## STRUCTURE AND PROPERTIES OF GARNET-TYPE LITHIUM ION CONDUCTORS Li7-xLa3Zr2-xTaxO12 AND THEIR APPLICABILITY IN LITHIUM-ION BATTERIES

By

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## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Materials Science and Engineering - Doctor of Philosophy

#### ABSTRACT

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Li-ion batteries have served as the primary energy storage units in portable electronic devices and will continue to play an important role in the sustainable energy future. Despite decades of developments, the energy density and safety of Li-ion batteries still cannot live up to the increasing demands of modern society. Many issues are related to the state-of-art liquid electrolyte due to its intrinsic volatility and flammability. Solidstate lithium ionic conductors have received much attention recently and the garnettype lithium ion conductors have emerged as the most promising candidate in the oxide system owing to their high conductivity and good chemical/thermal stability. This dissertation describes my PhD research work on the structure and properties of the garnet materials and their applicability in lithium-ion batteries.

In Chapter 3, a series of garnet compounds  $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$  (LLZTx, x= 0 – 2) were synthesized and their phases and transport properties were characterized. The highest bulk conductivity of 9.6 × 10<sup>-4</sup> S/cm is achieved for the composition  $Li_{6.7}La_3Zr_{1.7}Ta_{0.3}O_{12}$ which marks the highest value reported in the literature at the time of publication. Ta<sup>5+</sup> doping stabilizes the cubic garnet structure and the cation Ta<sup>5+</sup> and Zr<sup>4+</sup> form complete solid solutions for the cubic garnet compounds. A carefully conducted study of the LLZTx series reveals that pure cubic garnet phase forms only when  $x \ge 0.6$ .

To understand the transport properties of the LLZTx series, the structures of selected compositions in this series were studied by diffraction techniques and computer simulation. Neutron diffraction study provided information about the average structure whereas the pair distribution function (PDF) analysis shed light on the local structure. Atomistic simulation based on interatomic potentials was carried out and a statistical approach was employed to extract useful structural information. We found that both tetrahedral and octahedral Li display strong position disorders as visualized via nuclear density maps. The first-neighbor Li-Li interactions strongly influence the lithium distribution. PDF analysis and computer simulation results indicate that mobile Li ions hop through the tetrahedral-octahedral shared faces.

Finally, the applicability of the LLZTx compounds in lithium-ion batteries was evaluated. It was found that the LLZTx compounds were stable against Li metal but unstable against moisture and CO<sub>2</sub>. The composition LLZT0.3 is more compatible with the cathode material LiCO<sub>2</sub> than the LiFePO<sub>4</sub>. Partial success was achieved using sol-gel method. The pulsed electric current sintering was successfully applied to the densification of LLZT0.6 powder.

# DEDICATED TO FRIENDS AND FAMILIES

#### ACKNOWLEDGEMENTS

I am deeply grateful to my advisor Dr. Wei Lai for providing the valuable opportunity to conduct this research. Wei Lai has intrigued my interest in the current research field, set a good role model as a researcher and guided me through obstacles and difficulties. His work ethic, great responsibility, critical thinking skill, independence and pursuit of perfection all deeply influenced me. Personally, he has been kind and considerate to me. It is no exaggeration to say that without my advisor Dr. Wei Lai, I cannot possibly achieve what I have done and be who I have become.

I would like to thank my colleagues Rengarajan Shanmugam and Mattew Klenk. Rengarajan shared with me a lot of work and ideas since we got into this lab. He has been very helpful and wonderful to work with. I feel obliged to attribute many of my ideas to the inspiring discussions with him. Matt has been working with me on a similar research topic for the past year. Discussion with Matt helped me reexamine our work from a more objective perspective. I wish best luck to my colleagues in their PhD pursuits.

I'd like to acknowledge the financial support by the Ceramics Program of National Science Foundation (DMR-1206356). Many thanks to all the people that have provided supports during my PhD study. As my committee members, Prof. K Subramanian, Prof. Phillip M. Duxbury and Prof. Donald Morelli have advised me on various research issues and gave invaluable critique of my work. Prof. Andre Lee and Prof. Carl Boehlert have advised on my graduate program. Dr. Karl Dersch provided technical supports of the PECS sintering. I wish to acknowledge the High Performance Computing Center and the Institute for Cyber-Enabled Research, Composite Material & Structures Center and Department of Chemistry for granting me access to their instruments and resources.

I am grateful to all my friends who accompanied me through the hardship of PhD study. Among them, I am most indebted to my wife, Xue Li, who supported me immensely in many aspects. Last but not least, I want to thank my families in China. Although separated in great space, we share same goals, same concerns and same hearts for each other. I would have regretted so much if I hadn't listened to their advice on pursuing a PhD degree and I couldn't have achieved this goal without their materialistic and spiritual supports.

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#### **Chapter 1 Introduction and Motives**

### 1.1 Lithium-ion Battery: Significance and Status

Energy is the most fundamental element of human activities. Nowadays, our society relies on coal and petroleum for energy generation. However, climate change, pollution and limited reserves of fossil fuels all require us to find cleaner and more sustainable energy sources. Renewable energy sources such as solar[1-3]and wind power[4] are promising substitutes. However, unlike fossil fuels which both store and generate energy, the generation of solar energy and wind power depends largely on Mother Nature. As a result, there is a great mismatch between energy generation and energy consumption so energy storage devices are needed. Batteries, being the most successful electrochemical storage devices, have been and will continue to serve the purpose in the foreseeable future.

The global demand for batteries has been constantly on the rise owing to the insatiable appetite of information technology sectors.[5, 6] Secondary batteries (rechargeable batteries) are taking a larger global market share over time.[7] Despite being the young member of the battery family, Lithium-ion batteries (LIBs) have achieved tremendous growth since the commercialization of first LIB. Undoubtedly, the success of LIBs goes hand in hand with the success of portable electronic devices. Compared with conventional secondary batteries, LIBs have merits such as high energy

density, low discharge rates and little memory effects.[8-10] Figure 1.1 compares different battery technologies in terms of gravimetric and volumetric energy densities. Clearly, LIBs possess the highest energy density among common rechargeable batteries systems. LIBs are becoming increasingly competitive in terms of cost and performance as LIBs technology progresses. [11-20]



Figure 1.1 Volumetric and gravitational energy densities of various battery systems.[10]

The comeback of electric vehicles (EV) opens up a new market for LIBs. With a completely different design of powertrain systems, EVs deliver about 60% of energy from the grid; comparatively, conventional gasoline cars with internal combustion engines deliver only 20% of energy stored in gasoline.[21] Studies have shown that even if EVs run on electricity generated by coal, the overall greenhouse gas emission is still less than that by cars running on gasoline.[22] Drawbacks of EVs include limited

range[23], high cost of battery packages[24, 25] and safety issues[26]. Early models of EVs can only run a few tens of miles on a single charge, far inferior to conventional gasoline vehicles which have a minimum range of three hundred miles. Due to the flammable nature of battery components, worries of fire and explosions have been a constant setback for EVs despite numerous safeguards installed. The improvement of battery technologies holds the key to solving these issues.

LIBs, like most electrochemical cells, consist of three major components: cathode, anode and electrolyte. The cell potential originates from the chemical potential difference between the two electrodes which are electronically connected through the external circuit and ionically connected through the internal circuit (electrolytes). During the discharging cycles, electrons flow from the anode to the cathode, converting chemical energy into electrical energy. Meanwhile, Li ions move from the anode to the cathode through the electrolyte to balance the charge. The reactions in the case as shown in Figure 1.2, the reactions are:

Cathode:	$LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^-$	(1)

Anode: 
$$Li_x C \rightleftharpoons xLi^+ + C + xe^-$$
 (2)

Overall: 
$$C + LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + Li_xC$$
 (3)



Figure 1.2 Operational principle of lithium-ion batteries.[8]

Whether a cell is rechargeable or not depends on the reversibility of the chemistry of electrode materials. For primary batteries, the reactions in the electrode materials are irreversible under operational conditions. For secondary batteries, both the cathode and anode materials can extract and insert Li ions without causing irreversible changes so the batteries can be cycled many times.

Several parameters are used to evaluate battery performance. High gravimetric and volumetric energy densities are desirable which are largely dependent on the electrode materials. The internal resistance of a battery needs to be small to minimize energy waste and prevent overheating. The cycle life is defined as the number of complete cycles a battery can perform before the capacity falls below 80 % of the initial value. This is decided by the chemical stability and mechanical degradation of the electrode

materials. Other important aspects include rate capabilities (how fast batteries can be charged and discharged), specific power and voltage stabilities. Cost, environmental friendliness and safety are also important considerations from a practical point of view.

Common cathode materials include LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> and LiFePO<sub>4</sub>,[27, 28] all of which can deliver more than 100 Ah·Kg<sup>-1</sup> of commercial capacity. On the anode side, carbon-based materials are the most widely used anode materials due to the good cycle performance.[10] Despite the success that LIBs enjoy, there is still enormous potential energy density enhancement. We could see several folds increase in energy density if issues with conversion-chemistry-based lithium batteries can be properly addressed.

It is generally accepted that the causes for many issues in LIBs lie in the electrolyte materials. In contrast to the field of electrode materials, there hasn't been much breakthrough in the electrolyte technology. In the next section, details about the issues related to the use of liquid electrolytes will be discussed.

### **1.2 Liquid Electrolytes in Li Ion Batteries**

The electrolyte provides pathways for Li ion conduction between the two electrodes. Ideally, the ions pass through the electrolyte without altering the chemical compositions of the electrolyte and most of the 'interesting' reactions happen at the two electrodes. This seemingly suggests that electrolyte materials are not as important as electrode materials. In fact, the proper function of a cell is heavily dependent on the various properties of electrolyte materials.

The requirements for electrolyte materials are multifaceted and stringent.[9] Since the primary function of electrolytes is to conduct ions, the first criterion is high ionic conductivity. It is generally believed that a minimum bulk conductivity of 10<sup>-3</sup> S/cm is needed for the application of electrolyte materials in large-scale batteries. The second criterion is resistance against reduction and oxidation reactions. As electrolytes are in direct contact with the cathode and anode materials which are oxidative and reductive in nature, compounds that do not have sufficiently wide electrochemical window are susceptible to side reactions and decompositions which could result in irreversible loss of capacity, deterioration of transport properties and undesired heat generation[29-32]. Thirdly, electrolyte materials need to be thermally and chemically stable in itself or with other components such as separators and current collectors. Aside from these criteria, it is preferred that electrolyte materials are tolerant of abuses such as mechanical, electrical and thermal shocks.

Finding materials that meet all the criteria is no easy task. A lot of research efforts in the early days were put into the electrolyte formulation which led to the development of LiPF<sub>6</sub> dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC).[33-38] It is no exaggeration to say that the commercialization of first lithium-ion batteries was in large part due to the success of electrolyte materials research.

So how well do liquid electrolytes meet the criteria? It is far from perfect in a nutshell. The problem with liquid electrolytes lies in the thermal and chemical instability of both the solvent and solvate. If we look at the energy diagram of the liquid electrolyte relative to the cathode and anode materials (Figure 1.3), it is clear that the liquid electrolyte is thermodynamically unstable against either electrode. Therefore, at the surface of the anode, graphite for instance, a surface film forms due to the attack of highly reductive anodes.[39] This surface film is referred to as the solid electrolyte interface (SEI). The formation of the film is crucial for the cycle performance of the cell because it prevents any further reactions between electrolytes and anode materials which is the origin of capacity loss. [40] Similar to the graphite anode, a surface film also forms at the Li metal anode.[41] The issue with the Li metal anode is dendrite growth.[42] Upon cycling, lithium is unevenly distributed or stripped at the surface of the anode, leading to the growth of dendrites which eventually reach the cathode and short the battery. Catastrophic failures ensue. This dendrite issue remains unsolved today and carbonaceous anodes proved to be a safe alternative. Nevertheless, lithium plating can happen to a carbonaceous anode if the cell is overcharged and this sets the lower limit of the electrochemical window of liquid electrolytes.[9]

Similarly, the interface between cathode materials and liquid electrolytes is



Figure 1.3 Electrochemical window of liquid electrolyte LiPF<sub>6</sub> in EC/DEC compared to the electrochemical potential of common electrode materials.[43]

passivated by a surface film which forms at the first cycle.[44] The nature of the passivation film at the cathode differs from that at the anode.[45-48] It is believed that the formation of the film is due to reaction between the cathode material and the decomposition product of LiPF6.[49, 50] Reports[51-53] suggested that the passivation film at the cathode is not as stable as the SEI at the anode and the degradation at the cathode/electrolyte interface is responsible for power loss and capacity fade during prolonged cycles. The breakdown of the film is accelerated when the potential of the cathode surface is high which sets the upper limit of the electrochemical window to be 4.3 V. The instability of the liquid electrolytes limits the application of many high voltage cathode materials.[54-57]

Besides the electrochemical window, liquid electrolytes also have a small temperature window. EC in the electrolyte was found to be crucial to the formation of SEI layers.[40] However, the melting point of EC is only 36 °C and the liquidus temperature of EC/DMC mixture is roughly -20 °C[58] below which the bulk conductivity is severely compromised. This sets the lower temperature limit of the liquid electrolytes. The high temperature limit is determined by the instability between the LiPF<sub>6</sub> and the solvent.[59, 60] Though relatively stable at room temperature, the cyclic carbonates and the decomposition products of LiPF<sub>6</sub> can react at elevated temperatures. It is generally suggested that LIBs with liquid electrolytes should not be operated at temperatures above 50 °C. The small temperature window limits the application of liquid-electrolyte-based LIBs in military, space and traction related fields.

The worst things that could result from batteries are fire and explosions. Although this kind of disaster should not occur under normal operational circumstances, lithium ion cells are not designed to be immune to thermal runaway upon various forms of abuse. The safety of LIBs is a much greater concern in traction-related application because the cells are subject to much harsher mechanical and thermal environment in automobiles. Thermal runaway refers to a series of exothermic reactions which once triggered, could be self-sustained and generate heat faster than heat dissipation, causing an uncontrollable increase of cell temperature. The runaway process will not stop until all the reactive agents are consumed. In liquid-electrolyte-based LIBs, it is generally believed that the decomposition of SEI followed by reaction between intercalated lithium and electrolytes and the decomposition of cathode materials catalyzed by the presence of electrolyte solvents are responsible for the initiation of thermal runaway.[61, 62] In addition, liquid electrolytes contribute a significant portion of energy consumed in a thermal runaway process, making them the most dangerous components in the event of fire and explosions.

In summary, liquid electrolytes are the primary causes of many issues in LIBs such as capacity loss and safety. It is likely that the breakthrough of the lithium-ion battery technology requires a fundamentally different electrolyte system that is intrinsically more stable electrochemically and thermally.

#### **1.3 The Advantages and Limitation of Solid State Electrolytes**

The research efforts to improve electrolyte systems fall into three camps in general: 1) improve the liquid system by finding more stable lithium salts and organic solvents or introducing additives; 2) use polymer-based electrolytes; 3) use inorganic electrolyte systems. The first approach only solves the problem incrementally. Polymer-based electrolytes still cannot combine high conductivity and good stability. For the third approach, various types of inorganic lithium ionic conductors show good stability and excellent transport properties.[63-65] Nevertheless, technical issues still remain to be resolved for the wide application of inorganic solid electrolytes.

Inorganic solid electrolytes satisfy most of the requirements for electrolyte materials. [9] Some solid electrolyte systems have displayed exceptionally high conductivity (more than 10<sup>-3</sup> S/cm) and negligible electronic conductivity.[9, 64, 66] The transference number of most solid ionic conductors is very close to 1. The electrochemical windows of many solid systems are much wider than liquid electrolytes. Most importantly, inorganic solid electrolytes are much safer than liquid electrolytes due to the nonflammable nature. Good thermal stability of solids enables the operation of batteries in high-temperature environment. Lastly, solid electrolytes allow simpler cell design and packaging and they are more suitable for battery miniaturization.

The requirement that is not met by inorganic solid electrolytes is retention of electrode/electrolyte interface during cycling. With few exceptions[66], ceramic materials are rigid with high elastic modulus. Therefore, good contact between electrode and electrolyte particles is difficult to achieve and maintain for most ceramic systems. Currently, the main focus of research in the inorganic solid electrolyte field is still the search for high ionic conductivity compounds. Inorganic systems that have been investigated as promising solid electrolytes include superionic conducting sulfides, perovskite-type oxides, NASICON-type glass ceramics and garnet-type oxides.

Sulfide systems have long been known to possess high ionic conduction.[67-69] Following the report of superionic conductor Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub>-LiI glasses[70], many other glasses, glass-ceramics or crystalline materials based on sulfide systems were reported to have exceptionally high ionic conductivities.[66, 71-74] Another advantage of sulfide systems is the favorable mechanical property which allows the formation of good solidsolid interfaces at room temperature simply by mechanical milling and pressing.[75-77] The superionic conductor Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> and the glass-ceramics Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> have been reported to possess extremely high conductivity on the order of 10<sup>-2</sup> S/cm. [66, 73] However, Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> is likely be a metastable phase and readily decompose when in contact with Li metal or a high voltage cathode according to first-principle calculation[78]. For the glass-ceramics Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub>, heating at 550 °C results in the formation of Li<sub>4</sub>P<sub>2</sub>S<sub>6</sub> and Li<sub>3</sub>PS<sub>4</sub> crystals suggesting that it is also metastable. In addition, sulfides are extremely sensitive to moisture.

The perovskite-type oxides, Al-doped Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub> (0.06 < x < 0.14, short as LLTO), display excellent bulk conductivity (1 ×  $10^{-3}$  S/cm)[79, 80], but the grain boundary resistance of LLTO is relatively high.[81] The synthesis and densification of LLTO requires high temperature processes which make the control of stoichiometry very difficult due to the volatility of Li. Most importantly, Ti<sup>4+</sup> is readily reduced to Ti<sup>3+</sup> at low potential.

