Gallium Substitution in Zirconate-Based Fast Ionic Conducting Ceramics

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GALLIUM SUBSTITUTION IN ZIRCONATE-BASED FAST IONIC CONDUCTING CERAMICS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Changlong Li
August 2016

Accepted by:
Dr. Kyle S. Brinkman, Committee Chair
Dr. O. Thompson Mefford
Dr. Fei Peng
ABSTRACT

Garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) has been demonstrated as a promising solid-state electrolyte material for lithium ion batteries. Solid-state electrolytes with room temperature conductivities in excess of $10^{-4}$ S/cm are being considered as a substitute for the current liquid electrolyte and polymer based separators which would result in the enhanced safety. In the present work, the phase formation, sinterability and electrochemical properties of LLZO as a function of Ga dopant composition and synthesis route have been investigated. X-ray diffraction, combined with differential thermal analysis (DTA), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) characterization methods have been utilized to investigate the impact of Ga as a dopant.

Tetragonal-LLZO has been synthesized by conventional solid-state reaction process and conventional sintering method with a total conductivity $\sim 10^{-7}$ S/cm at 21°C. LLZO pellets with single cubic phase have been attained by quenching the t-LLZO in water at 600 °C exhibiting a conductivity of $\sim 10^{-4}$ S/cm at 21°C. The phase transition from tetragonal to cubic phase occurs when 0.1 mole of Ga was added to 1 mole LLZO powder (Li$_{6.7}$La$_3$Zr$_2$Ga$_{0.1}$O$_{12}$), however, the resulting phase assemblage is still a mixture of tetragonal and cubic phases. Calcined powders with a composition of 0.5Ga-LLZO exhibited a single cubic phase as verified by XRD, further proving the supposition that higher content of Ga is beneficial for cubic phase formation. At higher doping levels, an
excess of Ga in sample 1.0Ga-LLZO has been found as LiGaO\(_2\) in the powder, which works as a sintering aid and accumulates in the grain boundaries. Compared with conventional sintering process, pellets densified via spark plasma sintering displayed a higher relative density at a lower sintering temperature.

The highest total ionic conductivity at room temperature in the range of \(5.81 \times 10^{-5}\) S/cm for sol-gel synthesized \(\text{Li}_{5.5}\text{La}_{3}\text{Zr}_2\text{Ga}_0.5\text{O}_{12}\) and sintered by conventional sintering method in the air. Also, a total lithium ionic conductivity in the range of \(4.37 \times 10^{-6}\) S/cm at room temperature for SSR synthesized \(\text{Li}_{5.5}\text{La}_{3}\text{Zr}_2\text{Ga}_0.5\text{O}_{12}\) and sintered by conventional sintering method in the air. Grain growth investigation on 0.5Ga-LLZO sintered by SPS and following by conventional sintering has verified the suggestion that larger grains are beneficial to the total ionic conductivity.

In addition to room temperature Li-ion conductors, Ga doping in perovskite Yttrium-doped Barium Zirconate (BZY) serving as a high temperature proton conducting electrolyte material has been investigated. The sintering temperature was effectively decreased when Ga was doped into BZY structure, however, there was a concomitant decrease in the total conductivity.
ACKNOWLEDGEMENTS

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career, and wherever I will be in the following future, the studying and living experience at Clemson University will let me always remember to consistently live and work as a Clemson tiger.
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<tr>
<td>SG</td>
<td>sol-gel process</td>
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<td>CS</td>
<td>conventional sintering</td>
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<td>SPS</td>
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<td>Z</td>
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CHAPTER 1. INTRODUCTION

1.1 Background information

Based on the increasing demand for high energy density, long recycling life and safer batteries for portable electric devices and electric vehicles, rechargeable lithium ion batteries have attracted increasing attention. However, state-of-the-art electrolytes used in lithium ion batteries still employ an organic Li-ion salt electrolyte which has posed safety concerns arising from dendrite formation and issues with flammability. Possible Physical leakage of liquid [1, 2] during cell packing process, and the tendency to explode occurs when batteries with polymeric electrolytes are used in elevated temperature environments which lead to performance degradation and shortened recycling times. Meanwhile, the stability problem of the aqueous electrolytes with lithium metal has seriously limited the voltage range[3, 4]. Solid-state electrolytes with room temperature conductivities in excess of $10^{-4}$ S/cm are being considered as a potential substitute for current liquid electrolytes and polymer based separators which would result in enhanced safety. The employment of anode materials like LiC$_6$ and even lithium metals, and Nickle-, Cobalt-, Iron- or Manganese-containing oxides like LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_4$ as cathode results in much higher voltage and power densities as well as higher long-term stability [4].
A group of garnet-type fast lithium ionic conductor with chemical formula Li$_5$La$_3$M$_2$O$_{12}$ (M=Nb, Ta) was reported by Weppener et al. in 2003. Li$_5$La$_3$Nb$_2$O$_{12}$ and Li$_5$La$_3$Ta$_2$O$_{12}$ exhibited the same magnitude of bulk ionic conductivity \( \sim 10^{-6} \) S/cm at 25°C [5]. Li$_6$BaLa$_2$Ta$_2$O$_{12}$ possessed the higher conductivity of $4 \times 10^{-5}$ S/cm at 22°C with an activation energy of 0.40 eV [6]. Zirconium-containing garnet lithium has been investigated based on the good thermal and chemical stability against metallic lithium, as well the low cost and ease of preparation.

Murugan et al. have firstly reported LLZO with high bulk lithium ionic conductivity round $10^{-4}$ S/cm at 25°C via solid-state reaction procedure at 1230°C for 36 hours [7]. The diffraction pattern for a cubic cell with a lattice constant $a=12.968(2)$ Å was indexed by powder X-ray diffraction. High temperature and long sintering time are essential to gain dense pellets, however, lithium loss leading to the formation of pyrochlore phase La$_2$Zr$_2$O$_7$ usually initiates below this temperature[8].

Two phases of LLZO in different temperature range were confirmed by the work of Awaka et al. [3, 9]. Only LLZO with cubic symmetry shows high lithium ion conductivity has been experimentally confirmed, and theoretically explained by later researchers[9]. In general, lithium ions conductivity of cubic phase LLZO is higher than that of tetragonal LLZO by two orders of magnitude. However, the mechanism of the phase transformation between these two phases is not completely understood.
Studies on the structure of LLZO strongly indicated that the inclusion of foreign ions such as aluminum ions (Al\(^{3+}\)) helps to stabilize the cubic symmetry at high temperature. It has been found that Al\(^{3+}\) ions substitution for the Lithium ion in LLZO occurs when the alumina crucible was used in the sintering process at high temperature [7]. LLZO electrolytes doped with various contents of Al (0, 0.2, 0.7, 1.2, and 2.5 wt.%) were synthesized by a polymerized complex method (Penchini). High ionic conductivities on the order of 2.0×10\(^{-4}\) S/cm at room temperature were obtained. The density of the pellets increased from 2.6 g/cm\(^3\) to 4.4g/cm\(^3\) with the addition of 0.2 wt.% Al [10]. Some other trivalent ions like Ta-, Nb-, W-doped or co-doped LLZO attempting to improve both the sinterability and ionic conductivity [11]. Ga has been employed as a dopant in several types of ionic conducting materials such as perovskite and garnet. Ga\(_2\)O\(_3\) has a lower melting point (1,950\(^\circ\)C) relative to the other alternative metal oxides Al\(_2\)O\(_3\)(2,072\(^\circ\)C), Nb\(_2\)O\(_3\) (2477 \(^\circ\)C) which leads to the lower sintering temperature and better morphology.
### Table 1-1 modified lithium garnet-type LLZO with various dopants

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<th>Doping benefits</th>
<th>RT conductivity (S/cm)</th>
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<td>0.25Al-LLZO</td>
<td>Al</td>
<td>Increase sample density; create vacancies; stabilize cubic structure</td>
<td>$4.48 \times 10^{-4}$</td>
<td>Wenhao Xia, 2016 [12]</td>
</tr>
<tr>
<td>0.35W-LLZO</td>
<td>W</td>
<td>Create vacancies; stabilize cubic structure</td>
<td>$6.6 \times 10^{-4}$</td>
<td>Yiqiu Li, 2015 [13]</td>
</tr>
<tr>
<td>0.06Y-LLZO</td>
<td>Y</td>
<td>Stabilize cubic structure</td>
<td>$8.10 \times 10^{-4}$</td>
<td>Ramaswamy Murugan, 2011 [14]</td>
</tr>
<tr>
<td>Ta-LLZO</td>
<td>Ta</td>
<td>Create vacancies, stabilize cubic structure</td>
<td>$1.8 \times 10^{-4}$</td>
<td>Travis Thompson, 2014 [15]</td>
</tr>
<tr>
<td>0.25Nb-LLZO</td>
<td>Nb</td>
<td>Create vacancies</td>
<td>$8.0 \times 10^{-4}$</td>
<td>Ohta, 2012 [16]</td>
</tr>
<tr>
<td>0.4Ce-LLZO</td>
<td>Ce(IV)</td>
<td></td>
<td>$1.4 \times 10^{-5}$</td>
<td>E. Rangasamy, 2013 [17]</td>
</tr>
<tr>
<td>0.25Ga-LLZO</td>
<td>Ga</td>
<td>Create vacancies, stabilize cubic structure</td>
<td>$3.5 \times 10^{-7}$</td>
<td>J. Wolfenstine [18]</td>
</tr>
</tbody>
</table>
1.2 Experimental technologies

1.2.1 Principles and Mechanism of the Spark Plasma Sintering (SPS) Process

Spark Plasma Sintering (SPS) or Field Assisted Sintering Technology (FAST) is an electric current sintering method which employs a pulsed DC current to help to sinter[19]. Joule heat concentrates on powders where the electrical conductivity is much less than the graphite dies. A high power pulse source (typically from 1KA to 10KA) goes through the powder leading to effective joule heating [20] and high local heating rates. This pulsed direct current also results to cleaning and surface activation of the powders[21]. At the same time, the application of a uniaxial mechanical pressure enhances the densities of the sintered pellets(maximal loads typically between 50KN to 250 KN )[20].

