	6.729E-06	
Li	1.450E-10	3.229E-06	3.062E-06	2.958E-06	2.928E-06	2.908E-06	
La	1.950E-10	2.087E-06	1.999E-06	1.944E-06	1.928E-06	1.918E-06	
Та	1.450E-10	3.229E-06	3.062E-06	2.958E-06	2.928E-06	2.908E-06	
0	6.000E-11	9.422E-06	8.614E-06	8.131E-06	7.995E-06	7.906E-06	

## **Appendix II: Raster Kinematics from Target Diameter**

Calculation of the raster-motion kinematics is not as straightforward as it may seem. The initial instinct is commonly to assume that the diameter of the target is equal to the chord of the carousel diameter associated with rotation of the laser center point across the target. However as can be seen in Figure 11.1, this chord is not equivalent to the diameter of the target. This would be a reasonable approximation as the ratio of the target diameter to carousel diameter approaches zero but with similar diameters, the actual geometry must be considered.



Figure 11.1: Diagrams of the geometric relationships between the carousel rotation, target diameter, and point of laser impingement.

In order to generate kinematic information for the movement of the carousel axis such that the laser spot travels over the majority of the target surface, one must find the angle,  $2\theta$ . The key insight to complete this calculation is the realization that the triangle formed to the right side of
Figure 11.1 is formed from the angle  $\theta$  and the known diameters of the target and carousel. The law of cosines can then be applied as:

$$r_t^2 = r_c^2 + r_c^2 + 2 * r_c * r_c * \cos(\theta)$$
(11.3)

$$\theta = \cos^{-1} \frac{2r_c^2 - r_t^2}{2r_c^2} \tag{11.4}$$

Then the kinematic information can be calculated as a unit conversion, based on the known steps per revolution of the attached motors:

$$s_r = \theta * \frac{spr}{2\pi} \tag{11.5}$$

where  $s_r$  is the number of steps in the raster movement, spr is the steps per revolution of the motor and  $2\pi$  represents a full revolution. Then the motor must simply be instructed to move  $s_r$  steps clockwise,  $2s_r$  steps counterclockwise, and  $s_r$  steps clockwise to complete a raster motion cycle. In actual application, a utilization factor is added to the calculation to reduce the value of  $s_r$  by a percentage. This allows the user to adjust the raster-motion behavior for cases where the beam is not focused to a point, but to an elongated shape.

## **Appendix III: Computer Aided Design of Electrode Masks**



## III-i Bar Electrode Shadow Mask

## III-ii Photolithographic Mask Designs



Figure 11.2: Photolithography layout of four bars with width of 750  $\mu$ m and spacing of 200  $\mu$ m. Orange shaded area is the area written by the microwriter while the blue shaded area represents the eventual position of the metal electrodes. This mask was used for deposition on epitaxially grown LLTaO films.



Figure 11.3: Photolithography layout of a wide array of shapes, used for investigations of the role that electrode shape plays during in-plane impedance spectroscopy of LLTaO films. This mask illustrates the freedom of design that is afforded to electrode deposition when using photolithography.

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