The Li-conducting compounds with NASICON-type framework, Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) was reported to possess bulk conductivity of 7×10<sup>-4</sup> S/cm at 298 K. [64] Later,

The glass-ceramic route was adopted to solve the issue of large grain boundary resistance. Fu[82] achieved total conductivity as high as 1.3×10<sup>-3</sup> S/cm at room temperature. Using the glass-ceramic route, another system Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> showed even higher total conductivity (5×10<sup>-3</sup> S/cm) at room temperature.[83] Despite the high conductivity possessed by the LATP and LAGP systems, they are not suitable electrolyte materials due to the ease of reduction of Ti<sup>4+</sup> and Ge<sup>4+</sup>. For instance, the LAGP was found to have lithium storage capability by reducing Ge<sup>4+</sup>.[84]

### 1.4 Garnet-type Lithium Ion Conductors

Although the garnet structure is a well understood system, the capability of ion transport in Li garnets was demonstrated by Weppner et al. only in 2003.[85] The Li ion conductor Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> was shown to have bulk conductivity on the order of 10<sup>-6</sup> S/cm which was low compared to other Li ion conductors. However, two traits made the system very attractive: 1) small grain boundary resistance; 2) stability against Li metal. Later, another garnet-type Li ion conductor Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> with room temperature bulk conductivity as high as 5×10<sup>-4</sup> S/cm was discovered[86]. Garnet-type Li ion conductors are now considered the most promising oxide system for all-solid-state lithium-ion batteries.

The conventional garnet compounds with general formula of A<sub>3</sub>B<sub>2</sub>C<sub>3</sub>O<sub>12</sub> crystallize in the cubic system (space group  $Ia\bar{3}d$ , No. 230). In the Li garnet compound

Li<sub>3</sub>Nd<sub>3</sub>Te<sub>2</sub>O<sub>12</sub>[87], Li<sup>+</sup>, Nd<sup>3+</sup> and Te<sup>6+</sup> fully occupy the four-coordinated site 24*d*, eightcoordinated site 24*c* and six-coordinated site 16*a*. When Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> was found to also adopt the garnet framework, it was clear that some unconventional sites needed to be occupied to accommodate the extra Li atoms. The neutron diffraction study conducted by Cussen[88] showed that Li ions partially occupy the tetrahedral 24*d* sites and the octahedral 48g/96h sites. In a following study by Cussen, it was found that the octahedral site starts to get occupied with evacuation of the tetrahedral site as Li content exceeds 3 per formula unit.[89]

Interestingly, accompanied by the occupation of octahedral sites and the evacuation of tetrahedral sites, a sudden drop in the activation energy was observed indicating the opening of conduction paths. It was clear that the octahedral lithium ions are involved in the conduction but the role of tetrahedral lithium ions divides the opinions on the conduction mechanisms. In the first hypothesis, the tetrahedral lithium ions are mobile so the face sharing Li tetrahedra and octahedra form a continuous conduction network. The supporting evidences include Rietveld analysis on Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> which showed large thermal displacement factors of both tetrahedral and octahedral lithium sites indicating positional disorder.[88] In addition, a recent molecular dynamics study identified ion hopping between tetrahedral and octahedral Li sites.[90] The second hypothesis is that tetrahedral Li are not involved in the conduction and Li ions jump among octahedral sites directly. This is supported by NMR evidence that there was no exchange of lithium between different coordination environments.[91, 92]

Although a majority of Li-stuffed garnet compounds crystallize in the cubic symmetry, the Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> was found to crystallize preferentially in the tetragonal space symmetry[93] with space group  $I4_1/acd$  (No. 142) instead of the cubic symmetry as first reported[86]. Single crystal X-ray diffraction and neutron diffraction studies showed that Li atoms fully occupied *8a*, *16f*, *32g* sites which results in complete ordering of Li and vacancies. This is fundamentally different from its cubic counterpart where Li ions are disordered. Consequently, the tetragonal phase Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> exhibits a total conductivity of 10<sup>-6</sup> S/cm, about two orders of magnitude lower than its cubic symmetry counterpart.

#### **1.5 Research Problems and Dissertation Organization**

### 1.5.1 Composition optimization to achieve high ionic conductivity;

In 2003, the first garnet-type Li ion conductor Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> (LLT)was reported by Weppner et al.[85] with ionic conductivity of around 10<sup>-6</sup> S/cm at 25 °C. In 2007, the Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZ) was reported to possess bulk ionic conductivity of  $5\times10^{-4}$  S/cm at room temperature.[86] Given the high versatility of the garnet framework, it is likely that Ta and Zr atoms form good solid solutions. The intermediate compositions Li<sub>7</sub>-xLa<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> (LLZTx, 0 < x < 2) are expected to be single-phase compounds whose Li

content depends on the relative concentration of Ta and Zr. In many similar inorganic solid electrolyte systems, the optimal composition is usually not at the end members but at an intermediate composition where there was a trade-off between the mobile ion concentration and the vacancy concentration.[94, 95] There are 56 Li ions for the LLZ and 40 Li ions for the LLT on a total of 72 lithium sites. However, no research effort was made to elucidate how the phase and ionic conductivity evolve with Li content for the LLZTx series.

In Chapter 3, the results on the phase and ionic conductivity of the Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> series (x = 0 - 2) will be presented.

### 1.5.2 Better understanding of the average and local structure

The crystal structures of LLT and LLZ have been studied by Rietveld refinement based on neutron or x-ray diffraction data.[88, 93] However, the structures of the intermediate compositions Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> series (x = 0 - 2) have not been carefully studied. In addition, debates over whether the LLZ crystallizes in the tetragonal or cubic phase still exist. Following our study of the transport properties of the LLZTx series, a systematic study of the average structures of the series is needed to reveal the structure-property relation.

The classical Rietveld analysis of diffraction data is based on diffraction peaks (Bragg scattering) thus biased toward to long-range periodicity. This technique is proved

insufficient in dealing with ionic conductors[96-99] as structural disorder is a common feature of solid-state ionic conductors. In the average structure of lithium-stuffed garnets, partial occupancy over two distinct crystallographic sites (24d and 48g/96h) suggests substantial occupational disorder; large atomic displacement factors (ADPs), also called Debye-Waller Factors (DWFs), at ambient temperatures for both 24d and 48g sites suggest positional disorder. Therefore, the assumption of crystal symmetry for Li breaks down locally and the lithium arrangement resembles that of liquid or amorphous materials.

We used the total scattering combined with pair distribution function analysis to probe the local structure of Li-conducting garnets. Compared with conventional diffraction (Bragg scattering) combined with the Rietveld analysis, total-scattering combined with pair distribution function analysis studies both the long-range average structure from Bragg peaks and local short- and medium-range structure from diffuse scattering[100-102]. While the PDF analysis of neutron and X-ray scattering is an established method in the study of liquid and glasses, it has only recently been applied to the study of superionic conductors, such as Cu<sup>+</sup> superionic conductor CuI[103], Ag<sup>+</sup> superionic conductors Ag<sub>2</sub>Te[104], O<sup>2-</sup> superionic conductors La<sub>2</sub>Mo<sub>2</sub>O<sub>3</sub>[105], H<sup>+</sup> superionic conductors Y doped BaCeO<sub>3</sub>[106], Li<sup>+</sup> superionic conductor Li<sub>3</sub>La<sub>2/3</sub>x/3TiO<sub>3</sub>[107], etc. There has been no PDF analysis done on the lithium garnets to our knowledge. Computer modeling is now a well-established method to study the local structures of complex materials. Recently, calculations based on density-functional theory (DFT) have been performed to reveal the structure and lithium transport mechanisms of Li<sub>3</sub>Nd<sub>3</sub>Te<sub>2</sub>O<sub>12</sub>, Li<sub>5</sub>La<sub>3</sub>Nb<sub>2</sub>O<sub>12</sub>, Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>[108] and the origin of cubic-tetragonal phase transition in Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>.[109] However, the quantum mechanical method is computationally expensive and sometimes unfeasible for studying large systems and exploring a large number of configurations. For instance, only 10 configurations were studied by Bernstein[109]. The classical atomistic simulation based on interatomic potentials is much less computationally costly and provides adequate accuracy. However, exploration of energy landscapes of lithium-stuffed garnets with static energy minimization over a large number of configurations has not been performed, to our knowledge.

In Chapter 4, I will first present our time-of-flight (TOF) neutron diffraction study on the average structures of four compositions in the series  $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$  (x = 0, 0.3, 1, 2). These average structures are then used to generate initial configurations for the lattice energy calculation of eight compositions (x = 0, 0.125, 0.25, 0.5, 0.75, 1, 1.5, 2). The optimized structures are obtained by lattice energy minimization and the details of local arrangement of lithium ions and the lithium order/disorder across compositions are examined. To provide experimental evidence of the local structures, PDF analysis is performed on a model cubic garnet, Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> (LLT) using reverse Monte Carlo (RMC) modeling.

#### **1.5.3 Practical issues related to the application in LIBs**

The garnet type Li ion conductors have decent ionic conductivities. However, fulfilling the conductivity requirement is only the first step for the application in bulk lithium-ion batteries. Various practical issues need to be addressed.

For inorganic solid electrolytes, highly-dense samples are needed in order to achieve high ionic conductivity. However, the densification of lithium garnet powders is not trivial. The required temperature is usually so high that lithium evaporation becomes severe. This issue may be solved through 1) enhancing the sinterability of the powders; 2) employing advanced sintering techniques. The sol-gel method has been known to produce nano-scale powders with controlled morphology and high uniformity. Among many different categories of sol-gel synthesis routes, the Pechini method[110] is very suitable for the synthesis of multi-component complex oxides because of the non-ion selective nature of the chelating agents. As for advanced sintering techniques, the pulsed electric current sintering (PECS), also referred to as spark plasma sintering (SPS), has gained popularity recently. This technique utilizes electric current and high pressure to activate the sintering process. [111] It has proven records of achieving highly dense samples at a much lower temperature and shorter time.[112] The reduced
sintering temperature suppresses undesirable phase transformation, reactions, materials loss and grain growth.

Another practical issue with Li-conducting garnets is the stability with common electrode materials and the air. The electrodes of lithium ion cells are composite materials of active materials, electrolytes and conducting matrix. To build an all-solidstate battery, good contact between solid electrolytes and the electrode materials is required to reduce interfacial resistances. However, mechanical compression is not sufficient to build good contact between active materials and oxide-based solid electrolytes so a thermally activated diffusion process is needed. Consequently, the compatibility of electrolyte materials with active materials at elevated temperatures is a prerequisite for the application of solid electrolytes. The instability of LLZ against the air and proton exchange agents was recently reported[113-116] which led to tetragonal to cubic phase transition. However, no one has been able to reliably elaborate on the exact conditions in which the polymorphs transform so far.

In Chapter 5, our efforts on applying the sol-gel method and the PECS sintering to garnet compounds will be described. The compatibility of garnet compounds with several common electrode materials as well as the H<sub>2</sub>O and CO<sub>2</sub> effect on the phase stability of the LLZ are discussed.

#### **Chapter 2 Theories, Methods and Experimental Details**

### 2.1 The General Theories of Ionic Conduction in Solids

Atomic movement is a universal phenomenon in solids at temperature above 0 K. At 0 K, crystals are considered perfect (no point defects). At above 0 K, point defects are introduced which increases the entropy and lowers the free energy. The type of point defects most relevant to the atomic movement is vacancy defect. As thermally-activated atoms vibrate around their equilibrium positions, there is a finite probability for the atoms to hop to neighboring sites (given that there is a vacancy), leaving the original site vacant. This is the basic mechanism for atomic movement. Generally speaking, all ionic solids are capable of transporting ions. What separates the fast ionic conductors from ordinary solids is the magnitude of the ionic transport. To understand the massive scale of ion migration in ionic conductors, we need to first take a look at the classic model of mass transport.[117]

In the classic model, ions or vacancies move by a series of isolated jumps which are random and independent. The diffusion coefficient can be expressed as

$$D = \alpha d^2 \nu, \tag{4}$$

where  $\alpha$  is a geometric factor which is the reciprocal of the number of possible jump directions. *d* is the distance of each jump and *v* is the average jump frequency. *v* can be expressed as

$$v = \beta v_0 \exp(-\Delta G/RT) \tag{5}$$

where  $\beta$  is the fraction of species that are free to move (mobile species),  $\nu_0$  is the attempt frequency. The exponential term gives the success rate of the attempted jumps in which  $\Delta G$  is the free energy of migration. If we separate the entropy and enthalpy components of  $\Delta G$ , then

$$v = \beta v_0 \exp(\Delta S/R) \exp(-\Delta H/RT).$$
(6)

In conventional solids, only defects such as vacancies and interstitial atoms are considered mobile so  $\beta$  is essentially the defect concentration. For intrinsic defects

$$\beta = \exp(-\Delta G_f / RT). \tag{7}$$

 $\Delta G_f$  is the formation energy of the defect. Combining Equation 5, Equation 6 and Equation 7, the diffusion coefficient can be written as

$$D = \alpha d^2 v_0 \exp(\Delta S/R) \exp[-(\Delta H + \Delta G_f)/RT].$$
(8)

Let  $E_a$  be the sum of  $\Delta H$  and  $\Delta G_f$ , then we can call  $E_a$  the activation energy of the diffusion process.

The diffusion coefficient describes ion movement under chemical gradient where as the ionic conductivity describes ion movement under potential gradient. For ionic conductivity, the external electric field *E*increases/decreases the activation energy of diffusion along/opposite to the applied direction by  $z \mathcal{E}e_+a$ , where *z* is the charge number,  $e_+$  is the unit charge, *a* is the projection of each jump distance in the applied field direction. This imbalance gives a net flow of charges so the ionic conductivity is related the diffusion coefficient by the Nernst-Einstein relation

$$\sigma = DCz^2 F^2 / RT \tag{9}$$

where *C* is the concentration of mobile species and *F* is Farady constant. Combining Equation 8 and 9, we get the familiar Arrhenius relation

$$\sigma = (\sigma_0/T)\exp(-E_a/RT), \tag{10}$$

where  $\sigma_0$  is expressed as

$$\sigma_0 = C\alpha d^2 v_0 (z^2 F^2 / R) \exp(\Delta S / R). \tag{11}$$

Now let us examine why ionic conductors have exceptionally high ionic conductivity as compared to ordinary solids. In ordinary solids, defect creation is thermally activated and the defect concentration is many orders of magnitude lower than the mobile species concentration. In ionic conductors, the mobile species have large occupational disorder so defects can be considered as 'built-in'. The defect concentration ( $\beta$ ) is on the same order of magnitude as the mobile species concentration. In addition, the defect concentration is no long temperature-dependent so the defect formation energy term  $\Delta G_{f}$  vanishes which lowers the activation energy.

It is important to recognize the assumption in the random walk model that the jumping of ions is random, i.e., the jump frequency is independent of their surroundings. This assumption is largely true for ordinary solids because the defect concentration is so low that defects are essentially 'unaware' of one another. However, in ionic conductors, the jump frequencies are strongly affected by the interaction among mobile ions. So the proper modeling of the ionic conductivity in ionic conductors requires a more suitable diffusion theory which is beyond the scope of this dissertation.

#### 2.2 The Sol-gel Method

The sol-gel method is generally considered superior to the solid state method for the powder synthesis. In the solid state reaction, the mixing of precursors is at best at the particle level whereas atomic-level mixing can be achieved in the sol-gel method theoretically.[118] Powders prepared through solid state reaction are usually in the micron range. Using sol-gel method, nanoparticles of controllable sizes and morphology can be obtained. The enhanced sinterability of sol-gel powders due to chemical homogeneity and small particle size greatly reduces the energy barriers of densification thus lowers firing temperatures. Finally, novel forms of ceramic products such as fibers and film can be fabricated using the sol-gel method.

There are several different kinds of sol-gel processes.[118, 119] The Pechini method used in this thesis falls into the category of polymerized complex method.[110] First, the metal ions are added into citric acid (CA) solution to form metal chelate complexes. Ethylene glycol (EG) is then added while the whole solution is heated under constant stirring. The viscosity of the solution increases due to polyesterification and evaporation of solvents. Finally, a highly viscous gel of continuous polymer network with metal ions uniformly distributed and immobilized is formed. The metal oxides powder is obtained by breaking down the polymers at high temperature (usually above 300 °C).

The Pechini method is very suitable for the preparation of multi-component metal oxides because the CA has strong affinity to most metal ions and form stable metal chelates almost indiscriminately. In this dissertation, a modified version of the Pechini method, the EDTA/citrate complexing method,[120] was adopted. The chelation of Ethylene-diamine-tetra-acetic acid (EDTA) and metal ions is more tolerant to pH, temperature and metal ion concentration. The CA was used primarily as an esterification agent instead. This modified Pechini method has been successfully applied to a variety of complex metal oxides but not to the lithium garnet compounds yet.[121-123]

# 2.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an invaluable tool for electrochemical characterization. By measuring the electric response of an electrochemical system to certain stimulation, electrochemical processes within the system can be deduced. When a sinusoidal input signal, voltage for instance, is applied to a linear system, the output current has the same angular frequency

$$E(t) = \Delta E \cdot \exp(j\omega t) \tag{12}$$

$$I(t) = \Delta I \cdot \exp(j\omega t + \varphi) \tag{13}$$

And the impedance, in analogy to resistance, is given by

$$Z(\omega) = \frac{E(t)}{I(t)} = Z\exp(-j\phi) = Z\cos\phi - jZ\sin\phi = Z_R - jZ_I$$
(14)

There are several ways of graphically presenting EIS data. The most common way is to plot the imaginary component  $Z_I$  versus the real component  $Z_R$  in the complex plane. This kind of plot is call Nyquist plot, Cole-Cole plot or simply impedance plot. Figure 2.1 is an example of impedance plot of the simple circuit with a capacitor and a resistor in parallel.



Figure 2.1 An example of impedance plot (left) corresponding to the RC circuit (right).