Figure 1-1 shows the schematic of SPS process. The sintering instrument is assisted by a uniaxial press, two punch electrodes (upper electrode and lower electrode), dies, vacuum chamber, DC pulse generator and position, temperature, and pressure measuring units. Through setting working current and voltage, controlling of the temperature dwelling time, ramping rates can be realized. Spark plasma, as well as spark impact pressure, Joule heating, and an electrical field diffusion are generated during the DC pulse discharging process.
Figure 1-1 Schematic of SPS process.[19]

Figure 1-2 Schematic comparison between spark plasma sintering and conventional sintering with pressure.[19]
In general, there are four stages of the sparking plasma sintering process. Firstly, gases are extracted out and create a vacuum environment in the chamber. Then mechanical pressure is employed on the materials to form pellets in the second stage. Following is a joule heating process and cooling down process in the third and fourth stage [19].

Based on the highly effective utilization of energy employed in the local high-temperature regions, vaporization and melting of the surfaces of the powder particles occur. This leading to the constricted shapes or “necks” around the contact areas between the particles. When a spark plasma discharge occurs between these necks, a local high-temperature state formed with several to ten thousands of degrees centigrade in a short time[19], which resulting in a sintered compact with a relatively high density at much reduced time.

Meantime, the grain growth of the powder materials is controlled, due to the rapid heating process and shorter sintering time.
Figure 1-3 DC pulse current flow through the particles[19]
1.2.2 Principles of Electrochemical Impedance Spectroscopy

Electrochemical Impedance spectroscopy (EIS), also called AC impedance spectroscopy was used to determine the conductivity of ceramic based ionic conductors prepared in this work. Ohm’s law describes the resistance $R$ as the ratio between voltage $E$ and current $I$.

$$R = \frac{E(t)}{I(t)}$$  \hspace{1cm} (0.1)

When an AC excitation signal is applied to the system, the sinusoidal voltage can be expressed as

$$E(t) = E \sin(\omega t)$$  \hspace{1cm} (0.2)

where $\omega$ is the angular frequency.

The sinusoidal current can be expressed as

$$I(t) = I \sin(\omega t + \phi)$$  \hspace{1cm} (0.3)

where $\phi$ is a phase angle.

The impedance is a type of generalized resistance, which defined as $Z$.

$$Z(t) = \frac{E(t)}{I(t)} = \frac{E \sin(\omega t)}{I \sin(\omega t)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$  \hspace{1cm} (0.4)

Using Euler’s relation, $\exp(i\phi) = \cos \phi + i \sin \phi$, it is possible to express the impedance as a complex function. The voltage is described as

$$E = E_0 \exp(i\omega t)$$  \hspace{1cm} (0.5)
and the current is described as

\[ I(t) = I_0 \exp(i\omega t - i\phi) \]  

(0.6)

Then, the impedance can be represented as a complex number related to the frequency,

\[ Z(t) = E(t) = Z_0 \exp(i\phi) = Z_0 \exp(\cos \phi + i \sin \phi) \]  

(0.7)

where \( i^2 = -1 \).

In fact, \( Z(\omega) \) is composed of a real and an imaginary part. In general, the impedance can be represented as

\[ Z(\omega) = Z_{\text{Re}} - iZ_{\text{Im}} \]  

(0.8)

where \( i^2 = -1 \). The absolute value of \( Z \), written \( |Z| \), is given by

\[ |Z|^2 = (Z_{\text{Re}})^2 + (Z_{\text{Im}})^2 \]  

(0.9)

And the phase angle, \( \phi \), is given by

\[ \tan(\phi) = \frac{Z_{\text{Im}}}{Z_{\text{Re}}} \]  

(0.10)

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. An entire equivalent fitting circuit is the combination of several different components, which are composed of these common electrical elements.

Definitions and symbols of the basic components are shown in Table 1-2.

Table 1-2 Basic components: definition and symbols
<table>
<thead>
<tr>
<th>Component</th>
<th>Expression</th>
<th>Impedance</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>$E = IR$</td>
<td>$Z = R$</td>
<td>![Resistor Symbol]</td>
</tr>
<tr>
<td>Inductor</td>
<td>$E = L\frac{di}{dt}$</td>
<td>$Z = i\omega L$</td>
<td>![Inductor Symbol]</td>
</tr>
<tr>
<td>Capacitor</td>
<td>$I = C\frac{dE}{dt}$</td>
<td>$Z = \frac{1}{i\omega C}$</td>
<td>![Capacitor Symbol]</td>
</tr>
</tbody>
</table>
If the real part is plotted on the X-axis and the imaginary part on the Y axis of a chart, a plot termed the Nyquist plot is obtained. A typical and simple Nyquist plot for an RC circuit is shown in Figure 1-4(a). High-frequency data are on the left side of the plot and lower frequencies are on the right. Generally speaking, the impedance increases when frequency decreases. The value of $Z$:

$$\frac{1}{Z} = \frac{1}{R} + \frac{1}{i\omega C}$$

The corresponding equivalent circuit is a resistance and a capacitor in parallel, which is shown in Figure 1-4 (b)

**Figure 1-4 (a)** A typical Arrhenius plot of RC pattern; (b) The equivalent circuit for RC pattern.
However, RC equivalent circuit is just adoptable for standard semicircle plot. In most realistic situation, other phase constant elements like CPE, QPE, and Wo combined with resistance have been used to fit the curve of impedance plots for the refinement.

For a circuit sample with area $A$ and thickness $l$, the relationship between conductivity and resistance can be defined as\[22\]:

$$R = \rho \frac{l}{A} = \frac{1}{\sigma A} \quad \text{(0.12)}$$

Where $R$ is the resistance, $\sigma$ is the conductivity. The SI unit for $\sigma$ is Siemens per meter (S/m), however, unit S/cm is mostly used for the measurement of the ionic conductivity of small pellets.
CHAPTER 2. GARNET-TYPE LLZO

2.1 Structure of LLZO: tetragonal vs cubic Li$_7$La$_3$Zr$_2$O$_{12}$

High purity polycrystalline Li$_7$La$_3$Zr$_2$O$_{12}$ with tetragonal structure have been synthesized. The single crystal has been grown via flux method by Awaka et al.[3] This tetragonal structure has been verified by X-ray diffraction and neutron powder diffraction with a space group of I$4_1$/acd and lattice constants of $a=13.134(4)$ Å and $c=12.663(8)$ Å. In the tetragonal structure, two types of dodecahedral La$_8$O$_{18}$ and La$_8$(2)O$_{18}$, and one type of octahedral ZrO$_6$ construct the frame-work. Lithium atoms occupy three crystallographic sites in the interstices of this frame, which are one tetrahedral site Li(1)O$_4$, and two octahedral sites Li(2)O$_6$ and Li(3)O$_6$.

Lithium-ion migration pathway is decided by the arrangement of lithium ions in the structure. In tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$, the migration pathway of lithium ions can be described as in Figure 2-2 (merely in the structural view of lithium ions arrangement). The loop is constructed by three lithium sites, and a loop link to another to form the three dimensional network of the lithium-ion migration. However, all the three lithium sites are fully occupied by the lithium ions, which leading to the less vacancies for lithium ions migrating in the lattice[3].
Figure 2-1 Crystal structure of tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$. The solid box indicates the unit cell[3].

Figure 2-2 The loop structure of lithium atomic arrangement in tetragonal phase of Li$_7$La$_3$Zr$_2$O$_{12}$, g is the occupancy value[9].
Awaka et al. [9] determined the single crystal structure of the cubic form of \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) by X-ray diffraction in 2011. The cubic phase belongs to \( \text{Ia}3\text{d} \) group with cubic lattice parameter \( a=12.982(7)\text{Å} \). The garnet frame is composed of one dodecahedral \( \text{LaO}_8 \) site and one octahedral \( \text{ZrO}_6 \) site. Two lithium atoms were located at the tetrahedral \( \text{Li}(1)\text{O}_4 \) site and distorted octahedral \( \text{Li}(2)\text{O}_6 \) site, respectively. Compared with the framework of tetragonal \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \), two octahedral \( \text{Li}(2)\text{O}_6 \) and \( \text{Li}(3)\text{O}_6 \) become one equivalent position. The disordering and low occupation of lithium ions at \( \text{Li}(2)\text{O}_6 \) site were reported as a crucial role in the lithium ions transportation in these lithium ion conductors[23].

Lithium ions migration pathway is shown in Figure 2-4 (in the structural view of lithium ions arrangement). Because the low occupation (occupancy value: \( g=0.35 \)) in the equivalent \( \text{Li}(2)\text{O}_6 \) site, mobility of lithium ions will be increased due to the increased vacancies in the lattice for lithium ions hopping[9].
Figure 2-3 Crystal structure of cubic Li$_7$La$_3$Zr$_2$O$_{12}$, and the coordination polyhedral around Li(1) and Li(2) sites [9].

Figure 2-4 The loop structure of Lithium atomic arrangement in cubic Li$_7$La$_3$Zr$_2$O$_{12}$, g is the occupancy value[9].
2.2 Synthesis of Li$_7$La$_3$Zr$_2$O$_{12}$

2.2.1 Synthesis of Li$_7$La$_3$Zr$_2$O$_{12}$ raw powders via solid-state reaction (SSR) route

A mixture of the raw powders of Li$_2$CO$_3$ (99.9%, Macron Fine Chemicals), La$_2$O$_3$(99.99%, Alfa Aesar) and ZrO$_2$(99.7%, Alfa Aesar) with the ions ratio 7.7:3:2 were ball-milled with zirconia balls for 48 hours with ethanol as the dispersing reagent. The 10% excess of lithium carbonate was added in order to compensate for the loss of lithium in the heating process. The mixture was moved into a baker with a net filter and then dried into powder in the oven at 100°C for 12 hours.

According to the phase formation analysis via phase diagram[24], the target phase of LLZO is formed after 950°C. The dried powder was then pressed into pellets under isostatic pressure and heated at 950°C for 5 hours. Annealed pellets were ground again and pressed into pellets. Calcination was repeated at 950°C two times to ensure the reaction of starting materials.

2.2.2 Synthesis of Li$_7$La$_3$Zr$_2$O$_{12}$ raw powders via sol-gel (SG) route

The precursor of Li$_7$La$_3$Zr$_2$O$_{12}$ via sol-gel route was synthesized from the starting materials Li$_2$CO$_3$(99%, Alfa Aesar), La(NO$_3$)$_3$•6H$_2$O (99%, Alfa Aesar) and ZrO(NO$_3$)$_2$•xH$_2$O (99%, Sigma-Aldrich) in the stoichiometric proportions. First, citric acid was dissolved in water as the complexing reagent. ZrO(NO$_3$)$_2$•xH$_2$O was then dissolved in the distilled water and
nitric acid, in which nitric acid dissolved ZrO(NO$_3$)$_2$$\cdot$$x$H$_2$O. After that, the addition of LiNO$_3$ and La(NO$_3$)$_3$•6H$_2$O powder was dissolved in the mixture of ZrO(NO$_3$)$_2$$\cdot$$x$H$_2$O and citric acid solution. The transparent solution was stirred at room temperature overnight then heated to gel in the oven. The gel was kept in the oven at 100°C for several days with multiple grinding steps until all the gel became powder. The dried precursor of Li$_7$La$_3$Zr$_2$O$_{12}$ was synthesized in the box furnace at 950°C for 5 hours. The calcination process was repeated three times.

2.3 Sintering: conventional sintering (CS) and spark plasma sintering (SPS)

The synthesized powders with tetragonal phase were verified by X-ray diffraction. The calcined powder was ground into very fine particles and combined with 5 wt.% polyvinyl alcohol (PVA) as the ceramic binder during sintering. In general, the amount of PVA used was 0.15ml (3 drops) per gram Li$_7$La$_3$Zr$_2$O$_{12}$ powder. The powders were mixed with the binder until a wet paste was formed which was then dried under infrared light. The pellets were then isostatically pressed at 1400 psi for one minute.

Sintering was performed in air in a box furnace with the samples resting on an alumina plate with a covered alumina crucible. In addition, experiments were conducted with platinum foil between the pellets and the alumina crucible to limit incorporation of Al into the samples. The crucible and plate were sealed using a ceramic paste in order to avoid
excessive lithium loss during the sintering process at high temperature. The pellets were sintered at various temperatures from 950°C to 1200°C with 5°C/min utilized as the heating and cooling rate. A small boat of Li$_2$CO$_3$ was put next to the pellets producing a lithium rich vapor phase intended to further reduce lithium loss from the pellets during the high sintering temperature, similar work has been done in the previous work in lead process in our group[25].

For SPS processing, dried powders mixed with PVA binder were loaded into graphite dies. Graphite paper was placed on both the top and the bottom surfaces of the sample in order to avoid a reaction between the pellets and the graphite bars during the sintering process. Mechanical pressure of 3KN and 6KN, and two sintering times, 10 minutes and 5 minutes were used to investigate the optimal sintering conditions. The graphite papers were later removed by a post sintering heat treatment at 600°C for 2 hours in the furnace. SPS grain controlled study on BZY staff has been done in our group before[26].
2.4 Results and discussion

2.4.1 Phase characterization

The synthesized powders and sintered pellets were analyzed by X-ray diffraction (XRD) using CuKα radiation at room temperature in the 2θ ranges from 10° to 70° with 1°/min scanning rate.

The main impurity typically observed in Li7La3Zr2O12 is the pyrochlore phase La2Zr2O7[7, 27-40]. Pyrochlore is also the dominant impure phase in similar compositions such as perovskite type La0.5Li0.5TiO3[41]. This second phase is commonly observed after pellets are sintered due to the loss of lithium at high temperatures. Other impurities such as Li2ZrO3 have also been reported[8, 17, 28, 42-46].

Figure 2.5 shows the XRD pattern of powders synthesized at 950°C for 5 hours and the pellets sintered at 1000°C for 5 hours. A minor peak indicative of an impurity phase La2Zr2O7 was observed at 2θ=28.67°. The lattice parameters have been determined by the analysis of the XRD results after calibration with standard silicon powders. Two strong split peaks appear at 2θ=16.38° and 16.92°, which correspond to the two lattice parameters a=13.114(0) Å and c=12.690(7) Å. These lattice values matched well with the previous results (a=13.134(4) Å and c=12.663(8) Å)[3] in the literature.
Figure 2-5 X-ray patterns of LLZO powders calcined at 950℃ for 5 hours (red), pellets sintered at 1000℃ for 5 hours (blue), and standard tetragonal LLZO pattern (ICSD_183684)[47]. ●Li₂ZrO₃ (PDF 33-0843); ♦La₂Zr₂O₇ (PDF 71-2363)[48].
2.4.2 Morphology and elemental distribution study

a. Li$_7$La$_3$Zr$_2$O$_{12}$ powder

Li$_7$La$_3$Zr$_2$O$_{12}$ powders synthesized via a sol-gel and solid-state reaction process were dispersed in ethanol after ultrasonic treatment for 2 hours. The powders were deposited on a silicon plate and dried in the oven for 24 hours. Powders derived from a sol-gel (Fig 2.6a) and solid-state reaction (Fig 2.6c) were detected by scanning electron micro-spectroscopy (SEM) after coating with platinum. The distribution of particle sizes have been statistically analyzed by the ImageJ software[49]. The average size of particles synthesized by the sol-gel method is 0.7 um; the solid-state reaction process produced particles with an average particle size of 2.5~3.0 um. The results indicate that particles synthesized via the sol-gel are much smaller than those obtained from solid-state reaction route. This smaller size would affect the sintering process like elements distribution, grain growth, etc.
Figure 2-6 (a) Scanning electron microscopy (SEM) images of LLZO powders synthesized via sol-gel process; (b) Particle size distribution of powders synthesized via sol-gel process; (c) Scanning electron microscopy (SEM) images of LLZO powders synthesized via solid-state reaction (SSR) process; (d) Particle size distribution of powders synthesized via solid-state reaction (SSR) process.
For further study on the statistical data of the particle size, a table of t-test statistic shows in Table 2-1. In which, t statistic value for is -0.18 for sol-gel powders, while -0.06 for solid-state reaction powders, which means the tested mean size is very closed to the mean value for the whole population. The difference in particle between sol-gel process and solid-state process is signifcante.

Table 2-1 Statistical comparison of particle size for both sol-gel and solid-state reaction route.

<table>
<thead>
<tr>
<th>Sol-gel process</th>
<th>Descriptive Statistics</th>
<th>N</th>
<th>Mean (um)</th>
<th>SD (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>105</td>
<td>0.73</td>
<td>0.22</td>
</tr>
<tr>
<td>Test Statistics</td>
<td>t statistic</td>
<td>-0.18</td>
<td>104</td>
<td>0.85</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SSR process</th>
<th>Descriptive Statistics</th>
<th>N</th>
<th>Mean(um)</th>
<th>SD(um)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>128</td>
<td>2.47</td>
<td>0.70 um</td>
</tr>
<tr>
<td>Test Statistics</td>
<td>t statistic</td>
<td>-0.06</td>
<td>127</td>
<td>0.95</td>
</tr>
</tbody>
</table>
b. Li$_7$La$_3$Zr$_2$O$_{12}$ pellets

Microstructural observation of pellets synthesized via a solid-state reaction and sintered at 1100°C for 5 hours indicated residual porosity. Insufficient sintering is consistent with the low density (relative density~70%) measured by Archimedes’ method. Pellets fabricated via a SPS sintering process at 950°C exhibited higher density and a more uniform microstructure as displayed in Figure 2-7b.

![Figure 2-7](image)

Figure 2-7 Scanning electron microscopy (SEM) images of pellets synthesized via solid-state reaction sintered by (a) conventional sintering at 1100°C for 5 hours, magnitude 2K, and (b) Spark plasma sintering at 950°C for 5 minutes, magnitude 2K.

In comparison, powders synthesized via sol-gel process were sintered at 1000°C and 1100°C, respectively. The connectivity of grains and uniform grain size indicate that the sol-gel derived powders exhibited improved sinterability compared to those synthesized via the solid-state reaction process. Furthermore, the larger grain size of the pellets sintered at 1000°C (Figure 2.8a) compared to those sintered at 1100°C (Figure 2.8b). The higher
temperatures in excess of 1250°C may result in melting and decomposition of Li$_7$La$_3$Zr$_2$O$_{12}$ pellets[50-52].

Figure 2-8 Scanning electron microscopy (SEM) images of pellets synthesized via sol-gel process sintered by conventional sintering at (a) 1000°C, magnitude 2K, and (b) 1100°C, magnitude 2K.