The fundamental laws governing the relationship between charge transports and potentials in an electrochemical system is similar to that in an electrical circuit consisting of basic circuit elements. Therefore, real electrochemical systems are modeled using equivalent circuits. For example, the impedance of ionically conducting solids can be represented by RC circuits. For single crystals or polycrystalline materials whose grain boundary impedance is negligible, one RC circuit is sufficient and the resistive and capacitive components correspond to the ion transport process and the dielectric response of the bulk, respectively.[124] In most cases however, the grain boundary resistance cannot be ignored and an additional RC circuit is needed to describe the behavior at the grain boundaries.[125] As the time constants associated with the processes inside the grains and within the grain boundaries are usually different by more than two orders of magnitude, the semicircles corresponding to each RC circuit can be separated in the impedance plot.

## 2.4 Rietveld Refinement

Diffraction techniques are unarguably the most important tools to study crystal structures of materials. Rietveld refinement is the most popular method of characterizing crystal structures of crystalline materials based on diffraction data.[126] This method uses least square fitting to refine relevant parameters so the calculated diffraction pattern matches the experimental pattern. As many of the refinable parameters do not contain any structural information but are necessary merely for corrections and determination of the peak profile, these will be ignored for the current discussion. The terms that contain most of structural information are lattice constants and structure factors. The structure factors require special attentions in order to understand the strengths and limitations of the Rietveld method.

The intensity contribution of *hkl* plane is proportional to the square of the structure factor of *hkl* 

$$I_{hkl} \propto F_{hkl}^2 \tag{15}$$

where  $F_{hkl}$  can be calculated as

$$F_{hkl} = \sum_n f_n N_n \exp\left(2\pi i * (hx + ky + lz)\right) * \exp\left(-\frac{8\pi^2 u_n^2 \sin\theta}{\lambda}\right).$$
(16)

The summation is over all atoms in a unit cell.  $f_n$ ,  $N_n$  and  $u_n$  are x-ray atomic form factors (a measure of how well an atom scatters x-rays) or neutron scattering length (a measure of how well an atom scatters neutrons), site occupancy and isotropic atomic displacement parameters (ADPs) for the n<sup>th</sup> atom, respectively. *x*, *y* and *z* are coordinates of atoms.  $\theta$  and  $\lambda$  has the same definition as in the Bragg's law.

A number of approximation and assumptions are made in order to derive the above formula. In a conventional crystal, atoms vibrate around its equilibrium positions (x, y, z). The diffraction data contains the spatial and temporal average of all scattering contribution so the effect of thermal motions is accounted for by integration which gives rise to the second exponential term in Equation 16. In this process, it is assumed that the thermal motions of all atoms are independent of each other and the distribution can be approximated by Gaussian distribution. These assumptions may be invalid in some crystal systems.

## 2.5 Pair Distribution Function Analysis and Reverse Monte Carlo Modeling

Pair distribution function (PDF) analysis has been successfully applied to the study of liquids and amorphous materials for decades.[127] It has been proven a powerful tool for the characterization of disordered crystalline materials too.[128] The PDFs give the probability of finding a pair of atoms separated by distance *r*. They can be calculated given the complete structural information. The partial PDF  $g_{ij}(r)$  is defined as

$$g_{ij}(r) = \frac{n_{ij}}{4\pi r^2 dr c_j \rho_0} \tag{17}$$

where  $n_{ij}$  is the average number of type j atoms within a shell of r to r+dr centered at a type i atom;  $\rho_0$  is the total number density of all atoms;  $c_j$  is the number concentration of type j atoms.

The atomic pair distribution function (denoted as G'(r)) is the summation of partial PDFs for all pairs weighted by the concentration and scattering powers of the atom pairs:

$$G'(r) = \sum_{i,j=1}^{n} w_{ij} g_{ij} = \sum_{i,j=1}^{n} \frac{c_i c_j b_i b_j}{(\sum_{i=1}^{n} c_i b_i)^2} g_{ij}(r)$$
(18)

where  $b_i$  is the scattering length of type i atom in the case of neutron diffraction.

Two forms of the PDF will be used in this dissertation. The form used in the data reduction software PDFgetN[129] (denoted as  $G^{PDF}(r)$ ) is related to G'(r) as

$$G^{PDF}(r) = 4\pi r \rho_0 [G'(r) - 1]$$
(19)

whereas the form of PDF used in RMC modeling software RMCprofile[130] (denoted as G(r)) is related to G'(r) as

$$G(r) = (\sum_{i=1}^{n} c_i b_i)^2 [G'(r) - 1].$$
(20)

Experimentally, the pair distribution function is related to the normalized totalscattering function S(Q) by Fourier transform

$$G^{PDF}(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) \, dQ.$$
(21)

The reverse Monte Carlo method is a modeling tool for generating structural models of which the pair distribution function is consistent with the total scattering experiment. It is essentially a fitting scheme where a large number of atoms are allowed to move randomly to minimize the differences between calculated and experimental pair distribution functions.

## 2.6 Computational Methods

Computer simulation has become a powerful tool for studying the structure and properties of materials as the computational capabilities grow exponentially and our knowledge of computational chemistry advances. Nowadays, chemists and materials sciences use computational techniques to study structures of both crystalline and amorphous materials, behaviors at the interfaces and around defects and crystal properties such as ion diffusion.[131]

There are two main approaches in the field of computational chemistry differing in the way interactions of atoms are treated. The classic approach treats atoms as individual units with certain properties and use interatomic potentials to describe shorts range interactions of atoms. For solids, the most common model is the Born model[132] where atoms are treated as charged ions and the lattice energy is partitioned into the long-range electrostatic energy and the short-range interatomic interaction energy. The parameterization of interactomic potential models is largely empirical, although first principle calculations are increasingly applied to the fitting of potential models nowadays. By minimizing the lattice energy with respect to the coordinates of atoms, the most stable atomic configurations are determined. Subsequently, various materials properties can be calculated.

The second method employs quantum mechanical (QM) principles. According to quantum mechanics, the electronic structure of a system can be completely known by solving the Schrödinger equation. In contrast to the first approach where the interactions are approximated empirically, the second approach is founded on first principle. The main difficulty of this first-principle method lies in the mathematics as solving the Schrödinger equation of multiple-electron systems can be extremely challenging or impossible. In practice, a number of approximations and mathematical simplifications are used. Meanwhile, the method itself inevitably deviates from the first principle.

It is generally considered that results from QM calculations are more reliable. However, the classic approach requires much fewer computer resources than the QM approach. For this reason, the classic approach is still the practical choice when dealing with large systems. Energy minimizations with the classic approach are essentially done at zero Kelvin because no thermal effects are considered. Although it is possible to account for phonon contributions by 'quasi-harmonic' approximation at low temperature, the static-lattice model breaks down at high temperature. Molecular dynamics (MD) is a more suitable technique to study transport properties of materials, where the motion of atoms is simulated by numerically solving the Newton's equations of motion for a successive of time steps. In this disseration, only the classic approach (energy minimizations) is employed to study the lithium distribution of garnet compounds so I will dive a little deeper into the basics of this method here.

The first task of the energy minimization approach is calculation of lattice energy. The internal energy of the structure consists of many-body interactions of all ions:

$$U = \sum_{i=1}^{N} U_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} U_{ij} + \frac{1}{6} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} U_{ijk} + \cdots$$
(22)

Where  $U_{ij}$  represents interactions of pairs and  $U_{ijk}$  represents interactions of triplets, etc. The first term is generally ignored since it is independent of atomic coordinates. The inclusion of high-order terms in the calculation can be expensive. Fortunately for ionic solids, the interaction energies are dominated by pair-wise interaction so the pair-wise approximation is employed in this dissertation which neglects the energy contribution of third or higher order interactions.

As mentioned earlier, the lattice energy is partitioned into the long-range and shortrange interaction parts. The long-range interactions are essentially Coulomb interactions. The pair-interaction energy is expressed as:

$$U_{ij}^{c} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{23}$$

The short range interaction describes the bonding behaviors of atoms. For ionic solids, this term can be further divided into attractive and repulsive parts. The attractive part originates from the instantaneous dipoles of ions and is referred to as the Van der Waals-London interaction. The energy of this type of interaction depends on the separation of ions as  $r_{ij}$ . The repulsive part is mainly due to the Pauli exclusion

principle. Putting the two terms together, the short-range interaction can be expressed using the Buckingham potential:

$$U_{ij} = Ae^{-\frac{r_{ij}}{\rho}} - \frac{C}{r_{ij}^{6}}$$
(24)

A,  $\rho$  and C are parameters as model inputs.

An ion consists of a nucleus and an electron shell. Under the influence of an electric field, the centers of the nucleus and the electron shell do not overlap, giving rise to dipoles. Polarizability of ions is defined as the ability to form such dipoles. The accuracy of energy calculation may be improved by the inclusion of the shell model[133] where an ion is divided into a core and a shell, both carrying charge. The core and shell are Coulombically screened by each other but coupled via a 'spring', i.e., a harmonic force constant k so the motions are correlated:

$$\alpha = \frac{q_s}{k} \tag{25}$$

where  $q_s$  is the shell charge.

The structure can be optimized by minimizing the energy with respect to a number of variables such as coordinates and lattice constants. It is important to recognize that the optimized structure is a local minimum on the energy surface to which the initial configuration lies close. This minimum in many cases is not the global minimum which in principle is the true most stable structure. A number of approaches such as Monte Carlo or genetic algorithms are design to find the global minimum.[134-136]

#### 2.7 Experimental Details

#### 2.7.1 Powder synthesis via solid state reaction

In this thesis, two solid state synthesis routes differing in the crucible choice and the heating chamber atmosphere were employed. For the first route, the samples were calcined in Al<sub>2</sub>O<sub>3</sub> crucibles in air; for the second route, the samples were calcined in MgO crucibles under Ar flow. The Al<sub>2</sub>O<sub>3</sub> crucibles have been found to contaminate the garnet samples.[137] Instability of garnet compounds against the air was recently discovered.[138] The use of MgO crucible and the heat-treatment in Ar eliminate possibilities of Al contamination and air effects. Therefore, the second route is more rigorous than the first route. Samples for studying the transport properties of LLZTx series were prepared using the first route. Samples for other purposes (phase transition study, neutron diffraction, etc) were prepared using the second route.

The following procedure describes the typical procedures of the first route for the LLZTx series (x = 0, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1, 2). Starting materials of LiOH·H<sub>2</sub>O (Alfa Aesar, 99.995% purity), La<sub>2</sub>O<sub>3</sub> (Sigma Aldrich, 99.9% purity), ZrO<sub>2</sub> (Alfa Aesar, 99.7% purity), and Ta<sub>2</sub>O<sub>5</sub> (Alfa Aesar, 99.85% purity) were ball-milled (Jar mills, U.S.

Stoneware) in 2-propanol at the speed of 100 rpm for 24 hours with yttria stabilized zirconia balls in polyethylene jars. 10 wt% excess lithium starting materials were added to compensate for the evaporation during calcinations and sintering. The mixture was then dried with an IR lamp and heated in air (Carbolite CWF 1300 and Lindburg/Blue M BF51848A) at 900 °C for 10 hours in alumina crucibles with a heating rate 3 °C/min and then allowed to cool in furnace naturally. The ball-milling and heating were repeated once to enhance purity.

For the second route, the powder mixtures were calcined in MgO crucibles with a heating rate 3 °C/min and a cooling rate of 2 °C/min. A heat-treatment at 750 °C in a tube furnace under Ar flow was performed for 2 hours to eliminate the air effect. The samples were transferred to an Ar-filled chamber with moisture level less than 0.1 ppm for storage immediately after.

#### 2.7.2 Powder synthesis via sol-gel method

Two garnet compounds were synthesized using the EDTA-citrate complexing process (ECCP), Li<sub>7.2</sub>La<sub>3</sub>Zr<sub>1.8</sub>Sc<sub>0.2</sub>O<sub>12</sub> (LLZS0.2) and Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>. The general procedure is shown in Figure 2.2. To prepare the metal nitrate solution, LiOH, La<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub> were dissolved in diluted nitric acid completely; ZrO(NO<sub>3</sub>)<sub>2</sub> powder was dissolved in mixture of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O at 100°C. All solutions were then mixed well and added into EDTA/ammonia solution. This step was conducted very slowly and carefully so no

precipitates formed. Subsequently, the whole solution was heated at 80 °C for 30 minutes under constant stirring before citric acid/H<sub>2</sub>O solution was added. The pH value was adjusted into neutral or slight basic range by adding ammonia water. Finally, the solution was heated to 100 °C until a clear gel was formed, which was then heated at 350 °C on hot plate to obtain a black resin. The resin was calcined in open air in a furnace at 500 °C to burn off organic substances and obtain white fluffy powder. After grinding, the powder was heated to 800 °C to form the garnet phase.



Figure 2.2 Flow chart of a typical EDTA-citrate complexing process (ECCP).

# 2.7.3 Densification of garnet samples (cold press/sintering)

The LLZT*x* garnet powders prepared via the first powder synthesis route were sintered into dense pellets using conventional cold press/sintering method in order to

study the transport properties. Specifically, around 0.5 atomic % of NaHCO<sub>3</sub> (J.T.Baker, 99.7-100.3%) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar, 99.9%) were mixed with the obtained powders. Pellets were cold-pressed in a 1/2 inch die with a uniaxial press (Carver 3851) at 5 tons and then sintered in air at various temperatures in alumina crucibles for 36 hours. The heating rate was 3 °C/min before 900 °C and 1 °C/min to the desired temperature, and the cooling rate was 4 °C/min. For LLZT*x* compositions of *x* = 0.2 – 0.5, LLT, *i.e.* Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>, pellets were placed below the samples to prevent Al contamination from the crucible. All pellets were covered with powders of the same composition to minimize evaporations. The choice of NaHCO<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as sintering aid was semi-empirical.

## 2.7.4 Pulsed electric current sintering

In a typical PECS setup (Figure 2.3), the sample is confined in a carbon mold and a uniaxial pressure is applied. The whole setup is within a vacuum or inert gas chamber. The heating begins as pulsed direct electric current is applied. As most ceramic samples are electrically insulating, the current pulses cause discharge at the contact point of particles and generate local heat. Particles start to consolidate as necking and local melting occurs.



Figure 2.3 Schematics of pulsed electric current sintering setup.

For the sintering of garnet compounds Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> and Li<sub>6.4</sub>La<sub>3</sub>Zr<sub>1.4</sub>Ta<sub>0.6</sub>O<sub>12</sub> using the PECS, the powders were prepared via the second solid state route as described earlier. A cylindrical graphite mold with diameter 12.7 mm was used and subject to a 40 MPa uniaxial pressure. A typical heating rate of 100 °C/min was used with only slight variations in the heating profile from trial to trial. The holding time was 3 minutes at various temperatures.

# 2.7.5 Characterization of phase, gravimetric density and morphology

Powder X-ray diffraction (XRD) was used to characterize the phase of garnet samples with a Bruker D8 ADVANCE diffractometer using Cu-K $\alpha$  X-rays. The densities of the pellets were measured by the Archimedes' method in 2-propanol at room temperature. A scanning electron microscope (Carl Zeiss, EVO LS25) was used to characterize the microstructure of garnet samples.

# 2.7.6 Transport property characterization

For electrical characterization, pellets were pasted with gold ink (PELCO) and cured at 700 °C for 1 hour to improve adhesion, then assembled in Swagelok cells with stainless steel 316 rods as current collectors. Impedance measurements were performed in the frequency range 1 Hz to 500 kHz by a Bio-logic VMP 3multichannel potentiostat, with a peak sinusoidal amplitude of 20 mV. A BINDER ED23 heating oven and a freezer were employed for variable temperature impedance tests.

## 2.7.7 Hybrid cell testing

To test the applicability of solid electrolytes for lithium-ion batteries, a cell with a hybrid solid liquid electrolyte was assembled (section 3.1). A sintered pellet of composition Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub> was embedded in polyethylene (PE) and the whole disc was hermetically sandwiched by two liquid electrolyte compartments. The liquid electrolyte (LE) is 1 mol/L of LiPF<sub>6</sub> in dimethyl carbonate (DMC), dimethyl ethylene carbonate (DEC), and ethylene carbonate (EC) with a volume ratio of 1:1:1 (MTI). Lithium foil (Sigma-Aldrich, 0.38 mm thick) and LiFePO<sub>4</sub> composite film (MTI) were used as the anode and cathode, respectively. Both electrodes are 12 mm in diameter. Two pieces of polyethylene porous films (MTI) were employed as the separators.

Stainless steel 316 rods were used as current collectors. Electrochemical performance test was carried out at room temperature at a constant current of 100  $\mu$ A which corresponds to C/26 rate based on the active material of LiFePO<sub>4</sub>.

# 2.7.8 TOF neutron diffraction

The average structures of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZ), <sup>7</sup>Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub> (LLZT0.3), <sup>7</sup>Li<sub>6</sub>La<sub>3</sub>ZrTaO<sub>12</sub> (LLZT) and <sup>7</sup>Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> (LLT) were studied using the Rietveld refinement based on neutron diffraction data. Time-of-flight (TOF) neutron diffraction data over *d* range of 0.1 to 8.5 Å were collected with the POWGEN powder diffractometer at the Spallation Neutron Source of Oak Ridge national laboratory (ORNL). Measurements were made at 10 K and 300 K. Rietveld refinement was performed using the software package Jana2006.[139]

## 2.7.9 Atomistic simulation

All atomistic calculations were based on the static energy minimization algorithm implemented in the General Utility Lattice Program (GULP).[140] The ionic interactions were partitioned into long-range Coulombic interaction and short-range Buckingham interaction as  $U_{ij}=Aexp(-r_{ij}/\rho)-C/r_{ij}^{6}$ , where  $r_{ij}$  is the separation of ions and A,  $\rho$ , C are model parameters. The core-shell model[133] was employed to account for the polarization of Ta and O ions while Li, La, and Zr take their formal charges. Most of the interactomic potential parameters were taken from literature.[141-144] The preexponential terms *A* of Ta-O and Zr-O interaction were fitted to the structures (lattice parameters and atomic positions as determined experimentally at 10 K) of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> and Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> under the constant pressure condition. Table 2.1 summarizes the potential parameters.