The elemental distribution of Li$_7$La$_3$Zr$_2$O$_{12}$ pellet synthesized via sol-gel process and sintered at 1000°C for 5 hours has been analyzed in the SEM by energy dispersive X-ray spectroscopy (EDS) (Aztec, Oxford Instruments) mapping are shown in Figure 2-9. Mapping indicates oxygen, lanthanum and zirconium distribute uniformly in the grains and grain boundaries. Aluminum was found to be mainly concentrated on the boundaries. The reason for the incorporation of aluminum should be the contamination from the alumina crucible and plates used in the powders synthesis process. Lithium cannot be detected by EDS based on the low intensity due to the low excitation energy can be chosen in the EDS equipment.
2.4.3 Density measurement

Densities of Li$_7$La$_3$Zr$_2$O$_{12}$ pellets have been measured by Archimedes’ method. The relative density of each pellet was determined by dividing the theoretical density (tetragonal LLZO: 5.106 g/cm$^3$ [3] and cubic LLZO: 5.098 g/cm$^3$ [9]). In the comparison of Li$_7$La$_3$Zr$_2$O$_{12}$ pellets fabricated from the powders synthesized via solid-state reaction, pellet fabricated from the powders synthesized via sol-gel route achieved much higher density. Pellet fabricated by SPS holds a relative density close to 90% at 950°C for 5 minutes.
Table 2-2 Density and relative density of Li$_7$La$_3$Zr$_2$O$_{12}$

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Density (g/cm$^3$)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pellets sintered from the powders synthesized via solid-state reaction process</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLZO_CS1000</td>
<td>3.246</td>
<td>63.57%</td>
</tr>
<tr>
<td>LLZO_CS1100</td>
<td>3.277</td>
<td>64.19%</td>
</tr>
<tr>
<td>LLZO_SPS950</td>
<td>4.509</td>
<td>88.32%</td>
</tr>
<tr>
<td><strong>Pellets sintered from the powders synthesized via sol-gel process</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LLZO_CS1000</td>
<td>3.684</td>
<td>72.16%</td>
</tr>
<tr>
<td>LLZO_CS1100</td>
<td>4.308</td>
<td>84.37%</td>
</tr>
<tr>
<td>LLZO_SPS950</td>
<td>4.545</td>
<td>89.01%</td>
</tr>
</tbody>
</table>
2.5 Summary

Un-doped Li$_7$La$_3$Zr$_2$O$_{12}$ with single tetragonal phase has been synthesized from both a conventional solid-state reaction process and a sol-gel process. The size of the corresponding powders was investigated by scanning electron microscopy (SEM). Powders synthesized by the sol-gel process hold a finer average particle size in nano-scale (~0.7μm), while the powder synthesized by solid-state reaction process possess average particle size at micrometer level (2.5–3 μm). The elemental distribution of the powder synthesized via the sol-gel process are much more uniform than the those obtained by the SSR method. The finer and more homogenous elemental distribution of the powder prepared by the SG method contributed to better connectivity between trains leading to a higher relative density than samples processed by SSR at the same sintering condition.
CHAPTER 3. GA-DOPED Li7La3Zr2O12

3.1 Motivation and objectives

Since cubic phase Li7La3Zr2O12 possesses very high lithium ionic conductivity and the tetragonal phase is stable at room temperature, the transformation from tetragonal to a cubic structure is a crucial topic for this material system. Previous studies on Li7La3Zr2O12 discovered some unexpected elements incorporated from the sintering process (Al) were favorable for the stabilization of the cubic phase at low temperature[7]. Other alternative doping strategies like Iron(III) ions[53], Gallium(III) ions for Lithium(I) ions in A site, and Niobium(V)[5, 54, 55], Tantalum(V)[15], Antimony(V)[44], Yttrium(III)[14] for Zirconium(IV) in C sites have also been verified to improve the ionic conduction performance of this series of garnet-related zirconate ceramics.

In this work, intentional doping of Ga was pursued to maintain the cubic structure based on the trivalent chemical valence and suitable atom size. In addition, the lower melting point of Ga2O3 was thought to be helpful to lower the sintering temperature compared with similar trivalent elements such as Alumina ions[8, 30, 34, 36, 40, 43, 45, 56-64].
3.2 Synthesis of 0.1Ga-LLZO, 0.5Ga-LLZO and 1.0Ga-LLZO

3.2.1 Synthesis of Ga-LLZO powders via solid-state reaction

A conventional solid-state reaction approach has been used to prepare the Ga substituted Li$_7$La$_3$Zr$_2$O$_{12}$ garnet phases. 0.1-mole Ga was incorporated into 1 mole of Li$_7$La$_3$Zr$_2$O$_{12}$. Based on the study of Ga-substituted LLZO via Solid-state Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR), Ga atoms located in the tetrahedral positions promoted the distribution of lithium atoms [29]. Assuming this substitution pathway, the targeted formula of the Ga-substituted LLZO in this work would be Li$_{6.7}$La$_3$Zr$_2$Ga$_{0.1}$O$_{12}$. The starting material Li$_2$CO$_3$ (99.9%, Macron Fine Chemicals), La$_2$O$_3$ (99.99%, Alfa Aesar) and ZrO$_2$ (99.7%, Alfa Aesar), Ga$_2$O$_3$ (99%, Alfa Aesar) with the ions ratio Li:La:Zr:Ga=7.4:3:2:0.1 were ball-milled with zirconia balls for 48 hours with ethanol as dispersing reagent. Additions of 10% excess of lithium ions was added in order to compensate for the loss of lithium in the heating process. The mixture was moved into a baker with a net filter and then dried into powder in the oven at 100°C for 12 hours.

The structural change associated with Ga doping has been further investigated. In Li$_7$La$_3$Zr$_2$O$_{12}$ samples, all the lattices are verified as tetragonal structures. When 0.1 mole Ga was employed, the phases of 0.1Ga-LLZO consisted of both tetragonal structures and cubic structures. Increasing the contents of Ga leads to the increase of the ratio of cubic structures in tetragonal structures. By analysis of the XRD patterns, both 0.5Ga-LLZO and
1.0Ga-LLZO were found to be single phase cubic structures. In order to facilitate a comparison of samples with different content of gallium, all the powders of these sample were synthesized via solid-state route and calcined at 950°C holding for 5 hours and calcined three times with grinding between each steps. Pellets were fabricated at the same conditions and sintered at 1100°C. Therefore, the only variable in the process was the content of gallium. Li7La5Zr2O12 with various contents of Ga were investigated with targeted stoichiometry of Li6.7Ga0.1La3Zr2O12, Li5.5Ga0.5La3Zr2O12, and Li4GaLa3Zr2O12, which are denoted as 0.1Ga-LLZO, 0.5Ga-LLZO, 1.0Ga-LLZO in the following sections. To be brief, samples, which are labeled LLZO_SG_CS1100, 0.1Ga-LLZO_SG_CS1100, 0.5Ga-LLZO_SG_CS1100, 1.0Ga-LLZO_SG_CS1100, corresponding to 1 mole LLZO sample with 0 mole, 0.1 mole, 0.5 mole and 1.0 mole gallium doping in.

3.2.2 Synthesis of Ga-LLZO powders via sol-gel process

Powders synthesized from the sol-gel approach were fabricated for comparison with the solid-state reaction method. According to the analysis of the phase composition with different Ga contents, 0.1Ga-LLZO consisted of a mixture of tetragonal and cubic phases due to the small amount of Ga used. In the case of 1.0Ga-LLZO, the additional gallium resulted in the formation of LiGaO2. Hany El Shinawi and Jürgen Janek [42] also mentioned the function of the secondary phase LiGaO2 in Li7La5Zr2O12 structure can work
as the sintering aid to improve the densification of the pellets. However, in this work, no more talks in this part. In fact, there should be a transient point of the amount of gallium used to total stabilized the cubic structure as low as a point between 0.1~0.5 mole Ga, and as high as a point between 0.5~1 mole gallium. To be simplified, 0.5Ga-LLZO was chosen as the targeted composition for the synthesis of sol-gel derived powders.

The precursor was prepared by sol-gel method in the following steps: i) GaCl₃ solution was prepared with the original powder GaCl₃ dissolved in deionized (DI) water, ii) citric Acid was dissolved in DI water to serve as a complexing agent, iii) Li₂CO₃ and La₂O₃ were dissolved in dilute nitric acid, and ZrO(NO₃)ₓH₂O was dissolved in concentrated nitric acid and iv) the solution with ions was added to the citric acid solution with the ratios Li : La : Zr : Ga : citric acid= 6.1: 3: 2: 0.5 : 12. An addition of 10% excess of was used to compensate the loss of lithium during high-temperature treatments. The mixed solution was stirred overnight and dried at 100°C for several days in the oven until all the solvents were removed. The dried foam was ground and put into the oven until the powder become dry enough. Crystalline Ga-LLZO powder was fabricated by heating the precursor to 950°C for 5 hours.
3.2.3 Sintering Ga-LLZO via conventional sintering process

Green pellets were prepared by pressing the powder with PVA binder with an isostatic pressure of 1400 psi for 1 min. According to the previous studies on Li$_7$La$_3$Zr$_2$O$_{12}$ pellets, the sintering conditions for Ga-LLZO were 1000°C, 1100°C and 1200°C for 5 hours in air with a sealed alumina crucible. A ramping rate 5°C/min was adopted during both heating and cooling process. In addition, a small boat of Li$_2$CO$_3$ and mother powders were placed adjacent to the pellet in a sealed crucible to create a high lithium vapor pressure to reduce lithium loss during sintering as the same method as what used in the synthesis of undoped-Li$_7$La$_3$Zr$_2$O$_{12}$.

3.2.3 Sintering Ga-LLZO via SPS process

In addition to conventional sintering, pellets were sintered by SPS process at 950°C and 1000°C for 10 minutes and 5 minutes. Sintered pellets were reheated at 600°C in the conventional box furnace for 2 hours to remove the attached graphite paper used in the SPS process. After processing, it was observed that all the pellets sintered at 1000°C broke into very small pieces, and a majority of pellets sintered at 950°C for 10 minutes displayed similar behavior. Pellets sintered at 950°C for 5 minutes resulted in large sample pieces sufficient for measurement of ionic conductivity. Therefore, pellets sintered at 950°C for 5 minutes, which is label as SPS950_5min, has been chosen in the late grain growth study.
3.3 Results and discussion

3.3.1 Phase characterization

XRD of powders synthesized at 950°C indicated that the introduction of gallium strongly affected the phase formation of Li$_7$La$_3$Zr$_2$O$_12$. Ga doping at the level of 0.1 Ga resulted in a tetragonal to cubic transformation indicated by the presence of only one strong peak at $2\theta=16.72^\circ$, which is a characteristic peak for a cubic structure LLZO. Prior to doping, LLZO exhibited two strong split peaks around $2\theta=16.38^\circ$ and $16.92^\circ$ corresponding to the lattice parameters a and c in the tetragonal structure. That is, the 0.1Ga-LLZO powder is consisted of both tetragonal phase and cubic phase. Since Ga had a positive effect on tetragonal to cubic phase transformation of LLZO, it was hypothesized that single cubic phase sample could be fabricated by increasing the Ga content. The XRD pattern for the 0.5Ga-LLZO confirmed this hypothesis as displayed in Figure 3-1, where the structure consists of a cubic phase LLZO and evitable . At higher gallium doping levels (1.0Ga-LLZO) LiGaO$_2$ was found indicating the additional gallium additions resulted in secondary phase formation.

The lattice parameters of 0.5Ga-LLZO powder samples synthesized from the sol-gel process and calcined at 950°C (series of three calcination steps) have been calibrated by the addition of standard silicon powders. The XRD patterns display changes in peak position when comparing pure LLZO powders to 0.5Ga-LLZO powders. In the patterns of LLZO,
there are two strong split peaks at $2\theta=16.38^\circ$ and $16.92^\circ$, which correspond to the two lattice parameters in the tetragonal structure. However, the two split peaks merge into one strong peak at $2\theta=16.72^\circ$ after the addition of 0.5 moles Ga. By the combination of angle brackets from tetragonal-LLZO(ICSD_183684)[47], standard cubic-LLZO(ICSD_261302)[65] and the peak position in XRD patterns, the lattice parameters in this cubic structure was determined to be $a=12.980(4)\ \text{Å}$. The lattice values obtained in this work is much closer to the previous computational results ($a=12.982(7)\ \text{Å}$) in pure cubic structure LLZO[9].
Figure 3-1 X-ray diffraction patterns for LLZO, 0.1Ga-LLZO, 0.5Ga-LLZO, 1.0Ga-LLZO powders synthesized via sol-gel process, and the standard patterns for tetragonal-LLZO(ICSD_183684)[47], standard cubic-LLZO(ICSD_261302)[65]. Secondary phase La$_2$Zr$_2$O$_7$(PDF 71-2363); Li$_2$ZrO$_3$(PDF 75-2157); LiGaO$_2$(PDF 72-1640)
3.3.2 Morphology and elements distribution study

a. 0.1Ga-LLZO synthesized via solid-state reaction

Grain and grain boundary microstructure was determined by SEM and the elemental distributions were analyzed by EDS. SEM micrographs of 0.1Ga-LLZO pellets via solid-state reaction and sintered by the conventional sintering process at 1000°C, 1100°C and by SPS at 950°C are displayed in Figure 3-2. It was observed that spherical micro-sized grains were present with no sharp fringes for the three samples. Although pellets sintered by SPS method possess better sinterability than those sintered by conventional sintering process, the separate grains represent the pellets are not dense enough.
Figure 3-2 Scanning electron microscopy (SEM) images of (a) 0.1Ga-LLZO_SSR_CS1000, magnitude 2K; (b) 0.1Ga-LLZO_SSR_CS1000, magnitude 5K; (c) 0.1Ga-LLZO_SSR_CS1100, magnitude 2K; (d) 0.1Ga-LLZO_SSR_CS1100, magnitude 5K; (e) 0.1Ga-LLZO_SSR_SPS950, magnitude 2K; (f) LLZO_SSR_SPS950, magnitude 5K.
0.5Ga-LLZO was chosen as the target composition to compare the sol-gel process and solid-state reaction process due to the single cubic phase observed in calcined powders. For 0.5Ga-LLZO synthesized by solid-state reaction and sintered by conventional sintering at 1000°C Figure 3-3(a) and 1100°C Figure 3-3(b) for 5 hours, the spherical grains are in the ranges of 1 to 7 um. Grains grow connectively forming fringes just in partial regions. Compared with the pellets sintered at 1000°C by conventional sintering, pellets sintered at same temperature exhibited larger grains with obvious fringes. Figure 3-3(c) and Figure 3-3(d) shows the pellets synthesized by the sol-gel process have higher sinterability than those synthesized by solid-state reaction. The grains size is in the ranges of ~100um, which is much bigger than those synthesized by solid-state reactions. It is clearly visible that densification of the pellets and good inter-grains connectivity are achieved in the SEM images, which is in good agreement with the statement that finer particles in sol-gel synthesis process are favorable for sintering.
Figure 3-3 Scanning electron microscopy (SEM) images of (a) 0.5Ga-LLZO_SSR_CS1000, magnitude 5K (b) 0.5Ga-LLZO_SSR_CS1100, magnitude 5K (c) 0.5Ga-LLZO_SG_CS1000, magnitude 5K (d) 0.5Ga-LLZO_SG_CS1100, magnitude 5K.
Detailed SEM-EDS analysis revealed enrichment of gallium in grain-grain boundaries in 0.5-LLZO_SG_CS1100 pellets, which resemble glass-like inter-granular Ga-rich phases playing the role of sintering aids as reported by Shinawi et al.[42]. However, the majority of the gallium disperses uniformly in the garnet type structure indicating gallium substitution for the Li ions as discussed in previous reports.

Figure 3-4 Elements quantities analysis of 0.5Ga-LLZO_SG_CS1100 by Energy dispersive spectroscopy (EDS) mapping combined with SEM images. Al and Ga rich phases accumulate in the grain-grain boundary regions (brighter areas in the mapping for Ga and Al).
Figure 3-5 Elements quantities analysis of 0.5Ga-LLZO_SG_CS1100 by Energy dispersive spectroscopy (EDS) mapping combined with SEM images. SG represents powders synthesized via sol-gel process, CS1100 represents the pellets were sintered by conventional sintering at 1100°C. Composition can be expressed as \( \text{Li}_{7.7}\text{La}_{3}\text{Zr}_{1.3}\text{Ga}_{0.45}\text{Al}_{0.25}\text{O}_{12} \) by the charge balance and fixing the amount of lanthanum.
The existence of Al might be due to the Al substituting of Li ions during the sintering process. Because the lack of the information of lithium ions in the EDS, the exact composition of pellets cannot be acquired. However, the density measurement of the pellets by Archimedes’ method shows the pellets having a very high density (4.7325 g/cm³) among these pellets fabricated. According to the theoretical density of tetragonal LLZO (5.106 g/cm³) and cubic LLZO (5.098 g/cm³), the relative density of 0.5Ga-LLZO pellet is above 90%.

3.3.3 Density measurement

The theoretical density of 0.1Ga-LLZO, 0.5Ga-LLZO, 1.0Ga-LLZO were obtained by structural calculations based on the formula weight and lattice volume from EDS and XRD. Because lithium cannot be detected by X-ray, the precise compositions formula is not accessible at present. However, in this work, lanthanum was used to calibrate other elements and the total formula composition due to lanthanum is not volatile in the whole process. With the preceding assumptions, the theoretical density of the samples was calculated to be 4.893 g/cm³, 4.951 g/cm³, and 5.085 g/cm³ for the 0.1Ga-LLZO, 0.5Ga-LLZO, 1.0Ga-LLZO samples respectively. The density of each pellet and relative density are shown in Table 3-1.
Table 3-1 Density and relative density of Ga-doped LLZO

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density (g/cm³)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellets sintered from the powders synthesized via solid-state reaction process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1Ga-LLZO_CS1000</td>
<td>2.9233</td>
<td>59.75%</td>
</tr>
<tr>
<td>0.1Ga-LLZO_CS1100</td>
<td>3.0857</td>
<td>63.06%</td>
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<td>0.1Ga-LLZO_SPS950</td>
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<td>0.5Ga-LLZO_CS1000</td>
<td>3.1989</td>
<td>64.60%</td>
</tr>
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<td>0.5Ga-LLZO_CS1100</td>
<td>3.9454</td>
<td>79.69%</td>
</tr>
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<td>0.5Ga-LLZO_SPS950</td>
<td>4.1767</td>
<td>84.36%</td>
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<td>1.0Ga-LLZO_CS1000</td>
<td>3.2042</td>
<td>63.01%</td>
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<td>4.0136</td>
<td>78.93%</td>
</tr>
<tr>
<td>1.0Ga-LLZO_SPS950</td>
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<td></td>
</tr>
<tr>
<td>Pellets sintered from the powders synthesized via sol-gel process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5Ga-LLZO_CS1000</td>
<td>4.7623</td>
<td>96.18%</td>
</tr>
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<td>95.58%</td>
</tr>
<tr>
<td>0.5Ga-LLZO_SPS950</td>
<td>4.1767</td>
<td>82.13%</td>
</tr>
</tbody>
</table>
CHAPTER 4. ELECTROCHEMICAL STUDY OF LLZO AND GA-DOPED LLZO

The ionic conductivity of LLZO and Ga-LLZO pellets were investigated by AC impedance electrochemical spectroscopy (EIS) using silver electrodes. Heat treatment at 600°C for 2 hours (5 °C/min heating rate), was employed to remove the organic constituents in the silver paste.