Buckingham potential parameters								
Interactions	A (eV)	$\rho$ (Å)	$C (eV \cdot Å^6)$					
Li-O	632.102	0.2906	0					
La-O	4579.23	0.3044	0					
Ta-O	1152.34	0.3690	0					
Zr-O	1470.10	0.3500	0					
0-0	22764.3	0.1490	27.63					

Table 2.1 Buckingham potential and shell model parameters.

Core-shell model parameters						
Species	<i>Y</i> (e)	$k (eV \cdot Å^{-2})$				
Та	-4.596	30.2				
0	-2.760	5916.77				

Energy minimization under the constant volume condition (fixing lattice parameters as determined experimentally at 10 K) was performed on seven cubic compositions of Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub>, x=0.125, 0.25, 0.5, 0.75, 1, 1.5, 2 (named as LLZTx except for x=2, i.e. LLT) and one tetragonal composition, Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>. The multiplicity is 8 in each unit cell. In the 1×1×1 supercells, the total number of Li tetrahedral (24) and octahedral (48) sites was 72, within which *n* (40≤*n*≤56) lithium atoms were randomly distributed. Since the number of all possible combinations is very large, it is not possible to exhaust all configurations for the calculation of the lattice energy and a good statistical representation should suffice. Thus, 5000 initial structures were optimized for each composition in 1×1×1 cells with periodic boundary conditions. Lattice parameters were either directly taken from the Rietveld refinement results or calculated from linear interpolation of refinement results. Appropriate numbers of lithium atoms were randomly distributed into 72 tetrahedral and octahedral sites. La, O, Ta and/or Zr were initially placed at their ideal positions. Ta and Zr were randomly mixed for intermediate compositions. Structural optimization was performed in two steps. In the first step, only Li coordinates and Ta, O shell coordinates were relaxed; in the second step, all coordinates were relaxed. 3D crystal visualization program VESTA[145] or Crystalmaker[9] was used to visualize structures and nuclear density maps.

#### 2.7.10 Pair distribution function analysis

Pair distribution function analysis was carried out on a model cubic garnet material, Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>. Isotopically enriched <sup>7</sup>LiOH·H<sub>2</sub>O (Cambridge Isotope Laboratories, Inc.) was used as lithium precursors to minimize the absorption effect of <sup>6</sup>Li to neutrons. <sup>7</sup>LiOH·H<sub>2</sub>O was dried prior to use. The neutron total scattering data were collected at 15 K, 300 K and 550 K by NPDF (Neutron Powder Diffractometer) instrument at Lujan Neutron Scattering Center, Los Alamos National Laboratory. Around 5 grams of powders were sealed in a Vanadium container for the sample runs. Separate runs on empty chamber, empty container and vanadium rod were performed for background corrections. The data processing software PDFgetN was used to obtain the pair distribution functions. The choice of maximum Q (momentum transfer) strongly affects the noises in G(r) at low r. Too small a  $Q_{max}$  results in large termination ripples while too large a  $Q_{max}$  increases statistical noises. Therefore, the optimal  $Q_{max}$  was determined for each data set by minimizing the quality criterion term  $G_{low}$  [146] for the range of 1 Å < r < 1.75 Å. Scaled factors are also determined during the process. The effective density was manually adjusted so that the total structure function S(Q) oscillates around 1 at  $Q_{max}$ .

Rietveld refinement was performed using GSAS[147, 148] (general structure analysis system) to get the average structures which were then used to generate initial configurations for the reverse Monte Carlo modeling carried out with the software package RMCprofile. The 24d-48g model as described elsewhere [149] was used. A 5×5×5 supercell with lithium atoms randomly distributed at 24d and 48g sites under the constraints of fixed 24d occupancy was constructed as initial configuration for each temperature. Distance windows were applied and chosen to be sufficiently wide so that the peaks in the partial PDFs fall off naturally. The noises in G(r) at low r were truncated. 40 separate runs were performed to check the reproducibility of results derived from the stochastic modeling processes and to generate smooth density maps. The overall PDFs and partial PDFs of the average structures were simulated using PDFgui[150] for comparison where only structure-independent terms were fitted. Crystal visualization was enabled by VESTA[145] or Crystalmaker[151].

## Chapter 3. Phase and Ionic Conductivity of Ta-doped Li7La3Zr2O12

# 3.1 Abstract

The phase and ionic conductivity of the garnet oxide series  $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$  (x = 0 – 2) are studied through X-ray diffraction and impedance spectroscopy. Motivations and experimental details have been described in previous chapters. Ta-doping is found to be responsible for the stabilization of the cubic phase of  $Li_7La_3Zr_2O_{12}$ . Maximum ionic conductivity is achieved when Ta-doping level is 0.3. Electrochemical test on a hybrid cell proves that the solid electrolyte is suitable for the application in LIBs.

## 3.2 XRD Characterization

All the powders were prepared through the first solid-state route. Figure 3.1 shows the room temperature powder XRD patterns of LLZT*x* series calcined at 900 °C. The end-member Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> exhibits a tetragonal phase, consistent with literature reports that used similar processing temperatures. The peak positions of all compositions except x = 0 match with those in the cubic Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> (PDF: 45-0110).[88, 152] No additional peaks were observed indicating good solid solution of Ta and Zr was formed throughout the series. The peaks shifted to higher angles as more Ta was added, suggesting a decrease of lattice parameters, since the ionic radius of Ta<sup>5+</sup> (0.64 Å) is less than that of Zr<sup>4+</sup> (0.72 Å) under the same six coordination.[153, 154]



Figure 3.1 XRD patterns of powders calcined at 900 °C of LLZT*x* or Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> series.

Rietveld refinement with the General Structure Analysis System (GSAS) package was performed to obtain the lattice parameters of the cubic compositions. A structural model of space group of *Ia3d*, similar to that in Cussen et al[88], was used as the initial structure. La adopts a Wyckoff position of 24c and Zr/Ta are randomly distributed on *16a* site. It is generally agreed that lithium disorder in garnet oxides has a complex mechanism and lithium location on the tetrahedral 24d, center octahedral 48g, and displaced octahedral 96h sites has been reported.[154] Due to the low scattering factor of lithium to X-rays, lithium disorder was not the focus of the present XRD study; thus only 24*d* and 48*g* sites were adopted for Li in the refinement. The compositional dependence of lattice parameters is shown in Table 3.1. The lattice parameter decreases with the increase of Ta content and a rough linear relation was seen in consistence with the Vegard's law (Figure 3.2).

Table 3.1 Lattice parameter, sintering temperature, relative density, and room-temperature grain interior and total conductivity of Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> series.

Composition (x)	0.2	0.25	0.3	0.35	0.4	0.45	0.5	1	2
Lattice parameter (Å)	12.9780	12.9801	12.9721	12.9591	12.9470	12.9489	12.9187	12.8900	12.8311
Temperature (°C)	1130	1130	1100	1130	1130	1130	1130	1100	1230
<b>Relative density (%)</b>	91.7	92.7	92.5	92.8	92.8	93.6	94.1	95.0	93.8
GI conductivity (10 <sup>-4</sup> S/cm)	7.8	8.8	9.6	7.7	7.2	6.9	6.7	4.4	1.6
Total conductivity (10 <sup>-4</sup> S/cm)	7.3	6.3	6.9	4.6	4.7	4.0	2.8	3.5	0.34



Figure 3.2 Dependence of lattice parameters on Li content.

## 3.3 Sintering Behaviors

For the Zr-rich compositions (x < 0.5), the samples had strong tendency to react with Al introduced by the vessel during sintering and it was more so at elevated temperature. This was confirmed both by visual inspection and by the detection of high Al content with EDS (Figure 3.3) in the contaminated samples. In addition, the introduction of Al was also found to aid the densification. To minimize the Al contamination from the vessel, two measures were taken: 1) lowering sintering temperature by adding sintering aid; 2) putting LLT pellets, which showed little reaction with Al, below the to-besintered samples in all sintering processes. The Al content in both powders and pellet of composition LLZT0.25 were characterized by EDS. No Al was found in the powder



Figure 3.3 EDS results of (bottom) sintered LLZT0.25 sample without sintering aid but in direct contact with Al<sub>2</sub>O<sub>3</sub> crucible; (top) LLZT0.25 powders after calcined at 900 °C in Al<sub>2</sub>O<sub>3</sub> crucible

(Figure 3.3) and only small quantity (around 1at %) was detected in the pellet, which was roughly the amount of Al added as sintering aid.

It was observed that the density of sintered pellets affects both the bulk and grain boundary significantly. For instance, the pellet with composition LLZT0.25 sintered at 1100°C had percent theoretical density 87.7% and total conductivity more than one order of magnitude lower than the pellet sintered at 1130°C with percent theoretical density 92.7% (Figure 3.4). Thus, sufficiently high temperature was desirable for the sintering.



Figure 3.4 Impedance plots of LLZT0.25 samples sintered at different temperatures.

Optimized sintering temperatures and densities of sintered pellets (percent theoretical density) for all compositions are summarized in Table 3.1. Criteria for the

choices are conductivity, density and extent of Al contamination. Theoretical densities are calculated with formula

$$\varrho = \frac{MZ}{N_A a^3} \tag{26}$$

where *M* and  $\alpha$  are the formula weight and lattice parameter, respectively. *N*<sup>*A*</sup> is the Avogadro constant and *Z* is the number of formula units per cell.

Figure 3.5 shows the typical SEM images of the garnet powder and sintered pellets. Typical grain size of the powders is 1 to 5 microns and typical grain size of the sintered samples is 2 to 10 microns. Slight grain growth is observed as a result of sintering. The sintering process may be facilitated through the liquid-phase sintering mechanism due to the addition of sintering aids.



Figure 3.5 SEM images of (a) LLZT0.3 powder and (b) LLZT0.45 pellet (broken surface).

## 3.4 Electrical Characterization



Figure 3.6 Nyquist impedance plots of Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> pellets at room temperature. The imaginary part of the resistivity is plotted against the real part.

Figure 3.6 shows the Nyquist impedance plot of the LLZT*x* series from x = 0.2 to x = 1 measured at room temperature. Typical dimensions of the pellets are 10.8 mm in diameter and 3.5 mm thick. All resistance data were converted to resistivity for comparison. One arc was followed by a sloping line representing the blocking effect of gold paste to the ionic motion. The grain interior (bulk) and grain boundary resistivities were obtained by fitting the experiment data to a standard equivalent circuit  $C_{stray} || (L-R_{CI}-R_{CB})||Q_{CB}-R_{EL}||Q_{EL})$ , with the help of Zview program.[155] The dash and parallel represent the series and parallel connection, respectively. In the equivalent circuit, *L* and *C\_{stray* are the inductance and stray capacitance from the test leads, respectively. *R\_{CI*, *R\_{CI}*, *R\_{CI}*,

*R*<sub>GB</sub>, and *R*<sub>EL</sub> represent the grain interior, grain boundary, and electrode resistance (resistivity), respectively; *Q*<sub>GB</sub> and *Q*<sub>EL</sub> are the constant phase elements (CPE) for the grain boundary and electrodes, respectively. The CPE impedance takes the form of  $[(j\omega)^nQ]^{-1}$  where  $\omega$  is the applied angular frequency and *n* is the parameter for the homogeneity of the conduction and dielectric responses. The normalized dielectric capacitance *C* can be calculated as  $Q^{1/n}R^{1/n-1}$ .[156] The measurements in Figure 3.6 were performed with the calibrated cables and the stray capacitance was ignored. The inductance value was determined to be 2 × 10<sup>-7</sup> H from measurements on standard resistors. The normalized capacitance values from the fitting are on the order of 10<sup>-9</sup> F for the arcs in Figure 3.6, which is consistent with the expected grain boundary contribution.

The grain interior and total conductivity values are shown in Figure 3.7. The maximum room temperature grain interior conductivity is around 9.6 × 10<sup>-4</sup> S/cm for Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub>, which is comparable to 9.5 × 10<sup>-4</sup> S/cm reported for Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Nb<sub>0.25</sub>O<sub>12</sub>.[157] It is higher than ~5 × 10<sup>-4</sup> S/cm reported[86] for the "cubic" Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> and 4.3 × 10<sup>-5</sup> S/cm reported[158] for Li<sub>6</sub>La<sub>2</sub>BaTa<sub>2</sub>O<sub>12</sub>. Variation of conductivities was observed from batch to batch. For example, the bulk conductivity values between 6.5 and 9.6×10<sup>-4</sup> S/cm were obtained for Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub>. As discussed before, a tetragonal phase was obtained for Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (*x* = 0) in the present work so



Figure 3.7 Composition dependence of room-temperature grain interior (bulk) and total conductivity of Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> series. For composition Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>, data reported form the reference [86] was used.

the literature data[86] of the "cubic" phase were plotted. It is apparent that the peak grain interior was obtained at x = 0.3 while the peak total conductivity occurred at

x = 0.2, due to the lower grain boundary resistance, which might be caused by the cation segregation and reaction with sintering aids. A peak conductivity was reported at x=0.25 for the Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Nb<sub>x</sub>O<sub>12</sub> series.[157] A qualitative explanation of the observed composition dependent conductivity will be presented here. The lithium ionic conductivity is the product of lithium ion concentration and mobility. From nuclear magnetic resonance studies, it is generally accepted that the octahedral sites in lithium garnet oxides take part in the conduction mechanism.[89, 91, 154] It is expected that the mobility of a lithium ion on an octahedral site will be affected by the probability that the next octahedral jumping site is empty. Thus a maximum conductivity is expected at intermediate concentration values due to the trade-off between the carrier and vacancy concentrations.



Figure 3.8 Nyquist impedance of variable impedance measurements of Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub>. The imaginary part of the resistivity is plotted against the real part.

The variable temperature Nyquist impedance plot on the LLZT0.3 pellet is shown in Figure 3.8. Above 80 °C, the grain boundary arcs can't be observed so  $Q_{GB}$  was removed from the equivalent circuit. Thus only the total resistance can be obtained. The inductance value was 3 × 10<sup>-6</sup> H due to the extension test leads. The stray capacitance (4 × 10<sup>-11</sup> F) was determined by performing the measurement on the same sample at room temperature with and without the test leads. This capacitance causes the kink in the



Figure 3.9 Arrhenius plot for the grain interior and total conductivity of Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub>. The straight lines represent the fitting of Arrhenius relation with conductivity values.

high frequency data at 40 °C in Figure 3.8. The Arrhenius plot for the grain interior (< 80 °C) and total conductivity values is shown in Figure 3.9. Both the conductivity  $\sigma$  and product of conductivity and temperature  $\sigma T$  have been used for the Arrhenius relation in the literatures. For the conductivity  $\sigma$ , the activation energies of LLZT0.3 are 0.37 eV (35.6 kJ/mol) and 0.36 eV (34.6 kJ/mol) for the bulk and total conductivity, respectively. For  $\sigma T$ , the activation energies are 0.40 eV (38.5 kJ/mol) and 0.39 eV (37.6 kJ/mol) for the bulk and total conductivity, respectively. These values are comparable to those reported for the total conductivity  $\sigma$  of Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Nb<sub>0.25</sub>O<sub>12</sub> (~30 kJ/mol)[157] or  $\sigma T$  of Li<sub>6</sub>La<sub>3</sub>TaZrO<sub>12</sub> (0.42 eV).[159]
#### 3.5 Electrochemical Test



Figure 3.10 Schematic of the electrochemical cell with a sintered Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub> pellet. SS: stainless steel 316; LE: liquid electrolyte; PE: polyethylene.

An electrochemical cell with a hybrid solid electrolyte (SE)-liquid electrolyte (LE) configuration shown in Figure 3.10 was assembled and its electrochemical behaviors were studied. In this configuration, lithium ions have to move through the SE and SEILE interfaces since the center disc is hermetically sealed against the liquid electrolyte. The charge/discharge curves of the first cycle are shown in Figure 3.11(a), along with the impedance change before and after cycling in Figure 3.11(b). The charge capacity was 154 mAh/g and discharge capacity was 153 mAh/g. In the Nyquist plot, the high frequency arcs of all spectra display resistance of between 800 and 900 Ohms, which is on the order of the expected value of the solid electrolyte disc (600 Ohms). Both



Figure 3.11 (a) Charge/discharge curves of the electrochemical cell with solid electrolyte at room temperature. The charge capacity was 154 mAh/g and discharge capacity was 153 mAh/g. (b) Impedance evolution of the electrochemical cell in the first cycle.

the high frequency and low frequency features change with the cycling, which suggests complicated dynamics of the SEILE interface and possibly mixed conduction of the solid electrolyte. More detailed studies of interfacial behavior of SEILE interface and solid electrolytes are in progress. This experiment demonstrates that lithium garnet oxides support ionic transport that is relevant for lithium battery applications.

# 3.6 A Second Look at the Phase of LLZTx Series

In the study described above, all the powders of the LLZTx series were calcined in Al<sub>2</sub>O<sub>3</sub> crucible in air. In this section, the phase of the LLZTx series is studied more rigorously using the second solid state route which eliminates Al-contamination and air exposure. The MgO crucible do not react with LLZTx compounds at 900 °C which was

confirmed by LA-ICP-MS (Laser ablation-Inductively coupled plasma-Mass spectroscopy) experiment where very small quantity of Mg (10-20 ppm) was detected.



Cation Doping Induced Phase Transition

Figure 3.12 Powder X-ray diffraction patterns of  $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$  (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) taken with D8 ADVANCE diffractometer.

Surprising results were acquired for the new batch of LLZTx compounds. The XRD patterns of LLZTx series (x = 0 - 0.6) are shown in Figure 3.12. The x = 0 composition LLZ still has pure tetragonal phase; pure cubic phase is achieved only when x = 0.6. However, for x = 0.1 - 0.5, peaks of both tetragonal phase and cubic phase are present and overlap strongly. This is due to the close relation of the tetragonal and cubic lattices and poor angular resolution of the diffractometer. Nevertheless, it can still be seen



Figure 3.13 Zoomed-in version of powder x-ray diffraction patterns of  $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (x = 0, 0.3, 0.6).



Figure 3.14 Tetragonal phase fraction of composition  $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$  (x = 0 - 0.6) determined by Rietveld refinement.