Since the mechanism of lithium ion conduction is influenced by the migration of lithium ions, the structure of the lattice, the grain structure, the grain boundary structure, and residual porosity are important factors determining overall performance. In all of these cases, the amount of gallium dopant replacing lithium ions in lithium sites determines the lattice structure, grain size, the ratio of grain to grain-boundaries area, and the density of the samples. Therefore, these three important sample parameters have been investigated in this work.

4.1 Contents of gallium substituted in lithium sites

A typical Nyquist plot of LLZO measured at room temperature is displayed in Figure 4-1. The plot is mainly composed of a typical semicircle at high frequency and a tail at low frequency. Three contributions of the pellet can be referred to bulk, grain-boundary, and the electrodes. Therefore, the impedance data of these samples were fitted with an equivalent circuit of \((R_b)(R_{gb}Q_{gb})(Q_{electrode})\). R denotes the resistance and Q represent the
constant phase element contributions of the respective bulk ($R_b$), grain-boundary ($R_{gb}$), and the electrode contributions, which was also used in other related papers[66]. Two semicircles may be interpreted in terms of bulk and grain-boundary effect (for the high-frequency semicircle) and the electrode effects (for the low-frequency semicircle) if a lithium related electrode is employed.

Figure 4-1 A typical Nyquist plot of LLZO pellets measured at room temperature. $R_b(R_{gb}Q_{gb})Wo$ pattern is used to fit the experimental results, where $R_b$=bulk resistance, $R_{gb}$= grain-boundary resistance, $Q_{gb}$=consistent component to fit grain-boundary resistance, $Q_{electrode}$= consistent component to fit electrodes resistance.
Arrhenius plots for the total conductivity of different contents of gallium doping is shown in Figure 4-2. At the same measuring condition (20~120°C), total conductivity increases with the addition of gallium. For the LLZO_SG_CS100, with no dopant addition, the structure is totally comprised of a tetragonal phase, which results in a relatively low ionic conductivity (~1.3×10⁻⁶ S/cm at room temperature) than pellets with dopant additions. This is due to structural features of the tetragonal lattice where the three distinct lithium sites are highly occupied by lithium ions with limited space (vacancies) for ionic transport to occur.

With the introduction of gallium, the positions of the three lithium ions were occupied by gallium ions, leading to the structural transition from tetragonal to cubic resulting in Li vacancies which leads to higher level of ionic conductivity.

The 0.1Ga-LLZO_SG_CS1100 pellet which is composed of both tetragonal and cubic structures, displayed a higher level of ionic conductivity (2.0 ×10⁻⁶ S/cm at room temperature) than the LLZO_SG_CS100 pellet and lower ionic conductivity than the 0.5Ga-LLZO_SG_CS1100 pellet. The 0.5Ga-LLZO_SG_CS1100 pellet consisting of a single cubic structure possessed the highest total ionic conductivity (5.8×10⁻⁵S/cm at room temperature) of the above samples (LLZO_SSR_CS100 pellet and 0.1Ga-LLZO_SSR_CS1100 pellet).
Figure 4-2 Arrhenius plots for the total ionic conductivity of different gallium-containing LLZO sample which are sintered by conventional sintering process at 1100 °C for 5 hours.

4.2 Interfacial effects on ionic conductivity

Since 0.5Ga-LLZO samples exhibited the highest level of ionic conductivity among targeted compositions in this work, further observations and analysis about the grain and grain boundaries were pursued. Previous studies about the powders synthesized via both sol-gel route (SG) and by solid-state reaction (SSR) method showed the powders from SG resulted in finer particle size (600–700nm), compared with SSR powders (2–3 um). In general, finer particles are more beneficial for sintering resulting in lower the sintering
temperature and enhanced grain growth. Sintering temperature for the powders synthesized via sol-gel process is much lower than those synthesized via solid-state reaction process due to the higher energy activity of the smaller particles. Meantime, these finer particles also promote the grain growth when prorogating sintering time.

Obviously, a large ratio of gain/grain-boundaries can be realized by increasing the grain size. Compared with the pellets fabricated from the SSR powders, the pellets fabricated by SG powders possessed larger grains. All the grain sizes discussed here are statistical data instead of single particles.

Investigations on the impact of grain growth on conductivity initiated with the 0.5Ga-LLZO_SG_SPS950_5min, which represents the pellets fabricated with sol-gel powders and sintered by the spark plasma sintering (SPS) method for 5 minutes. After the initial SPS treatment, the pellets were subjected to conventional sintering at 950°C, 1000°C, 1100°C for 5 hours consequently. SEM images of the surface of these pellets are shown in Figure 4-3.

The particles size distributions were analyzed by ImageJ software[49] and the plots of particle size distribution are presented in Figure 4-4 (a) and (b), particle size did exhibit significant change due to the same sintering temperature employed as the starting SPS samples. The grain size changed from 1 um to 3 um, and then from 5 um after the heat
treatment at 950 °C, 1000°C and 1100°C respectively. Grain and grain size distribution analysis of 0.5Ga-LLZO_CS1100_5h have been discussed in Figure 3-3.
Figure 4-3 Scanning electron microscopy (SEM) images of (a) 0.5Ga-LLZO_SG_SPS950_5min,2K, (b) SPS+CS950_5h, 2K, (c) SPS+CS1000_5h, 2K, (d) SPS+CS1000_5h, 2K. In which, SG means the powders synthesized via sol-gel route, CS950_5h, CS1000_5h, and CS1100_5h represents the SPS950 dealt with reheating treatment at 950°C, 1000°C and 1000°C consequently for 5 hours.
Figure 4-4 Particle size distribution plots of 0.5Ga-LLZO pellets sintered by (a) SPS950_5min (b) SPS+CS950_5h (c) SPS+CS1000_5h (d) SPS+CS1000_5h.

Table 4-1 Statistic data for SPS pellets: number of grains, mean size, standard deviation, t-test statistic, degree of freedom, and probability >|t|

<table>
<thead>
<tr>
<th></th>
<th>SPS950_5min</th>
<th>SPS+CS950_5h</th>
<th>SPS+CS1000_5h</th>
<th>SPS+CS1100_5h</th>
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<tr>
<td>N (numbers of grains)</td>
<td>129</td>
<td>100</td>
<td>104</td>
<td>52</td>
</tr>
<tr>
<td>Mean size</td>
<td>1.01</td>
<td>1.33</td>
<td>3.51</td>
<td>7.03</td>
</tr>
<tr>
<td>SD (standard deviation)</td>
<td>0.46</td>
<td>0.51</td>
<td>1.63</td>
<td>3.58</td>
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<td>t-statistic</td>
<td>3.88E-4</td>
<td>-3.29E-2</td>
<td>-4.88E-2</td>
<td>2.25E-3</td>
</tr>
<tr>
<td>DF</td>
<td>128</td>
<td>99</td>
<td>103</td>
<td>51</td>
</tr>
<tr>
<td>Probability &gt;</td>
<td>t</td>
<td></td>
<td></td>
<td>0.99</td>
</tr>
</tbody>
</table>
Nyquist plots of the pellets measured at room temperature are shown in Figure 4-5. From the microstructural perspective, there was no obvious changes from SPS950_5min to SPS+CS950. However, electrical measurements indicate that the bulk conductivity ($\sigma_b$) became larger and grain boundaries conductivity ($\sigma_{gb}$) became smaller after prolonged annealing at 950°C. This is potentially due to the enhanced re-distribution of gallium atoms at the grain boundaries after longer time leading to the higher resistance in the boundary areas. This is supported by the gallium accumulation observed at the grain boundary in or prior mapping results. For 1000°C, 1100°C, both the $\sigma_b$ and $\sigma_{gb}$ ionic conductivity have been improved as a result of the enhanced grain growth. The larger grain sizes lead to an enhancement in the ratio of grain/grain boundaries are, leading to the improvement in the total ionic conductivities.