(Figure 3.13) that the peak positions of both tetragonal and cubic phase match well with the two end members LLZ and LLZT0.6. Therefore, we hypothesize that the tetragonalcubic phase transition due to Ta-doping occurs through a two-phase mechanism. The relative tetragonal-cubic phase fractions were determined using Rietveld refinement implemented by GSAS. The results are shown in Figure 3.14. The tetragonal phase fractions are largely consistent with the lever rule assuming the two end members are LLZ (T) and LLZT0.6 (C).

#### 3.7 Summary

Lithium garnet oxides with formulas Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>3</sub>O<sub>12</sub> (x = 0 - 2) were successfully synthesized by the solid state reaction method. For the first batch of powder prepared in Al<sub>2</sub>O<sub>3</sub> crucible in air, single cubic phases were observed in the composition x range between 0.2 and 2, while Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (x = 0) displayed a tetragonal structure. The lattice parameters decreased with the addition of Ta due to the smaller ionic radius of Ta<sup>5+</sup> compared with Zr<sup>4+</sup>, following the Vegard's law. For the second batch of powder prepared in MgO crucibles in Ar, tetragonal and cubic phases coexist for x = 0.1 - 0.5. The discrepancy can be attributed to the Al-contamination and air exposure effect. Nonetheless, pellets with relative density above 91% were obtained through sintering using the first batch of powder. The maximum bulk conductivity was achieved for x =0.3, with a value of 9.6×10<sup>4</sup> S/cm at room temperature and an activation energy of 0.37 eV. The total conductivity of the x = 0.3 composition was  $6.9 \times 10^{-4}$  S/cm at room temperature with an activation energy of 0.36 eV. These lithium garnet oxides exhibit lithium ionic transport that is relevant for lithium battery application.

### Chapter 4 Structural Study by Neutron Diffraction and Computer Simulation

## 4.1 Abstract

In previous chapter, the phase and ionic conductivity of the LLZTx series have been discussed. This chapter focuses on the structural aspect of the garnet series to shed light on the compositional dependence of the conductivity, tetragonal-cubic phase transition and the conduction mechanism. In the first part, the average structures of the LLZTx series studied by Rietveld refinement based on TOF neutron diffraction are discussed which is complemented by lattice energy calculation. In the second part, pair distribution function analysis based on total neutron scattering data is performed on a model cubic garnet Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> to probe the local lithium environment.

4.2 Neutron Diffraction and Atomistic Simulation of Lithium Garnets Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> Series

#### 4.2.1 Average structure study by neutron diffraction

## 4.2.1.1 Cubic garnets

For cubic garnets, unanimously, tetrahedral lithium atoms were considered to reside at 24d site. Several structural models[88, 154, 160-162] differing in the assignment of octahedral Li have been used in literature. Two crystallographic sites have been used for the octahedral Li: ideal 48g site and two split, i.e. 96h, sites (Figure 4.1a,b). Each Li octahedron (Oh) shares faces with two Li tetrahedra (Td). Each Li tetrahedron share faces with four Li octahedra. All reports treated ADPs of all Li sites isotropic.



Figure 4.1 Schematics of three Li sites: 24d (pink), 48g (blue) and 96h (yellow). (a) One Li octahedron (Oh) shares faces with two Li tetrahedra (Td). (b) One Li tetrahedron share faces with four Li octahedra. (c) Connectivity of Td and Oh lithium atoms shown schematically in 2D.

In our study, six structural models for lithium disorder at Td and Oh sites have been used in the Rietveld refinement. 1) lithium at 24d Td site and 48g Oh site as 24d-48g model; 2) 24d-96h model; 3) 24d-48g/96h model; 4) 24d-48ganis in which anisotropic ADPs were used for 48g site; 5) 96h-96h in which split-site model was applied at Td site as well; 6) 24danis-48ganis in which anisotropic ADPs were used for both sites. Partial occupancy and ADPs of lithium from Rietveld refinement on neutron data of compositions LLT, LLZT and LLZTO.3 at 10 K were shown in Table 4.1, for the first five

models. Td 24*d* or 96*h* occupancy was normalized to a total number of 24 lithium atoms while Oh 48*g* or 96*h* occupancy was normalized to a total number of 48 lithium atoms.

For all three cubic compositions, the models that split sites or use anisotropic ADPs for Oh site (24d-96h and 24d-48ganis) generally fit experimental data better than 24d-48g model, indicating that at least a portion of octahedral lithium ions are displaced. Adding 48g site to the 24d-96h model improved the fit slightly. It was difficult to judge whether the improvement reflected the intrinsic advantage of the 24d-48g/96h model or was simply the result of more refinable terms. The reduction of  $R_{wp}$  and  $\chi^2$  by adopting the split-site model was more pronounced for LLZT and LLZT0.3, compared to LLT. It seemed clear that there was a tendency to favor the split-site model or anisotropic model as Li content increased. This suggests that the nuclear density at the octahedral site becomes more dispersed at higher Li content. This is indeed observed in our simulation results and will be revisited in later sections.

For the disorder at Td site, there was no obvious advantage of using the *96h-96h* model since negative  $U_{iso}$  appeared and/or the  $R_{wp}$  and  $\chi^2$  were not improved. Model with anisotropic ADPs at the *24d* site, i.e. *24d*anis-*48g*anis model, gave negative  $U_{11}$ . However, this does not completely exclude the possibility of these two disorder models. If we manually set  $U_{iso}$  or  $U_{11}$  at *24d* site to a small positive number, disc-shape atomic Table 4.1 Comparison of 10 K refinement results of cubic compositions Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>, Li<sub>6</sub>La<sub>3</sub>ZrTaO<sub>12</sub> and Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub>

with different models.

	Li <sub>5</sub> La <sub>3</sub> Ta <sub>2</sub> O <sub>12</sub>					Li <sub>6</sub> La <sub>3</sub> ZrTaO <sub>12</sub>				Li <sub>6.7</sub> La <sub>3</sub> Zr <sub>1.7</sub> Ta <sub>0.3</sub> O <sub>12</sub>					
Model	24d- 48g	24d- 96h	24d- 48g/96h	24 <i>d</i> - 48g anis	96h- 96h	24d- 48g	24d- 96h	24d- 48g/96h	24 <i>d</i> - 48g anis	96h- 96h	24d- 48g	24d- 96h	24d- 48g/96h	24d- 48g- anis	96h- 96h
$R_{wp}$	4.33	4.32	4.29	4.32	4.30	5.20	5.02	5.01	5.06	4.99	3.93	3.82	3.81	3.83	3.79
$\chi^2$	1.76	1.76	1.74	1.76	1.75	1.98	1.91	1.91	1.93	1.91	1.92	1.86	1.86	1.87	1.85
24d/96h (Td) occu.	0.75	0.73	0.72	0.72	0.73	0.61	0.57	0.57	0.51	0.56	0.61	0.55	0.56	0.49	0.53
$24d/96h$ (Td) $100 \cdot U_{iso}$ (Å <sup>2</sup> )	2.0	1.9	1.8	1.8	0.02	3.3	2.6	2.6	2.6	-0.3	3.7	2.7	2.9	2.8	-0.9
48g (Oh) occu.	0.46	-	0.23	0.47	-	0.70	-	0.14	0.74	-	0.81	-	0.40	0.87	-
$48g$ (Oh) $100 \cdot U_{iso}$ (Å <sup>2</sup> )	8.0	-	12.0	*	-	5.6	-	1.9	*	-	6.8	-	3.9	*	-
<i>96h</i> (Oh) occu.	-	0.46	0.24	-	0.48	-	0.72	0.58	-	0.72	-	0.84	0.44	-	0.86
96h (Oh) $100 \cdot U_{iso}$ (Å <sup>2</sup> )	-	5.1	1.1	-	5.5	-	1.8	1.3	-	1.9	-	2.6	0.4	-	2.8
* Anisotropic ADPs ( $100 \cdot U_{ij}$ ) in the order of $U_{11}$ , $U_{22}$ , $U_{33}$ , $U_{12}$ , $U_{13}$ , $U_{23}$ of (a) LLT: 11.6, 8.4, 8.4, -4.1, -4.1, -1.2; (b) LLZT: 18.1, 3.1, 3.1, -4.9, -4.9, 2.1; (c) LLZT0.3: 24.4, 2.5, 2.5, -3.5, -3.5, 2.5.															

displacement was obtained, similar to that that from atomistic simulation, to be discussed later. In our opinion, this suggests one of the limitations of only applying one technique, e.g. the Rietveld refinement, to study disorder in complex materials.

Comparing the results from 24d-96h model, tetrahedral Li occupancy dropped from 73% to 57% as Li content increased from 5 to 6; the drop was minimal as Li content increased from 6 to 6.7. The overall negative correlation is consistent with literature results.[154] However, the occupancy values extracted from diffraction techniques should not be blind-trusted, and indeed they were quite model-dependent as shown in Table 4.1.

The lattice parameters displayed good linearity with respect to Ta doping level, obeying the Vegard's law. Marginal change of tetrahedral occupancy was observed with results refined using 300 K data. The *U*<sub>iso</sub> of tetrahedral Li and octahedral Li increased only slightly from 10 K to 300 K, which is characteristic of positional disorder.

## 4.2.1.2 Tetragonal garnet Li7La3Zr2O12

The refinements for both 10 K and 300 K data were initiated with Awaka et al.'s refined structure[93] where *8a*, *16f*, *32g* sites of space group *I*4<sub>1</sub>/*acd* (No. 142) were fully occupied by Li. Satisfactory fit was achieved. Parameters of refined structure of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZ) at 10 K are tabulated in Table 4.2.

Atom	Pos.	Frac.	Х	У	Z	$\frac{100 \cdot U_{iso}}{(\text{\AA}^2)}$					
La1	8b	1	0	0.25	0.125	0.024(16)					
La2	16e	1	0.1274(8)	0	0.25	0.076(13)					
Zr	16c	1	0	0	0	0.099(13)					
Li1	8a	1	0	0.25	0.375	0.42(9)					
Li2	16f	1	0.1798(3)	0.4298(3)	0.125	1.11(10)					
Li3	32g	1	0.0813(3)	0.0871(3)	0.8057(3)	0.80(6)					
01	32g	1	0.9655(1)	0.0555(1)	0.1529(1)	0.276(16)					
O2	32g	1	0.0544(1)	0.8527(1)	0.5343(1)	0.283(16)					
O3	32g	1	0.1499(1)	0.0280(1)	0.4471(1)	0.232(16)					
$I4_1/acd, a$	$I4_{1}/acd, a = 13.1065(1), c = 12.6143(1), R_{wp} = 4.21, \chi^{2} = 1.36$										

Table 4.2 Parameters of refined structure of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> at 10 K.

Coordinates and lattice parameters are in rather good agreement with the literature results. Space group of No. 142 belongs to subgroups of space group No. 230. Upon symmetry reduction, 24d site in space group No. 230 splits into 8a and 16e sites; 48g site splits into 16f and 32g sites. The octahedra (Oh) hosting 32g site are sandwiched by one tetrahedron hosting 16e site and one tetrahedron (Td) hosting 8a site whereas the octahedra hosting 16f site are sandwiched by two tetrahedra hosting 16e site. With full population of 8a, 16f and 32g sites, the occupancy of octahedral sites and tetrahedral sites in the tetragonal LLZ phase are 1 and 1/3. This kind of Li ordering ensures that an occupied Td-Oh-Td lithium triplet is avoided. Close inspection reveals that Li ions in 32g octahedra are pushed off center by neighboring 8a Li to give a Li-Li separation distance of 2.551 Å. As a result, the distance between empty 16e site and 32g Li ions is only 1.448 Å. In an attempt to fit the neutron diffraction data with a model where 16e

site was also accessible to Li, the refinement process reduced the *16e* occupancy to zero along with a very large *U*<sub>iso</sub>, both diminishing the scattering contribution of *16e* sites. It is safe to conclude that there is no experimental evidence on occupation of *16e* site in tetragonal LLZ. Refinement on neutron data at 300 K was performed with the same *8a-16f-32g* model. The lattice expanded 0.06% along *a*-axis and 0.34% along *c*-axis. Change in coordinates of all atoms is minimal.

#### 4.2.2 Local structure study by atomistic simulation

#### 4.2.2.1 Validity of potential models

Table 4.3 Comparison of experimental and simulated structures using interatomic potential parameters in Table 2.1.

	$\frac{\text{LiTaO}_3}{\text{Expt.}  \text{Calc.}}$		$\frac{\text{La}_2\text{Zr}_2\text{O}_7}{\text{Expt.}  \text{Calc.}}$		La <sub>3</sub>	TaO <sub>7</sub>	Li7La	$_{3}$ Zr <sub>2</sub> O <sub>12</sub>	Li <sub>5</sub> La <sub>3</sub> Ta <sub>2</sub> O <sub>12</sub>		
					Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	
Lattice	Rhomb	Rhombohedral		Cubic		Orthorhombic		Tetragonal		Cubic	
a (Å)	5.1543	5.1051	10.8042	10.7459	11.1863	10.9026	13.1065	13.0834	12.7889	12.748	
b (Å)	-	-	-	-	7.6152	7.6546	-	-	-	-	
c (Å)	13.7835	13.6921	-	-	7.7556	7.7371	12.6143	12.6249	-	-	

To test interatomic potential parameters in Table 2.1, we performed structural optimization of three known structures, rhombohedral LiTaO<sub>3</sub>,[163] cubic La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>,[164] and orthorhombic La<sub>3</sub>TaO<sub>7</sub>[165] along with the end members in the garnet series, Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (in space group No. 142) and Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> (in space group No. 1) under the constant pressure condition. Table 4.3 compares experimental and simulated lattice

parameters of all five structures. The optimized structures are in good agreement with experimental results.



#### 4.2.2.2 Energy distribution of ordered Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>

Figure 4.2 Static energy versus structure number plot (left) and energy probability distribution (right) of tetragonal Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>. Structures at the highest peak have the same lithium distribution as the Rietveld refined structure.

5000 initial structures were employed and optimized with the interatomic potential parameters and around 5000 structures were optimized successfully. These structures were ranked in increasing energy values. Figure 4.2 shows the energy versus structure number plots (energy plot) and energy probability distribution histogram of tetragonal LLZ. The energy distribution charts were generated by binning the energy with a bin width of 0.025 eV and normalizing the count to the total number of optimized structures. Each of the optimized structures represents a local minimum that the initial structure lies close to. The probability distribution charts could provide a rough idea of the energy landscape of a system. For instance, the probability distribution of tetragonal LLZ has three sharp peaks on the low end of energy spectrum and the plateaus on the energy plot indicates that the structures at each of the three peaks have exactly the same energy value. So the energy landscape consists of three large local minimums with low energy values and multiple local minimums with high energy value.

Table 4.4 Static structure information of tetragonal Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> from atomistic simulation (asterisk peak in Figure 4.2). Lattice parameters and space group are the same as those in Table 4.2.

Atom	Pos.	Frac.	Х	У	Z
La1	8b	1	0	0.25	0.125
La2	16e	1	0.1261	0	0.25
Zr	16c	1	0	0	0
Li1	8a	1	0	0.25	0.375
Li2	16f	1	0.1787	0.4287	0.125
Li3	32g	1	0.0847	0.0856	0.8047
O1	32g	1	0.9650	0.0555	0.1557
O2	32g	1	0.0561	0.8516	0.5339
03	32g	1	0.1517	0.0277	0.4469

Although no symmetry constraints were imposed on atomic positions during the energy optimization of tetragonal LLZ (*P1* space group was used), it was found that all atoms in structures of the asterisk-labeled peak in Figure 4.2 are ordered and follow exactly the crystal symmetry of space group No. 142. The obtained atomic coordinates,

very similar to those in Table 4.2, are listed in Table 4.4. For the other two smaller peaks with lower energies, small displacement from the ideal sites in Table 4.4 was observed. Thus structures at the asterisk peak can be considered to represent the static structure, while structures at two other peaks represent the dynamic displacement. The matching between the atomistic simulation results and diffraction/Rietveld refinement results provides additional validation of our potential models.

#### 4.2.2.3 Energy distribution of disordered Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>

The energy landscape of LLT in cubic lattices is very different from that of tetragonal LLZ, as can be deduced from the energy and probability plots in Figure 4.3. The energy plot is smooth and continuous with no plateaus, which indicates that no structures have exactly same energy. The probability distribution chart is characterized by a single Gaussian peak. Thus the energy landscape comprises of large number of local minimums with energy values close to the mean value of the Gaussian peaks and few local minimums with lower or higher energies. No lithium ordering was observed in any of the simulated structures.

While the real ordered LLZ crystal can be represented by a single asterisk peak in Figure 4.2, how are different 1×1×1 cell structures in Figure 4.3 related to real LLT crystals? We further performed the energy minimization of LLT in 2×2×2 cells with 1000 initial structures. The lattice energies of 2×2×2 structures were divided by 8 to compare

those of 1×1×1 cells. The distribution can also be fitted to a Gaussian distribution function, as shown in Figure 4.3. The mean values for the 1×1×1 (-4899.96 eV) and 2×2×2 cells (-4900.02 eV) are almost the same, indicating that the average lattice energy of a unit cell did not change much with the increasing box size. The standard deviation is reduced by a factor of 2.8 by increasing the box size 8 times (0.18 eV vs 0.50 eV). This value is very close to  $\sqrt{8}$ .



Figure 4.3 Static energy versus structure number plot (left) and probability distribution (right) of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>. The lines are fitted curves by a Gaussian distribution function.

In the context of statistics, this dependence reminds us of a special property of Gaussian distribution[166]:

Suppose that the random variables  $X_1$ , ...,  $X_n$  form a random sample from the normal distribution with mean  $\mu$  and variance  $\sigma^2$ , and let  $\overline{X_n}$  bar denote their sample mean. Then  $\overline{X_n}$  has the normal distribution with mean  $\mu$  and variance  $\sigma^2/n$ .

The fact that the standard deviation of the energy distribution of  $2\times 2\times 2$  cells is  $\sqrt{8}$ times of that of 1×1×1 cells implies that 2x2x2 calculations have no significant correlations between the unit cells so that the energy contribution of one unit cell is completely independent of the energy contribution from a neighboring cell. The 2×2×2 configurations could be considered as eight 1×1×1 structures which are randomly selected from the 1×1×1 configuration space merged into one block. This is surprising for ordinary crystals. This weak correlation between neighboring unit cells can be understood by the disordered nature of the LLT. In the context of statistical thermodynamics, the energy fluctuation of a canonical ensemble has the same square root dependence on the sample size.[167] It is to be noted that we were probing the energy probability distribution and not the density of state in Figure 4.3, so we will not carry out the Boltzmann averaging. Instead, our hypothesis is that structure of a macroscopic LLT crystal can be approximated by stitching 1×1×1 cells in real space. In other words, we will apply unit-weighting to study the structure of these disordered solids. The unit-weighting method is by no means the most correct choice but it facilitates us to understand the structure evolution with composition variation.

#### 4.2.2.4 Energy distribution of intermediate compositions.

The energy plots and energy distribution histograms of intermediate compositions are shown in Figure 4.4. The probability distributions (Figure 4.4) can be viewed as a gradual evolution from that of disordered LLT to ordered LLZ. Specifically, from LLZT1.5 to LLZT0.75, they are characterized by a single Gaussian peak as in LLT. From LLZT0.5 to LLZT0.125, a second peak appears on the lower end of energy spectrum and grows at the expense of the first Gaussian peak. Eventually, the high-energy peak gives way to the low-energy peak completely and the peak becomes increasingly spiky. Careful inspection of the energy plots reveals the fundamental difference of the two peaks: in the region of Gaussian peaks, the curve is smooth and continuous; in the region of the low energy peaks, the curves comprises of plateaus on which structures have exactly the same energy. The size of plateaus becomes larger as Li content increases and LLZT0.125 has a low-energy plateau similar to that in LLZ.

We think the tendency for lithium order is positively correlated to the Li content from 5 to 7 and the order-disorder transition is smooth rather than abrupt. For these disordered solids with intermediate compositions, we will apply the same unitweighting to study their structural features.



Figure 4.4 (a) Static energy versus structure number plot and (b) probability distribution of intermediate compositions,  $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$  (x=0.125, 0.25, 0.5, 0.75, 1, 1.5).

# 4.2.2.5 Average structure (partial occupancy and nuclear density map) from atomistic simulation

Before examining local lithium disorder at the tetrahedral (Td) and octahedral (Oh) sites, we will compare site occupancies from averaging the energy landscape (labelled as Sim in Figure 4.5) with those from the Rietveld refinement (labelled as Exp in Figure 4.5) and exclusion principle[160, 162] (labeled as Exc in Figure 4.5).[160] The simulated Td(Li) occupancy was calculated by counting the number of lithium ions within spheres of 0.75 Å radius centered at ideal 24d positions. The idea of exclusion principle originated from Cussen and O'Callaghan, [162] who proposed that out of three neighboring Td-Oh-Td lithium sites, only two at maximum could be occupied to avoid short Li-Li interaction. Based on this exclusion principle, predictions of tetrahedral Li occupancy as a function of Li content were made which proposed that Li content could not exceed 7.5.[160] Our simulation predicted an overall sharper decrease of tetrahedral Li occupancy with increasing Li content than our refinement results and exclusion principle prediction. We think that Cussen's argument has merits which are evident in understanding the negative correlation of Td lithium site occupancy and Li content, but it may be an over-simplification of the real case. In later section, we will see that the Td-Oh-Td lithium triplets are actually viable local configurations in cubic structures.



Figure 4.5 Simulated (labeled as Sim) compositional dependence of Td and Oh lithium site occupancies. Results from Rietveld refinement of experimental diffraction data (labeled as Exp) and from exclusion principle (labeled as Exc) are also presented.



Figure 4.6 Simulated nuclear density maps of La (a) and Ta (b) of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>. Isosurface level 0.8 Å<sup>-3</sup>. Density maps are isolated spheroids centered around positions from the Rietveld refinement.

In addition to partial occupancy, the average structure from atomistic simulation can be better visualized in the form of 3D nuclear density maps/probability density functions (pdfs) of specific atoms. These density maps were generated by dividing the unit cell into  $128 \times 128 \times 128$  pixels and calculating pdfs of atoms of interest within each pixel over optimized structures. The 3D density maps of La and Ta (Figure 4.6) at an isosurface level of 0.8 Å<sup>-3</sup> consist of small isolated spheroids centered around the Rietveld refined positions, suggesting that the movements of these atoms are small during the optimization and the overall *Ia-3d* space group symmetry are retained for these elements.

The 3D density maps of Li in cubic garnets (Figure 4.7 left) are much more delocalized. The shape of nuclear density in the Td regions resembles a flat square pulled at the ends of two diagonals in different directions. As discussed in earlier section, the Rietveld refinement showed signs of similar disc-shape displacement. In comparison, the nuclear density in the Oh regions is rod-like. From LLT to LLZT0.25 (a to c), the density in the Oh region grows while the density in the Td region shrinks, consistent with the Rietveld refinement results. The density maps of high Li content compositions, e.g. LLZT0.25, connect to form a continuous channel-like network even at high isosurface levels. The 2D density maps on slices cutting through Td-Oh-Td sites (Figure 4.7 right) reveal that the nuclear density at the Oh site is more dispersed as the



Figure 4.7 Isosurfaces (level of 0.8 Å<sup>-3</sup>) of simulated Li nuclear density map and 2D maps (saturation levels from 0.5 Å<sup>-3</sup> to 5 Å<sup>-3</sup>) on slices cutting through Td-Oh-Td sites of (a) LLT (b) LLZT (c) LLZT0.25 in the static limit.



Figure 4.8 Isosurfaces (level of 0.8 Å<sup>-3</sup>) of nuclear density maps and 2D maps (saturation levels from 0.5 Å<sup>-3</sup> to 5 Å<sup>-3</sup>) generated from Rietveld refinement results of (a) LLT (b) LLZT (c) LLZT0.25 in the static limit.

lithium content increases. Overall, lithium distribution in these lithium garnet oxides exhibits features that can be expected in liquid and amorphous materials. Apparently, models based on harmonic ADPs (as in the standard Rietveld refinement) cannot capture the complicated shape of these nuclear density maps. However, it is still worthwhile comparing density maps from two approaches. 3D nuclear density maps of lithium and 2D slices generated from Rietveld refinement results using 24d-48ganis model are shown in Figure 4.8. Lithium distribution from two approaches is qualitatively similar. It is noted that the density at the octahedral region of Figure 4.8 also increasingly elongates towards the tetrahedral region as Li content increases. From the nuclear density maps we can infer the possible conduction pathways. In the literature, two conduction mechanisms have been proposed based on diffraction and nuclear magnetic resonance (NMR) studies[91, 92] on various garnet compounds: the direct Oh-Oh jump and the correlated Oh-Td-Oh route. NMR results[91, 92] that the locations and dynamics of Li ions in Li5La3Nb2O12 depended on thermal history and further concluded that octahedral lithium ions were the mobile species whereas tetrahedral lithium ions were immobile on the time scale of NMR experiment. However, the determined occupancies of 24d site and 48g site were at odd with results of diffraction studies. MD simulation showed that the hopping between Td and Oh sites were likely responsible for Li-ion transport.[90] Judging from the nuclear density maps,

we highly favor the Oh-Td-Oh route although the present structure study does not provide direct information on the Li conduction pathway.

## 4.2.2.6 Local clusters around Td lithium sites

As shown in Figure 4.1, lithium Td sites are connected to four Oh sites by shared faces. We define the 'coordination' number (CN) of an occupied or unoccupied Td site density resembles a small tetrahedron summing up contributions from all 6 configurations. The repulsion from La bends the two edges inward and flattens the whole tetrahedron, giving the simulated shape. The shape with other CNs can be explained in the same fashion. as the number of lithium Oh atoms within a 2.5 Å distance. Figure 4.9 shows the compositional dependence of the fractions of empty Td sites (Figure 4.9a) and occupied Td sites (Figure 4.9b) with different CNs. Nearly all



Figure 4.9 Compositional dependence of fractions of (a) empty tetrahedral Li sites (b) occupied tetrahedral Li sites with different 'coordination' numbers (CNn) (n = 0, 1, 2, 3, 4).



Figure 4.10 Simulated density maps of tetrahedral Li with (a) CN2 in Li<sub>6</sub>La<sub>3</sub>ZrTaO<sub>12</sub> (b) CN3 in Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.75</sub>Ta<sub>0.25</sub>O<sub>12</sub>. (c) Schematic explanation of the shape of Li density map with CN2.

empty Td sites are surrounded by three or four Oh lithium atoms. At high Li contents, the CN4 fraction is nearly 1. For the occupied Td sites, the curves of CN0, CN1, CN3, CN4 are monotonically increasing or decreasing except the curve for CN2, i.e. nearest-neighbor (Oh, $\Box$ )-Td-(Oh, $\Box$ ) lithium cluster, which maximizes at Li content 6.75. The shape of the curve is reminiscent of the conductivity dependence on compositions in Chapter 3. It is likely that (Oh, $\Box$ )-Td-(Oh, $\Box$ ) lithium clusters are most advantageous for conduction. The disc-like tetrahedral lithium distribution in is strongly shaped by Li-Li

and La-Li Coulombic repulsion. This is evident in the density maps where only tetrahedral lithium ions with specific CN, e.g. CN2 and CN3 in Figure 4.10a and Figure 4.10b, respectively, are counted. CN2 has the overall disc shape while CN3 resembles a distorted cross. Figure 4.10c illustrates how Li-Li and La-Li repulsion shape the density map of CN2 Li. Two octahedral lithium ions push the tetrahedral lithium onto a line as shown in red, and the shape of nuclear

#### 4.2.2.7 Local clusters around Oh lithium sites.

As shown in Figure 4.1 lithium Oh sites are connected to two Td sites by shared faces. The nearest-neighbor CNs for Oh sites are thus 0, 1, and 2. Figure 4.12 shows the compositional dependence of the fractions of occupied Oh sites with different CNs. The exclusion principle places the Td lithium at ideal 24d site. If the nearest-neighbor Oh lithium is occupied, it has to be displaced to 96h site and the next Td lithium site has to be empty, as shown schematically in Figure 4.11a. Such pairs were observed in our simulation as CN1, i.e. Td-Oh- $\Box$ , although tetrahedral lithium was displaced from 24d site. The CN2 clusters, i.e. Td-Oh-Td lithium triplets, are not allowed in the exclusion principle. However, we observed many such triplets in cubic garnets and the triplet fraction decreases with increasing lithium content. As can be seen in Figure 4.12, the exclusion principle is only valid at the highest lithium content, i.e. tetragonal LLZ. In Td-Oh-Td lithium triplets, Td lithium atoms are displaced away from 24d site and Oh

lithium atoms lie closer to ideal octahedral site, i.e. *48g*, as shown in Figure 4.11b. Similarly, Oh lithium in CN0 cluster is close to *48g* site as well.



Figure 4.11. Li distributions in neighboring Td-Oh-Td sites (a) based on exclusion principle (b) observed in our simulation.



Figure 4.12 Compositional dependence of fractions of occupied octahedral Li sites with 'coordination' numbers (CNn) (n=0, 1, 2).

#### 4.2.2.8 Nearest-neighbor Td-Oh lithium pairs

In addition to local environment around Td and Oh lithium atoms, the study of overall nearest-neighbor Td-Oh lithium pairs could also provide insight into lithium distribution. The average distance of the nearest-neighbor Td-Oh lithium pairs varies from 2.42 Å to 2.58 Å depending on the composition (Figure 4.13). The initial increase with Li content is likely due to the lattice parameter increase. When Li content is above 6.5, the average Li-Li distance decreases despite the increase in lattice parameter. This reduction may be a result of space limitation as the number of lithium increases and this inevitably increases the repulsion of Td-Oh lithium pairs. We further calculated the average number of such lithium pairs for all compositions. The number of pairs increases monotonically with Li content for the disordered systems, which also results in increase of Li-Li repulsion. In the ordered tetragonal phase (lithium content 7), the largest separation distance of 2.58 Å and the smallest number of Li-Li pairs, e.g. 32, was observed. Based on these observations, it is possible that the minimization of Td-Oh lithium pair repulsion is the driving force to the disorder-order transition. On the other hand, a certain amount of repulsion between Li ions may be a key to destabilize the Li ions and enhance mobility which is strongest for the cubic compositions with high Li content. This is largely consistent with conclusion from our conductivity study that the bulk conductivity is highest around Li content 6.7.



Figure 4.13 Simulated compositional dependence of nearest-neighbor Li-Li average distances and number of Td-Oh lithium pairs.

# 4.2.2.9 Cubic-tetragonal phase transformation in LLZ

The cubic-tetragonal phase transformation has two important aspects: the change in crystal symmetry and the order-disorder transition of Li ions. As illustrated in earlier section, the ordering of Li is simply the result of Li-stuffing. As the number of Li in a unit cell increases, the constraints on Li distribution imposed by Li-Li repulsion becomes so stringent that lithium ions order in a fashion that reduces the total lattice energy. In the extreme case of LLZ, a nearly complete ordering occurrs under cubic symmetry which proves that tetragonal lattice is not a necessary condition of Li-ordering. Manual analysis of structures at the highest peak of cubic LLZ revealed that the Li distributions are very similar to that in tetragonal LLZ. All the octahedral sites

are occupied; the remaining eight Li ions occupy the tetrahedral sites in a manner similar to *8e* sites. After reorienting all the structures according to the unique axis, the density map of tetrahedral Li was generated (Figure 4.14). All the nuclear densities inside the tetrahedra are concentrated at two very small regions which are roughly 0.25 Å away from the ideal *24d* sites. Density map including octahedral Li showed that the nuclear densities of octahedral Li are also very concentrated. These density maps are in stark contrast with the disordered structure, marking the disorder-order transition.



Figure 4.14 Comparison of 24*d* Li density maps of LLZ under (a) tetragonal lattice and (b) cubic lattice.

# 4.3 Pair Distribution Function Analysis of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>

# 4.3.1 Rietveld Refinement

The average structure of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> was determined by Rietveld refinement. Although study of the average structure is not the focus of this section, it is performed for the purpose of generating initial structures and comparing the average and local models.

When the ADPs of all atoms are set to be isotropic, La, Ta and O atoms have normal values of atomic displacement factors for thermal vibrations of crystalline materials; the ADPs for lithium (Table 4.5) are unusually large for both sites, characteristic of positional disorder. Therefore, the garnet structure consists of frameworks composed of ions other than lithium and channels in which lithium ions behave in a diffused manner. As the temperature increases, the lattice expands and the ADPs of both lithium sites increase. The occupancies of 24d site remain largely unchanged. Attempts to split the 24d sites into four 96h sites led to unphysical and unstable results. These results are consistent with conclusion from previous section.

Table 4.5 The Rietveld refinement results of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> collected at 15 K, 300 K and 550 K using isotropic model.

	15 K	300 K	550 K
Lattice parameter (Å)	12.7409(12)	12.7702(12)	12.7989(14)
24d occupancy	0.749(12)	0.757(12)	0.757(15)
48g occupancy	0.458(6)	0.454(6)	0.454(7)
$24d \ 100 \cdot U_{iso} \ (\text{\AA}^2)$	2.56(14)	3.29(15)	3.99(19)
$48g \ 100 \cdot U_{iso} \ (\text{\AA}^2)$	4.59(23)	5.02(25)	5.56(30)

Using an alternative model where the ADPs of all atoms except 24*d* Li are set to be anisotropic, the goodness of fit was greatly improved (from 13.3 to 9.75). All atoms

display certain degree of anisotropy with 48g Li being the strongest. The relative values of  $U_{ij}$  (Table 4.6) are in qualitative agreement with O'Callaghan's refinement[87] on garnet compound Li<sub>3</sub>Nd<sub>3</sub>Te<sub>2</sub>O<sub>12</sub>.

Table 4.6 Anisotropic ADPs (in Å<sup>2</sup>) of Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> at 15 K derived from Rietveld refinement

<i>48g</i> Li			La			Ta		0						
100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.
$U_{11}$	$U_{22}$	$U_{12}$	$U_{23}$	$U_{11}$	$U_{22}$	$U_{23}$	$U_{11}$	$U_{12}$	$U_{11}$	$U_{22}$	<i>U</i> 33	$U_{12}$	$U_{13}$	$U_{23}$
14.3	1.7	-35	0.4	1.0	0.4	0.2	0.3	0.03	0.9	0.5	0.9	-0.01	0.04	-1.1

## 4.3.2 Experimental Data

The normalized total-scattering intensity S(Q) of 15 K data is shown in Figure 4.15. Ideally, S(Q) should remain flat at 1 for large Q. In this experiment, the S(Q) value slowly decreases with Q at high Q. We speculate that an artificial background is present in the whole Q range and likely to be due to incorrect absorption corrections as deduced from the differences of the experimental S(Q) and fitted S(Q). Fortunately, this kind of artificial background is usually a slow varying function of Q which only modifies the low r end of the PDFs where no structural information is contained. The effect can be seen from the noises in G(r) at low r (discrepancy of the dotted baseline and experimental pattern below the first peak). Nevertheless, the low r noise have negligible effects on the high *r* region so the effect of noise is minimized by fitting over the whole range of *r* (1.75 Å < *r* < 20 Å).



Figure 4.15 (a) Reduced S(Q) of 15 K data. The dotted red line is the baseline to which S(Q) should approach at high Q. (b) A comparison of experimental G(r) of three temperatures. Experimental data and fitted curves are represented by circle symbols and lines. The baseline has the value of  $(\sum_{i=1}^{n} c_i b_i)^2$ . The 300 K and 550 K curves are shifted vertically for clarity.

# 4.3.3 RMC Modeling and Partial PDFs

Good fit was achieved for all temperatures using RMC modeling. There are 22000 atoms in the model, each having three degrees of freedom. The total number of variables is much larger than the number of uncorrelated data points, so the fitting problem is severely under-constrained, i.e., many solutions satisfy the experimental constraints. Nevertheless, different solutions may give us equivalent structural
information such as partial PDFs if these quantities are obtained by summation or integration. In this sense, there may be one unique solution to each data set. To check if this is the case, results from 40 separate trials with the same initial condition were compared. Furthermore, the correctness of the solution should be judged from the soundness of the physical meanings.