The sample 0.5Ga-LLZO_SG_CS1100_5h, which was made from sol-gel powders and sintered by the conventional sintering process resulted in the highest ionic conductivity bulk and grain boundary conductivity measured in this study. Compared with the 0.5Ga-LLZO_SPS+CS1100_5h pellet (average grain size~7um), the LLZO_SG_CS1100_5h exhibited much larger grains (average grain size~104um), resulting the far better performance. The equivalent circuits of $R_b(R_{gb}Q_{gb})$ have been employed here to fit the experimental data.
Figure 4-5 Nyquist plots of 0.5Ga-LLZO_SPS950 pellets dealt under spark plasma sintering for 5 minutes, CS950_5h (Conventional sintering at 950°C for 5h), CS1000_5h (Conventional sintering at 1000°C for 5h), CS1100_5h (Conventional sintering at 1100°C for 5h) and 0.5Ga-LLZO_CS1100 (Conventional sintering at 1100°C for 5h directly from calcined powders) measured at room temperature (RT). All the powders are synthesized via sol-gel process.
Arrhenius plots of bulk ionic conductivity, grain-boundary ionic conductivity and total ionic conductivity of the pellets measured at a temperature range from 20°C to 100°C are shown in Figure 4-6, Figure 4-7 and Figure 4-8 and correspondingly. For pellet 0.5Ga-LLZO_SG_SPS950_5min and 0.5Ga-LLZO_SG_SPS+CS950_5h, the temporal effects of elevated temperature annealing on the elemental re-distribution and changes in bulk, grain-boundary, and the total ionic conductivities have been found. By extending the sintering time from 5 minutes to 5 hours at 950°C, \( \sigma_b \) changes from \( 1.6091 \times 10^{-5} \) S/cm to \( 2.1585 \times 10^{-5} \) S/cm; \( \sigma_{gb} \) changes from \( 3.0713 \times 10^{-6} \) S/cm to \( 2.213 \times 10^{-6} \) S/cm. Grain growth occurs when increasing the sintering temperature and holding for 5 hours in each step.
Figure 4-6 Arrhenius plots of bulk ionic conductivities of 0.5Ga-LLZO pellets: SPS950_5min (sintered by spark plasma sintering process for 5 minutes), SPS+CS950_5h (conventional sintering at 950 °C for 5h), SPS+CS1000_5h (conventional sintering at 1000 °C for 5h), SPS+CS1100_5h (conventional sintering at 1100 °C for 5h) and CS1100 (conventional sintering at 1100 °C for 5h directly from calcined powders) measured at temperature range 20~100°C.
Figure 4-7 Arrhenius plots of grain-boundary ionic conductivities of 0.5Ga-LLZO pellets: SPS950_5min (sintered by spark plasma sintering process for 5 minutes), SPS+CS950_5h (conventional sintering at 950°C for 5h), SPS+CS1000_5h (conventional sintering at 1000°C for 5h), SPS+CS1100_5h (conventional sintering at 1100°C for 5h) and CS1100 (conventional sintering at 1100°C for 5h directly from calcined powders) measured at temperature range 20~100°C.
Figure 4-8 Arrhenius plots of total ionic conductivities of 0.5Ga-LLZO pellets: SPS950_5min (sintered by spark plasma sintering process for 5 minutes), SPS+CS950_5h (conventional sintering at 950℃ for 5h), SPS+CS1000_5h (conventional sintering at 1000℃ for 5h), SPS+CS1100_5h (conventional sintering at 1100℃ for 5h) and CS1100 (conventional sintering at 1100℃ for 5h directly from calcined powders) measured at temperature range 20~100℃.
4.3 Effects on ionic conductivity brought by the densities of pellets

Density is critical to this kind of material based on the assumption that a pellet of 100% relative density is used in the conductivity calculation. A low relative density means less ion migration pathways exist in the pellet. Increasing sintering temperature and time leads the shrinkage of the pellets and resulting in the samples with higher density. It was observed that pellets sintered by SPS possessed higher density than those sintered via conventional sintering process at the same sintering temperature.

Ionic conductivities for 0.5Ga-LLZO pellets with various relative densities 70%~90% have been investigated and analyzed that total ionic conductivities increased from $2.40 \times 10^{-6}$ S/cm to $5.80 \times 10^{-5}$ S/cm at room temperature (25°C). However, the grain growth and relative density are closely connected, so it is not easy to separate these two effect entirely.
In summary, though the individual effect on the total ionic conductivity of LLZO cannot be separately investigated with the controlling of other aspects, the trend for each aspect can still be investigated. In Table 4-2, the overall relationship of total ionic conductivity at room temperature and grain size, relative density for each 0.5Ga-LLZO SPS and SPS+CS pellets have been shown. A general trend increase with increased average grain size and increased relative density can be observed.

Table 4-2 List of the comprehensive relationship between compounds, grain size, relative density and ionic conductivity at room temperature.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Average grain size (um)</th>
<th>Relative Density (g/cm³)</th>
<th>RT Ionic conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5Ga-LLZO SPS950 pellets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPS950_5min</td>
<td>1.0</td>
<td>81%</td>
<td>2.40×10⁻⁶</td>
</tr>
<tr>
<td>CS950_5h</td>
<td>1.3</td>
<td>81%</td>
<td>2.57×10⁻⁶</td>
</tr>
<tr>
<td>CS1000_5h</td>
<td>3.5</td>
<td>83%</td>
<td>4.52×10⁻⁶</td>
</tr>
<tr>
<td>CS1100_5h</td>
<td>7.0</td>
<td>89%</td>
<td>5.06×10⁻⁶</td>
</tr>
<tr>
<td>0.5Ga-LLZO CS1100 pellets</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25Ga-LLZO Hot Press 1000 [18]</td>
<td>3.0</td>
<td>91%</td>
<td>3.5×10⁻⁴</td>
</tr>
<tr>
<td>1.0Ga-LLZO _CS1085_6 h</td>
<td></td>
<td>92.5%</td>
<td>5.4×10⁻⁴</td>
</tr>
</tbody>
</table>
The obvious trend of increase in ionic conductivity both with increased mean grain size and density have been observed and shown in Figure 4-9 (a) and (b), respectively. Larger mean grain size means there are less interfacial areas in the pellets, the contribution from grain-grain boundaries become less than bulk. Higher density provides more pathways for ions to choose from as the transporting routes, and the total ionic conductivity increases when more pathways provided.

![Figure 4-9](image_url) The relationship between ionic conductivity at room temperature with (a) mean grain size and (b) density of the SPS and SPS+CS 0.5Ga-LLZO pellets.
CHAPTER 5. GA-DOPED BZY

5.1 Motivation and objectives

Based on the increasing demand for energy with advantages such as environmental benefits, cost-effectiveness in operation and high efficiency, hydrogen working as a fuel has attracted cumulative attentions from many scientists. As the crucial component in fuel cells, the electrolyte, which conducts ions has a number of challenges such as maintaining high ion conductivity with the appropriate chemical or mechanical stability over the operating temperature range of interest[67].

Investigations on proton-conducting electrolytes materials have been reported including polymer, metallic and ceramic membranes[68]. Each of these material systems has different applications due to differences in the working temperature range. Polymer membrane like Nafion developed by DuPont company [69] are suitable for low-temperature applications[70]; metallic and ceramic membranes are suitable for intermediate and high-temperature applications[71, 72].

Intermediate temperature solid oxide fuel cells (IT-SOFC) has benefits of longer life time and reduced cost of operating system due to its relatively lower working temperature (100-600 °C). Generally speaking, there are two types of ionic conductors working as electrolytes: protonic conductor and oxygen ionic conductors. Protons have higher mobility and lower
activation energy than oxygen ions due to much smaller size[67]. Therefore, proton type electrolytes have a higher conductivity at intermediate temperature[73].

5.2 Structure of perovskite-type ceramics

Perovskite materials are a common class of electroceramics with applications in ferroelectrics and energy conversion and storage materials. The general composition can be written as $\text{A}_{1-x}P_x\text{B}_{1-\beta}\text{Q}_\beta\text{O}_{3-\delta}$. In this expression, A represent atoms in A-site, which are bivalent cation such as Barium (Ba), Strontium (Sr), Calcium (Ca) or Magnesium (Mg); P is bivalent cation working as dopants in A-site; B represent atoms in B-site, which are tetravalent cations mainly included in Group IV such as Titanium (Ti), Zirconium (Zr) or the elements in Lanthanum (La) series such as La and Cerium (Ce); Q is B-site dopant, which could be chosen from Group III or La series such as Ytterbium (Yb), Gadolinium (Gd), Neodymium (Nd) and Europium (Eu). The addition of aliovalent dopants into the lattice is aiming to help the formation of oxygen vacancies and leading to an increase the concentration of oxygen vacancies, which is beneficial for the motion of protons in ceramics. The Roman character $\delta$ show this composition is non-stoichiometry with the number of oxide ion vacancies per perovskite-type oxide unit cell.
The cubic structure of perovskite-type AZrO₃ is represented Figure 5-1. In which, A represents A-site atoms like Ba, Ca, Sr or Mg; O represents oxygen atoms. Roman characters (i-iv) represent the positions of protons [74].

Figure 5-1 The structure of perovskite-type AZrO₃

5.3 Fabrication of BaZr₀.₈Y₀.₂O₃-δ and BaZr₀.₈Y₀.₁Ga₀.₁O₃-δ via solid-state reaction

The powders of BZY and Ga-doped BZY were synthesized from the starting materials BaCO₃, ZrO₂, Y₂O₃ and Ga₂O₃ in stoichiometric proportions. The mixed raw powders were ball-milled for 48 hours with ethanol as the dispersing agent. Then powder was dried and reground before calcination. The calcining conditions were investigated in the temperature range from 950°C to 1200°C. Temperature 1450°C and 1500°C have been chosen as the
sintering temperature for the fabrication of BZY, BZGY, and BZG. In order to obtain dense pellets, sintering time are 10 hours for each pellet.