It was found that the partial PDFs did not vary much from trial to trial. We obtained the partial PDFs by averaging over all trials (Figure 4.16). The partial PDFs involving La and Ta, as shown in Figure 4.16a, consist of distinct Gaussian-type peaks at both short and long distances, characteristic of long-range ordering in typical crystalline materials. Partial PDFs of pairs involving O atoms exhibit short-range ordering (strong peaks at short distances) and oscillation around 1 at long distances in Figure 4.16b. For the pairs involving Li atoms (Figure 4.16c), partial PDFs have broader peaks with smaller values



Figure 4.16 Partial PDFs of (a) pairs containing La and Ta, (b) pairs containing O but no Li and (c) pairs containing Li at 15 K. The flat portion before the first peak in all partial PDFs has value of 0. The red dotted line has value of 1.

at both short and long distances. Figure 4.16 suggests that the structure is composed of solid-like atoms such as La/Ta, liquid-like atom such as Li, and intermediate atom such as O. the overall LLT structure can be viewed as amorphous lithium phase within a crystalline framework agreeing well with the Rietveld refinement results.

## 4.3.4 Selection of Li-O Partial for Determining Li Environment

Apparently, the local lithium environment information is contained in the partial PDFs of pairs containing Li atoms. Table 4.7 compares the weighting factor of  $g_{ij}(r)$ , i.e.  $c_i c_j b_i b_j$ , to the overall PDF. The weighting factors of pairs containing Li are relatively small due to the small scattering power of Li atoms. On the other hand, the Li-O pairs contribute to the overall PDF significantly due to the high concentration of O. Another fortunate fact is that the first distinct peak in the overall PDF, i.e. negative peak around 1.8 Å in Figure 4.15b, is mainly due to Li-O pairs, while most other peaks are the synthesis of several partial PDFs. This enhances the fitting accuracy of Li-O partial PDF. Similar partial PDFs as those in Figure 4.16 can be calculated from the average structure obtained by the Rietveld refinement (Figure 4.16), by applying occupancy/ADPs and

Table 4.7 Weighting factors of partial PDFs of all pairs.

Pairs	Li-Li	Li-La	Li-Ta	Li-O	La-La	La-Ta	La-O	Ta-Ta	Ta-O	0-0
100 <i>·cicjbibj</i> (Å-2)	0.255	-1.13	-0.63	-3.19	1.26	1.41	7.11	3.95	3.98	10.0
Fraction (%)	1.3	-5.8	-3.6	-16.4	6.5	7.3	36.5	2.0	20.4	51.5



Figure 4.17 (a) Li-O partial PDFs derived from average structure and RMC modeling of 300 K data. Tetrahedral and octahedral Li environment determined by Rietveld refinement (b, c) and RMC modeling (d, e).

assuming zero atomic correlation. Figure 4.17a shows the comparison of Li-O partial PDFs from the average structure in a unit cell and from the local structure of 5x5x5 supercell fitted by RMC modeling. In the simulated curve, there are two well separated peaks centered at 1.9 Å and 2.4 Å. This can be understood from the examination of Li environment in the average structure. In the average structure, Li at 24d site (pink in Figure 4.17) are coordinated with four oxygen with equal bond distances 1.92 Å whereas Li at 48g site (blue in Figure 4.17) have six Li-O bonds, two short ones (1.93 Å x2) and four long ones (2.34 Å x2 and 2.50 Å x2, Table 4.8). Thus the peak at around 1.9 Å in Li-O partial PDF corresponds to the four bonds at the 24d site and the two short

Table 4.8 Bond distances of Li tetrahedral and Li octahedra determined by Rietveld refinement and RMC modeling (averaged).

	LiOl (Å)	LiOs (Å)	OOl (Å)	OOs (Å)
Li tetrahedra (RR)	1.92	1.92	3.14	3.14
Li tetrahedra (RMC)	2.15	1.86	1.94	2.15
*The Li-O bond lengths	(Å) of Li oct	ahedra (from sl	hortest to long	est) are 1.93,
1.93, 2.34, 2.34, 2.50, 2.50	) for RR and 1	.88, 2.01, 2.14,	2.29, 2.49, 2.6	59 for RMC.

bonds at the *48g* site, while the peak at around 2.4 Å corresponds to the four longer bonds at the *48g* site.

In the local structure, both peaks show considerable shifts toward to smaller distances, i.e., 1.8 Å and 2.2 Å. In addition to peak positions differences, the sharpening of peaks was also observed which is usually indicative of correlated motions. These discrepancies clearly suggest that the average structure does not reflect the local environment of Li. We inspected the optimized RMC model visually to look for the cause of the shift. The typical Li tetrahedra and octahedra are shown in Figure 4.17. The tetrahedral Li move towards the center of the face resulting in three short Li-O bonds (denoted as LiOs) and one long Li-O bond (LiOl). The bond distances listed as RMC are from averaging over all local Li-O pairs in the supercell. At the Oh site, several short Li-O bond distances are close to those at the Td site. From this examination, it seems that the peak at 1.8 Å is mainly due to the short bonds LiOs while the peak at 2.2 Å is mainly

due to LiOl andlong Li-O bond at Oh. The overlapping region between these two peaks was caused by the intermediate Li-O bond distances.

The tetrahedral Li displacement towards the faces is also evident from the distances of Li ions to the closest triangular face. According to the average structure, tetrahedral Li is at the geometric center of the tetrahedron so the Li-to-face distances are all roughly 0.63 Å for all temperatures. Figure 4.18 shows the distribution of Li-to-face distances obtained from RMC modeling for all temperatures. Clearly, there are almost no Li at the tetrahedral center and most tetrahedral Li shift towards one of the four triangular faces giving rise to average shortest Li-to-face distance of around 0.4 Å. This observation of tetrahedral Li displacement is consistent with our previous atomistic simulation and Xu's first principle calculation.[108] The displacement is more pronounced as temperature increases which can be seen from the increasing fractions of Li with short Li-to-face distances. A small portion of Li are essentially on the triangular face (distance



Figure 4.18 Fractions of Li as a function of the shortest distances of Li and triangular faces at 15 K, 300 K and 550 K.

close to 0 Å) so the coordination number should best be considered as three rather than four.

The origin of tetrahedral Li shift can be deduced considering the neighboring Li atoms. The occupied Li tetrahedron is surrounded by four octahedra that can accommodate Li atoms. The electrostatic interaction of the tetrahedral Li and Li in partially filled octahedra is likely to break the ideal tetrahedral symmetry, i.e. *24d* in space group 230, and lead to displacement of Li from the center of the tetrahedron. The octahedral Li environment difference between the average structure and the RMC local model is quite subtle. Disordering within the octahedra is best envisioned with the following discussion of Li density maps.

## 4.3.5 Li Density Maps

The method of generating nuclear density maps (atomic probability density functions or atomic p.d.f.) is described in previous section. Each pixel is a small cube with 0.1 Å in length. The atomic coordinates of the 5x5x5 supercells used in RMC modeling were condensed into a 1x1x1 cell to compare those from the RR. Figure 4.19 compares the Li density isosurfaces in 3D and 2D cross sections determined by Rietveld refinement and RMC modeling. Anisotropic ADPs were used for all atoms except 24d Li due to unphysical U<sub>ij</sub> values. Only Gaussian/harmonic (isotropic or anisotropic) density maps are allowed from Rietveld analysis as shown in Figure 4.19. The ellipsoids

within octahedral regions approximately elongate towards adjacent tetrahedral sites. On the other hand, shapes of enclosed regions within Li tetrahedra and octahedra derived from RMC modeling (Figure 4.19b, c, d) show much greater complexity. Tetrahedral Li regions have four 'fingers' sticking out towards the center of the tetrahedral faces, representing off-center Li atoms as discussed in the earlier section.



Figure 4.19 Nuclear density maps of Li at (a) 15 K derived from Rietveld refinement, (b) 15 K, (c) 300 K and (d) 550 K derived from RMC modeling. Isosurface level 0.5 Å<sup>-3</sup>. 2D Li density maps of (111) plane cutting through *24d-48g-24d* sites at (e) 15 K derived from Rietveld refinement, (f) 15 K, (g) 300 K and (h) 550 K derived from RMC modeling with saturation levels from 0 Å<sup>-3</sup> to 1 Å<sup>-3</sup>.

Apparently, this type of nuclear distribution can neither be explained simply by thermal vibration nor modeled by simple Gaussian distribution. Instead, it reflects complex positional disorder as a result of interaction with its environment. Comparing the nuclear density maps at different temperatures, high temperature ones are more spread and noisier suggesting stronger positional disorder.

As seen from the 2D density maps, the density regions within tetrahedra and octahedra connect at low enough isosurface levels, more so for the high temperature data. This is a vivid depiction of the conduction path of lithium garnet system. No nuclear density was observed between the adjacent octahedra, which eliminates the possibility that octahedral Li jump directly to next octahedral site. All the above results qualitatively agree with our atomistic simulation results. In addition, closer inspection of a cluster of Td-Oh-Td region reveals a "sine wave" shape through a trajectory of (Td



Figure 4.20 Geometric relations of Li nuclear density and Oxygen cages (a) at 15 K and (b) at 300 K. Isosurface level of 0.5 Å<sup>-3</sup>. The blue lines are added to facilitate the visualization of object shapes and conduction pathway.

center)-(triangular O face)-Oh-)-(triangular O face)- (Td center) as shown in Figure 4.20 for 15 K and 300 K. Summing up Li distribution results from RMC modeling, we conclude that the conduction path (shown as blue line in Figure 4.20) involves direct hopping between tetrahedral and octahedral sites.

### 4.3.6 Li Site Occupancy

Integration of density maps around each tetrahedral and averaging over all sites yield "site occupancy" values that can be compared with those from Rietveld refinement (Table 4.9). We counted the number of lithium atoms within a sphere of radius 0.75 Å centered at the 24*d* position and averaged over 40 RMC trials.

Table 4.9 The tetrahedral site occupancies determined by RMC modeling and Rietveld refinement for all temperatures.

	15 K	300 K	550 K
RMC modeling	0.629	0.558	0.553
Rietveld refinement	0.749	0.757	0.757

There are two obvious discrepancies between the RMC modeling and the Rietveld refinement results: 1) the occupancy values obtained using RMC modeling are lower; 2) the occupancies decrease as the temperature increases in RMC modeling whereas they remain largely the same for Rietveld refinement. The lower tetrahedral site occupancy reflects the biases of RMC method towards maximization of entropy as the accessible volume in the octahedral cages is larger. The negative correlation of tetrahedral site occupancy with temperature makes more physical sense in our opinion. It is expected that the Td site has lower site energy compared with the Oh site due to its higher symmetry. At low temperature, the tetrahedral sites are preferred; at high temperature, the preference is offset by thermal agitation and the ions tend to have more uniform distribution.



#### 4.3.7 Anisotropy of Framework Atoms

Figure 4.21 Density maps of La, Ta and O derived from Rietveld refinement and RMC modeling. Isosurface level of 0.5 Å<sup>-3</sup>. The red arrow in La RMC plot incate the elongated direction of the circled density region.

Figure 4.21 compares the density maps of La, Ta and O derived from Rietveld refinement and RMC modeling. Unlike the lithium density maps, these density maps agree fairly well between the two techniques, which demonstrates that RMC modeling of PDF data is capable of capturing the average features of nuclear densities. In contrast to the Ta densities which are roughly spherical, the La density shows considerable elongations in certain directions. The O density derived from RMC modeling appears to be quite noisy reflecting some degree of disorder. This O disorder is consistent with the partial PDFs shown in Figure 4.16.

## 4.4 Summary

TOF neutron diffraction study on the tetragonal phase Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> confirmed the previously reported structural refinement results. No evidence was found on the population of *16e* site. Different models were attempted for the structural refinement of three cubic compositions Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub>, Li<sub>6</sub>La<sub>3</sub>ZrTaO<sub>12</sub> and Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub> using neutron diffraction data. The improvement on the fit by adopting a dispersed lithium nuclear density at the ideal octahedral site, i.e. through splitting site or anisotropic ADPs, was greater for compositions with high Li content. There were signs of dispersed lithium nuclear density at the ideal tetrahedral site as well, although the split-site model or anisotropic ADPs yielded unphysical parameters. No significant structural change was observed from 10 K to 300 K in all compositions.

Atomistic simulation based on interatomic potentials shed light on the Li disorder/order and local structures of Li-stuffed garnet series  $Li_{x}La_{x}Zr_{x}Ta_{x}O_{12}$  (x = 0, 0.125, 0.25, 0.5, 0.75, 1, 1.5, 2). The energy distribution plot of end member LLT is characterized by a single Gaussian peak. The appearance of sharp peaks that are discrete on the energy spectrum in the distribution plots of high Li-content compositions is the sign of Li-ordering. The tendency of Li-ordering is progressively stronger as Li content increases. Complete lithium ordering was observed for the other end member LLZ. Simulation results suggest an overall lower Td lithium occupancy than those based on the exclusion principle prediction or our refinement results. We conclude that the previously proposed exclusion principle is an over-simplification only valid for tetragonal LLZ and Td-Oh-Td lithium triplets are common in cubic compositions. On the other hand, we believe the nearest-neighbor Td-Oh lithium pairs and  $(Oh,\Box)$ -Td- $(Oh,\Box)$  lithium clusters appear to be the characteristic local features contributing to the structure and conduction of these lithium-stuffed garnet oxides.

PDF analysis using reverse Monte Carlo modeling was successfully applied to the Listuffed garnet compound Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> to understand the structural disorder. Local Li environments determined by RMC modeling are quite different from the average structure. The tetrahedral Li atoms are displaced from the center to the faces of the tetrahedra. A negative correlation of the tetrahedral site occupancy with temperature was observed. The nuclear density maps which are useful in visualizing the distribution of Li agree well with the atomistic simulation results. We proposed the conduction path of Li which involves both tetrahedral and octahedral Li. Framework atoms also show a certain degree of anisotropy evident from the density maps.

#### Chapter 5 Practical Aspects of Applying Garnet Compounds in LIBs

## 5.1 Abstract

Up to this point, all the discussions have focused on ionic conductivities and structures of Li-stuffed garnet compounds. I have shown that decent ionic conductivity of 1 mS/cm can be achieved. However, fulfilling the conductivity requirement is only the first step to the application of inorganic electrolyte in bulk lithium-ion batteries. Various practical issues need to be addressed. This chapter discusses some of the practical issues and our efforts to solving these issues. Two main aspects about Listuffed garnet compounds are investigated: 1) sintering and 2) chemical and electrochemical stabilities. Sol-gel synthesis was attempted to improve the sinterability of the garnet powder; the applicability of the pulsed electric current sintering is investigated. For the second topic, issues of instability against H<sub>2</sub>O/ CO<sub>2</sub> and the chemical stability against Li or common electrodes materials are discussed.

## 5.2 Sol-gel Synthesis of Garnet Compounds

## 5.2.1 Li<sub>7.2</sub>La<sub>3</sub>Zr<sub>1.8</sub>Sc<sub>0.2</sub>O<sub>12</sub>

The compound LLZS0.2 has never been reported in literature. The attempt to synthesize LLZS0.2 using conventional solid state method resulted in a tetragonal phase with small quantity of Sc<sub>2</sub>O<sub>3</sub> phase suggesting that the Sc ions were not completely

incorporated in the garnet structure. Therefore, the EDTA-citrate complexing process was attempted.



Figure 5.1 Image of transparent gel of Li7.2La3Zr1.8Sc0.2O12 after evaporation of solvents.

A transparent yellowish gel with high viscosity was successfully formed (Figure 5.1), which suggests that a three dimensional interconnected polymeric matrix was formed with metal cations well dispersed and immobilized. XRD (Figure 5.2) results showed that the powder calcined at 500 °C clearly consists of two phases. The broad peaks largely match with the phase La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (PDF: 73-0444) which has a pyrochlore structure whereas the narrow peaks belong to the Li<sub>2</sub>CO<sub>3</sub> phase. The broadening of the pyrochlore peaks is due to the small crystallite size as described through the Scherrer equation

$$\tau = \frac{K\lambda}{\beta\cos\theta} \tag{27}$$

Where  $\tau$  is the mean crystallite size, *K* is a dimensionless shape factor,  $\lambda$  is the X-ray wavelength,  $\beta$  is the line broadening at half the maximum intensity and  $\theta$  is the Bragg angle. The crystallite size determined from the XRD data is around 6 nm. However, the crystalline phase Li<sub>2</sub>CO<sub>3</sub> has much larger crystallite size as deduced from the sharp diffraction peaks.



Figure 5.2 The powder XRD results of calcined Li<sub>7.2</sub>La<sub>3</sub>Zr<sub>1.8</sub>Sc<sub>0.2</sub>O<sub>12</sub> powders at different temperature.

The powder turned into a single tetragonal phase after calcined at 800 °C. Further calcinations at 1000 °C convert LLZS0.2 into cubic phase. Both powder at 800 °C and 1000 °C showed no peak broadening indicating that they are of micron sizes. The SEM image (Figure 5.3) on the 800 °C powder confirmed that majorities of the particles are 1

to 5 micron in size. Therefore, it is evident that there was severe particle growth or merging upon heating to 800 °C which may be facilitated by the melting of Li<sub>2</sub>CO<sub>3</sub> (m.p. 733 °C). A small amount of Sc<sub>2</sub>O<sub>3</sub> impurity was observed in the 1000 °C sample. Considering the low doping level of Sc, it is likely that the Sc element was not incorporated at all. The LLZS0.2 may not be a thermodynamically stable phase.



Figure 5.3 SEM image of LLZS0.2 powders calcined at 800 °C.

## 5.2.2 Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>.

The solid state method was used in reports of tetragonal phase garnet Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>. We attempted to synthesize LLZ using the ECCP with slight modification to the previously presented procedure. The lithium precursor was not added to the EDTAmetal complex solution initially so fine powder with nominal composition La<sub>3</sub>Zr<sub>2</sub>O<sub>8.5</sub>



Figure 5.4 The powder XRD results of calcined Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> powders at 500 °C and 800 °C. LZO stands for La<sub>3</sub>Zr<sub>2</sub>O<sub>8.5</sub>.

was formed after 500 °C calcinations. Then LiOH was mixed well with the nanopowders before final firing step.

Similarly, a highly-viscous transparent gel was formed. Calcination of the gel at 500 °C gave rise to an amorphous phase powder evident from the XRD results (Figure 5.4). Contrary to the LLZS0.2 case, neither the nanocrystalline pyrochlore phase nor the Li<sub>2</sub>CO<sub>3</sub> was observed. After the amorphous powder was mixed with LiOH and heated to 800 °C, a pure tetragonal phase LLZ was formed. Again, the peaks showed no broadening similar to the LLZS0.2 case.

The SEM images (Figure 5.5) on the 500 °C amorphous powder and the 800 °C garnet powder revealed drastic morphology evolution of the powder. Close inspection of the

SEM image indicates that the 500 °C powder consists of agglomerates of uniform particles with diameters around 20 nm whereas the 800 °C powder is composed of micron range particles with a broad particle size distribution.



Figure 5.5 SEM images of LLZ powders calcined at (a) 500 °C and (b) 800 °C.

In summary, the synthesis of lithium garnet powder using the EDTA-citric acid complex process was only partially successful. The garnet phase can be formed after a two-step reaction. However, the final powder has micron-range irregularly-shaped particles and broad size distribution.

#### 5.3 Pulsed Electric Current Sintering of Garnet Compounds

The PECS was applied to the sintering of LLZ, and LLZT0.6 powder as described in Chapter 2. The phases and densities of the PECS sintered sample are summarized in Table 5.1. For the sintering of the LLZ powder, complete or partial melting the powder was observed in the trials with sintering temperature above 1000 °C. In comparison, using conventional sintering method without sintering aids, the LLZ sample cannot be consolidated even at above 1200 °C. XRD results (Figure 5.6) indicate that the LLZ changed from pure cubic phase to mostly pyrochlore phase corresponding to the composition La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>.

		LI	LLZT0.6	LLZT0.6 with LiF		
Temperature (°C)	1100	1000	800	500	950	950
Phase	$P + G^{\dagger}$	P+G	P+G	P+G	G	G
Density (g/cm <sup>3</sup> )	-	-	4.76	3.55	4.63	5.12
<sup>+</sup> P and G standand for pyrochlore phase and garnet phase respectively						

Table 5.1 Summary of PECS experiment results applied to garnet materials.

In the subsequent trial, the sintering temperature was lowered to 800 °C. Despite showing no sign of melting, the pellet was mechanically weak suggesting the sintering was not successful. In addition, the garnet phase decomposition was evident from XRD with slightly less pyrochlore phase fraction. The density was more than 90% of the theoretical density (5.12 g/cm<sup>3</sup>). However, considering that there was large amount of pyrochlore phase which has a higher theoretical density, the sample was in fact not dense. The phase decomposition problem persisted even when the sintering temperature was lowered to 500 °C at which very little densification occurred.



Figure 5.6 XRD patterns of PECS sintered pellets. Symbols o and x correspond to the strongest peak in the garnet and pyrochlore phase, respectively.

In comparison, the sintering of LLZT0.6 at 950 °C was more successful. XRD pattern showed that the cubic garnet phase did not decompose under the PECS condition. The pellet has good mechanical strength and reasonable density. The bulk ionic conductivity characterized by impedance spectroscopy was  $5 \times 10^{-4}$  S/cm. It was observed that the pellet was darkened due to the carbon contamination from the graphite die. Similar problem has been reported in literature.[169] LiF has been shown to facilitate mass transport and eliminate residual carbon during the sintering of transparent yttrium aluminum garnet by SPS process.[170] Therefore, 1 wt% of LiF was added to the LLZT0.6 powder for the subsequent trial. The density of the pellet was

enhanced greatly to 5.12 g/cm<sup>3</sup> or 93.7% (theoretical density 5.47 g/cm<sup>3</sup>). The bulk ionic conductivity was enhanced slightly to  $6 \times 10^{-4}$  S/cm.

In summary, the densification of garnet materials LLZ and LLZT0.3 using PECS have been attempted. We found that the LLZ garnet phase undergoes phase decomposition into pyrochlore phase even at 500 °C under the PECS condition. In comparison, the cubic phase LLZT0.6 sample is stable under the PECS condition. Highly dense pellets can be obtained with LiF additive at 950 °C which is much lower than that required in the conventional sintering technique.

## 5.4 Compatibility of Garnet Compounds with Common Electrode Materials

In this section, the compatibility of garnet compounds with common electrode materials is evaluated.

## 5.4.1 LiCO<sub>2</sub>

LiCO<sub>2</sub> (LCO) is a cathode material with layered-structure, high electronic conductivity and good structural stability.[38] It has been widely used in the commercial Li ion batteries. To evaluate the compatibility of LiCO<sub>2</sub> with the garnet oxides, a mixture of LiCO<sub>2</sub> (purchased from MTI) powder and LLZT0.25 powder in a 1:1 weight ratio was heated at 1000 °C and 1080 °C. XRD was used to characterize the phase of the mixture. The XRD pattern of the mixture after being heated to 1000 °C

(Figure 5.7) was very similar to that of original mixtures. A small double-peak corresponding to the LaCoO<sub>3</sub> phase was observed. The LaCoO<sub>3</sub> phase grew substantially after the mixture was heated to 1080 °C and the garnet phase disappeared completely. Therefore, we conclude the garnet powder is largely compatible with LiCO<sub>2</sub> at temperature below 1000 °C but incompatible at temperature above 1000 °C.



Figure 5.7 XRD patterns of the LCO and LLZT0.25 mixture as mixed (bottom), after heated to 1000 °C (middle) and after heated to 1080 °C (top). The x, o and \* symbols correspond to the strong peak of the garnet phase, LCO phase and LaCoO<sub>3</sub> phase.

## 5.4.2 LiFePO<sub>4</sub>

LiFePO<sub>4</sub> (LFP) is another type of widely commercialized cathode material.[13] It has advantage over LiCO<sub>2</sub> in terms of safety and cost. The LiFePO<sub>4</sub> (purchase from MTI) powder was mixed with LLZT0.25 powder in a 3:7 weight ratio. The mixture was then heated at 1000 °C and 1080 °C. XRD (Figure 5.8) was used to characterize the phase of the mixture.

After the mixture of LFP and LLZT0.25 was heated to 500 °C, the garnet phase almost completely disappeared and an amorphous background was present. Further heating to 850 °C and 950 °C restored the garnet phase, but the LFP phase disappeared completely. In addition, impurity phases including the pyrochlore phase and LaFeO<sub>3</sub> phase appeared. We conclude that the garnet compound is incompatible with LFP at temperature as low as 500 °C.



Figure 5.8 XRD patterns of the LFP and LLZT0.25 mixture as mixed (bottom), after heated to 500 °C, 850 °C and 950 °C. The x, o, Y and \* symbols correspond to the strong peaks of the garnet phase, LFP phase, LaFeO<sub>3</sub> phase and pyrochlore phase.

### 5.4.3 Li metal

The metallic Li is an ideal anode in terms of energy density. However, Li ion batteries using Li metal as anode have serious safety issues due to the dendrite formation.[42] The solid electrolyte, if fully dense, may act as a mechanical barrier to the dendrite growth and enable the application of Li metal. In addition, the solid electrolyte material may also find potential use in Li-air batteries.

We studied the stability of garnet compounds against the Li metal using electrochemical impedance spectroscopy. The preparation of LLZT0.3 sintered pellet is described in Chapter 2. A symmetrical cell was assembled by attaching Li foil on both sides of the pellet in a Swagelok setup. Stainless steel rods were used as current collectors.

Figure 5.9 shows the impedance evolution of the symmetrical cells. The frequency range was 1 Hz to 500 KHz. In all impedance plots, there was only one semicircle that could be attributed to the interfacial resistance of Li foil and solid electrolyte. The left intercept gave the resistance of the electrolyte pellet. Immediately after the cell was assembled, the interfacial resistance was quite large suggesting slow kinetics between the Li metal and the electrolyte pellet. Heating the whole system to 140 °C greatly reduced the interfacial resistance. However, as the cell aged for one week, the interfacial resistance resistance grew by almost ten times. The left intercept of the arc did not move much so

the resistance of the electrolyte layer was largely stable. After the cell was cooled to room temperature, the interfacial resistance was 10 ten times of that immediately after assembly. Visual inspection of the Li foil indicated reaction between the Li foil and the stainless steel rods. No color change on the electrolyte pellet was observed. Therefore, the growth of interfacial resistance was due to the deterioration of the Li foil caused by the current collectors rather than reaction with the electrolyte. The stability of the electrolyte resistance over one week at 140 °C suggests that the garnet compound is stable against Li metal.



Figure 5.9 Impedance plots of the Li-LLZT0.3-Li cell right after assembly, heated to 140 °C (blue line), aged for one week (red line) and cooled to room temperature.

#### 5.5 Effects of H<sub>2</sub>O and CO<sub>2</sub> on Tetragonal Phase Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>

The phase and ionic conductivity of the garnet compound Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> have been controversial.[86, 93, 137, 171] Both cubic and tetragonal phase has been reported with conductivity discrepancy by two orders of magnitude. The reports that discovered the role of H<sub>2</sub>O/CO<sub>2</sub> in the tetragonal-cubic phase transition in LLZ[114, 116] were published while I was conducting independent research on this effect.

The second solid state synthesis route was adopted for the preparation of LLZ so theexposure to air was strictly controlled. According to XRD, all samples calcined at 900 °C, 950 °C and 1000 °C exhibit pure tetragonal phase immediately after synthesis. Interestingly, the samples after wet-milled in anhydrous acetone all exhibited cubic phase. Subsequent calcinations of the wet-milled powder restored the tetragonal symmetry (Figure 5.10). To evaluate the effect of wet-milling, TG experiment was carried out on the sample with and without wet-milling. The as-prepared sample had almost no weight loss upon heating to 400 °C whereas the wet-milled sample had a nearly 5% weight loss. It was obvious that the garnet LLZ powder interacted and absorbed species either from acetone or air during the ball-milling step which induced phase transition.

In order to identify the species that interacted with the LLZ powder, the powder was dry-milled (no acetone solvent) for 24 hours in a jar filled with air or with Ar. The trial



Figure 5.10 Ball-milling effects on the phase of garnet LLZ powder.

with air yields similar pattern as that ball-milled in acetone whereas the trial with Ar showed no phase transition. Therefore, it was clear that the interaction with species in the air was responsible for the phase transition in LLZ.

The phase transition temperature of pure LLZ was determined by in-situ impedance measurement. A porous LLZ pellet was obtained by sintering at 1000 °C. The sample was subject to constant Ar flow during the impedance measurement. Figure 5.11 shows the Arrhenius plot of the LLZ pellet upon cooling. The slope below the transition temperature 630 °C is much larger than that above 630 °C, indicating greater activation energy in the low temperature region. The sudden change of the activation energy can be attributed to the phase transition from tetragonal phase to cubic phase. As the Al contamination and air exposure are strictly excluded in the whole process, we expect



Figure 5.11 Arrhenius plot of Li7La3Zr2O12 upon cooling.

the stoichiometry of the LLZ sample to be close to ideal. Therefore, this tetragonalcubic/order-disorder phase transition is due to the increasing entropic contribution to free energy with temperature which is an intrinsic thermodynamic property of the LLZ.

In contrast to the uncontaminated LLZ which undergoes phase transition at 630 °C, the LLZ samples contaminated by H<sub>2</sub>O or CO<sub>2</sub> undergo phase transition at a much lower temperature. The process occurs even at room temperature if the LLZ sample is exposed to air long enough. Heating accelerates the process and leads to a complete phase transition in a much shorter time as seen in Figure 5.12. The sample exposed to H<sub>2</sub>O for 1 day at 250 °C or exposed to CO<sub>2</sub> for 2 day at 350 °C transformed to cubic phase nearly completely. Therefore, the H<sub>2</sub>O and CO<sub>2</sub> can individually induce tetragonal -cubic phase transition of LLZ. There is an important distinction between the



Figure 5.12 The effects of H<sub>2</sub>O and CO<sub>2</sub> on the phase of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> material.

induced transition and intrinsic transition that is the stoichiometry is unchanged in the intrinsic transition whereas the H<sub>2</sub>O or CO<sub>2</sub> modifies the stoichiometry in the induced transition.

In summary, the intrinsic phase transition temperature of uncontaminated LLZ is around 630 °C. H<sub>2</sub>O and CO<sub>2</sub> may individually induce phase transition of LLZ at temperature as low as 298 K.

#### **Chapter 6 Conclusions and Future work**

#### 6.1 Conclusions

The garnet-type lithium ion conductors are promising solid electrolyte candidate for lithium-ion batteries. In this dissertation, the garnet series Li<sub>7-x</sub>La<sub>3</sub>Zr<sub>2-x</sub>Ta<sub>x</sub>O<sub>12</sub> (LLZTx) were subject to a comprehensive study. We discovered the fast ionic conductor Li<sub>6-7</sub>La<sub>3</sub>Zr<sub>1-7</sub>Ta<sub>0-3</sub>O<sub>12</sub> with bulk ionic conductivity of 0.96 mS/cm, which is still among the highest values reported in the garnet family so far. Our structural study through advanced diffraction techniques and computer simulation provides insights into structure-property relation in garnet oxides and the method developed here may be transferred to the research of other solid-state ionic conductor systems. Our investigation in the practical aspects of garnet oxides will be beneficial to application-oriented research.

The two end members of the LLZTx series, Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZ) and Li<sub>5</sub>La<sub>3</sub>Ta<sub>2</sub>O<sub>12</sub> (LLT), crystallize in the tetragonal phase (*I*4<sub>1</sub>/*acd*, space group No. 142) and cubic phase (*Ia-3d*, space group No. 230) at room temperature, respectively. The cubic phase lithium garnet compounds generally possess higher ionic conductivity. For the intermediate compositions, it was found that pure garnet phase forms when  $x \ge 0.2$ . The highest bulk conductivity is achieved at the composition Li<sub>6.7</sub>La<sub>3</sub>Zr<sub>1.7</sub>Ta<sub>0.3</sub>O<sub>12</sub> (LLZT0.3). The sintering temperatures of LLZTx can be reduced to around 1100 °C using appropriate sintering

aids. Unintentional Al contamination helps stabilize the cubic structure and facilitates the sintering process. In a more carefully conducted experiment where measures are taken to minimize Al contamination and air exposure, the LLZTx compounds are found to form pure cubic phase only when  $x \ge 0.6$ . When x < 0.6, the tetragonal and cubic phases coexist.

According to the average structures determined by neutron diffraction and Rietveld refinement, the tetrahedral site occupancy decreases and the octahedral site occupancy increases as lithium content, i.e., 7 - x, increases. Both sites have unusually large atomic displacement parameters indicating strong positional disorder. The Li density maps obtained from atomistic simulation provide visualization of lithium distribution. At low isosurface levels, the density regions within Li tetrahedra and octahedra connect to form a continuous three-dimensional network. From the probability distributions of lattice energies which shed light on the energy landscape of a particular system, it is clear that the tendency of Li-ordering increases with lithium contents. The firstneighbor Li-Li repulsions play a key role in determining the distribution of Li. The pair distribution function analysis was conducted for the first time on garnet oxides and proven to be a valuable tool in studying the local structure. It revealed that the lithium ions exist almost as an amorphous phase. The tetrahedral Li prefer to stay at the offcenter position inside the tetrahedra, which can be explained by the imbalance of Li-Li repulsion due to Li disorder. The Li density maps are in good agreement with those

from atomistic simulation, further confirming the tetrahedral-octahedral-tetrahedral conduction pathway.

The garnet compounds are compatible with Li metal and LiCO<sub>2</sub>. The pulsed electric current sintering can be employed to sinter the garnet compound Li<sub>6.4</sub>La<sub>3</sub>Zr<sub>1.4</sub>Ta<sub>0.6</sub>O<sub>12</sub>. These favorable characteristics make it very suitable for the application in lithium ion batteries. Nevertheless, attention should be paid to the downside such as instability in air.

## 6.2 Future Work

Despite the accumulated knowledge about garnet-type lithium ion conductors, there is still much unfinished work to do to achieve the ultimate goal. Because of the aluminum contamination and air stability issues, there exist discrepancies between the nominal composition and the real composition in the transport properties study of the LLZTx series. It is still an open question what the optimal composition is in contamination-free samples. The challenges with characterizing the transport properties of 'ideal' samples lie in the difficulty of the sintering process. We have demonstrated the PECS sintering can be used to achieve contamination-free LLZT0.6 dense samples. If the procedure with further optimization of PECS experimental conditions is applied to the complete LLZTx series ( $0.6 \le x \le 2$ ), the compositional dependence of transport properties of 'ideal' samples can be determined.

The lattice energy calculation presented in this dissertation only probes the configuration at the static limit. Molecular dynamics simulation is more suitable to understand the transport properties of real-world samples. The pair distribution function analysis is only applied to LLT. However, the approach used here is perfectly transferrable to other high Li content garnets. We expect that a thorough study of the relation between local Li distribution and Li content will provide the structural information needed to better understand the compositional dependence of transport properties in garnet oxides.

We have investigated the air stability of the LLZ samples. More need to be known about the H<sub>2</sub>O/CO<sub>2</sub> effect on the phase and transport properties of other high ionic conductivity garnets. This can be achieved through in-situ impedance measurement on garnet samples under controlled gas environment.

Finally, the next phase of garnet oxides research should focus on the engineering approach of constructing all-solid-state batteries. Foreseeable challenges include ensuring good solid-solid contact among the solid components, minimizing polarization effects due to large solid electrolyte resistance and optimizing overall energy density.

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