5.4 Results and discussion

5.4.1 Phase characterization

The phases of BaY\(_{0.2}\)Zr\(_{0.8}\)O\(_{3-\delta}\) powders have been identified by X-ray diffraction spectroscopy in the range of 2\(\theta\) = 20° ~ 80°. As shown in Figure 5-2, the peaks of starting material BaCO\(_3\) remained in the patterns after calcination at the lower temperature such as 950°C and 1000°C. All impurities disappeared when the calcination temperature was increased up to 1000°C and 1100°C, and the targeted phases of BaY\(_{0.2}\)Zr\(_{0.8}\)O\(_{3-\delta}\) was obtained. The material displayed a cubic structure with a lattice parameter of a=4.1950 Å. When 1.0 mole gallium was doped in 1 mole BaY\(_{0.2}\)Zr\(_{0.8}\)O\(_{3-\delta}\), the targeted composition BaZr\(_{0.8}\)Y\(_{0.1}\)Ga\(_{0.1}\)O\(_{3-\delta}\) was formed with a lattice parameter of a=4.185(9) Å. The slight shift of the XRD pattern could be explained as the doping of gallium in the BaY\(_{0.2}\)Zr\(_{0.8}\)O\(_{3-\delta}\) lattice. When Yttrium doped in BaZrO\(_3\), oxygen vacancies formed due to the charge balance, leading to the change of parameters. On the other hand, the slight difference of the radius between gallium and yttrium also leads the change of parameters. In the view of XRD pattern, slight shift of the peak positions means these changes of parameters.
Figure 5-2 X-ray diffraction pattern for BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ powders calcined at a) 950°C, b) 1000°C, c) 1100°C and d) 1200°C for 10 hours in sealed crucible. Diamonds represents the standard peaks of BaY$_{0.2}$Zr$_{0.8}$O$_{3-\delta}$, • represent BaZrO$_3$(PDF 70-3667)
Figure 5-3 X-ray patterns for powders of BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$ (BZG), BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$ (BZGY), and BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BZY) synthesized at 1200°C via solid-state process.
5.4.2 Morphology study and density measurement of Ga-doped BZY

Observation of surface of pellets are shown in Figure 5-4 (a)BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$(BZY), (b)BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$ (BZGY), and (c)BaZr$_{0.8}$Ga$_{0.2}$O$_{3-\delta}$(BZG) sintered at 1500℃ for 10 hours. Obviously, the visibility of the single grain shows the pellets are just a pack of grains instead of sintered pellet.

Density measurement has been done by Archemede’s method in the water. Boiling water treatment was employed to get rid of the effect brought by the open pores in the pellet. Low relative density around 75% for BZY and BZGY have been obtained via the calculation by comparing with undoped BaZrO$_3$. This low relative density represents the pellets have not been sintered.
Figure 5-4 Scanning electron microscopy (SEM) images of pellets sintered at 1500°C for 10 hours: (a) BaZr_{0.8}Y_{0.2}O_{3-δ}(BZY), magnitude 5K; (b) BaZr_{0.8}Y_{0.1}Ga_{0.1}O_{3-δ}(BZGY), magnitude 5K; and (c) BaZr_{0.8}Ga_{0.2}O_{3-δ}(BZG), magnitude 5K
The relative density of sample respect to the theoretical density for un-doped BaZrO$_3$ (6.21 g/cm$^3$) is shown in Table 5-1 [75].

Table 5-1 Density and relative density of BZY, BZGY, BZG pellets measured by Archemede’s method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density (g/cm$^3$)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZr$<em>{0.8}$Y$</em>{0.2}$O$_{3-\delta}$, 1500$^\circ$C, 10h</td>
<td>4.5415</td>
<td>73.13%</td>
</tr>
<tr>
<td>BaZr$<em>{0.8}$Y$</em>{0.1}$Ga$<em>{0.1}$O$</em>{3-\delta}$, 1500$^\circ$C, 10h</td>
<td>4.6873</td>
<td>75.48%</td>
</tr>
<tr>
<td>BaZr$<em>{0.8}$Ga$</em>{0.2}$O$_{3-\delta}$, 1500$^\circ$C, 10h</td>
<td>5.1589</td>
<td>83.07%</td>
</tr>
</tbody>
</table>
5.4.3 Electrical conductivity measurements

Ionic conductivities of pellets BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$(BZY), BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$(BZGY), and BaZr$_{0.8}$Ga$_{0.2}$O$_{3-\delta}$(BZG) have been obtained via electrochemical impedance measurement as similar as what have been done for LLZO. Ag electrodes have been pasted on both side of the pellets. The difference is the measuring temperature range. For LLZO, which is normally used at room temperature, low measuring temperature range from 20°C to 100°C has been used. For BZY, high measuring temperature range from 600°C to 800°C have been employed.

In general trend, ionic conductivities of the pellets drop along with the doping level of gallium in the range of 600°C~ 800°C. Compared with the line of Arrihenius plot for BZY in the paper[76], the low conductivity should be due to different sintering process. In the paper, a high sintering temperature at 1670°C for 24 hours has been employed, while in the work 1500°C and 10 hours have been employed.
Figure 5-5 Arrhenius plot for total ionic conductivity of BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BZY), BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$ (BZGY) and BaZr$_{0.8}$Ga$_{0.2}$O$_{3-\delta}$ (BZG) sintered at 1500°C for 10 hours.
CHAPTER 6. CONCLUSIONS AND FUTURE WORK

6.1 Ga-doped Li$_7$La$_3$Zr$_2$O$_{12}$

The investigation of both Ga-doped and undoped LLZO demonstrated that the addition of gallium had a beneficial effect on both the structure and electrochemical performance of LLZO.

Two separate routes (solid-state reaction and sol-gel process) were employed to synthesize the powders with targeted compositions of both Li$_7$La$_3$Zr$_2$O$_{12}$ and Ga-doped Li$_7$La$_3$Zr$_2$O$_{12}$ with different gallium contents. The crystalline phase content of the powders was examined by powder X-ray diffraction studies. For undoped LLZO powders, the XRD patterns exhibited peaks matching the tetragonal structure, which was consistent with literature values [47, 65]. A structural transformation from tetragonal symmetry to cubic symmetry was observed with increasing amount of gallium substitution. In this work, 0.1 mole gallium doped LLZO (Li$_{6.7}$La$_3$Zr$_2$Ga$_{0.1}$O$_{12}$), resulted in powders which were composed of a mixture of tetragonal and cubic structure. Increased level of substitution in the amount of 0.5 moles gallium LLZO(Li$_{5.5}$La$_3$Zr$_2$O$_{12}$) resulted in the XRD pattern indicating a pure cubic phase. At higher doping levels of 1 mol% gallium, LLZO:1.0Ga (Li$_4$La$_3$Zr$_2$GaO$_{12}$) sample there was a formation of a secondary phase identified as LiGaO$_2$. Therefore, powders of undoped-LLZO and LLZO with 0.5 mole gallium dopant were discussed and compared in the following studies both as powders and pellets.
Powders synthesized via the sol-gel process resulted in smaller average particle sizes (~0.7um) than those synthesized via solid-state reaction process (2.0~3.0um). A smaller particles size means more surface area in the powders, which results in larger grains and a more uniform grains distribution in the sintered pellets.

The pellets were sintered by both a spark plasma sintering (SPS) process and a conventional sintering (CS) method. For SPS pellets, higher densification with smaller grain size was obtained, compared with those fabricated by a conventional sintering process. Density measurements of sintered pellets measured via Archimedes’ method revealed that the SPS pellets had higher densities than CS pellets at the same sintering temperature even at the shorter sintering times utilized.

The grain-growth of the Li$_{5.5}$La$_3$Zr$_2$Ga$_{0.5}$O$_{12}$ SPS pellets with sol-gel powders has been investigated by the combination of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electrochemical impedance spectroscopy (EIS). Grain growth occurs when the sintering temperature and sintering time are increased. Pellets sintered at 950°C for 5min had the smallest average grain size ~1.0 um. Following the initial SPS process, pellets were gradually sintered in a conventional box furnace at 950°C, 1000 °C, and 1100°C in air for 5 hours. The average grain size grew from ~ 1.0 um to ~7.0 um. In comparison, pellets directly sintered by a conventional sintering process at 1100°C for 5
hours displayed an average grain size of approximately 102.4 um. This large grain growth was due to the large driving force of starting powders with small nominal grain size.

In general, there will be an optimum trade-off between lithium-loss, sintering temperature, phase composition and the ionic conductivity of the pellets. The highest total ionic conductivity at room temperature was found to be in the range of $5.81 \times 10^{-5}$ S/cm for the sol-gel synthesized Li$_{5.5}$La$_3$Zr$_2$Ga$_{0.5}$O$_{12}$ sintered by conventional sintering in the air. The total lithium ionic conductivity was found to be in the range of $4.37 \times 10^{-6}$ S/cm at room temperature for the SSR synthesized Li$_{5.5}$La$_3$Zr$_2$Ga$_{0.5}$O$_{12}$ sintered by conventional sintering method in the air. It is believed that differences in characteristics of the original powders, like particle size and uniformity, led to the higher ionic conductivity of the pellets fabricated via sol-gel synthesized powders. High sintering temperatures in excess of $1100^\circ$C led to the loss of lithium ions, which also resulted in a degradation of the ionic conductivity. DTA/TG studies of the LLZO powders revealed that approximately 1% weight loss occurs from $400^\circ$C to $1300^\circ$C, which may correspond to the loss of lithium ions in the powders during the heating process. Also, secondary phases such as La$_2$Zr$_2$O$_7$ and very low conductivity values were measured for pellets sintered at $1200^\circ$C for 5 hours.

In the pellets, bulk (grain) or grain boundaries have both contributed to the total ionic conductivity. Generally speaking, the bulk region displayed a 1 to 2 order magnitude increase as compared to the grain-boundary ionic conductivity pointing to a metric
consisting of the ratio of grain/grain-boundaries for optimization of the total ionic conductivity. Samples with a large ratio of grain/grain-boundaries are expected to have high values of total ionic conductivity. This was verified and discussed in the section discussing grain growth. The LLZO:0.5Ga pellets sintered by SPS process for 5 minutes at 950°C, following by conventional sintering process at box furnace at the same temperature for 5 hours resulted in an ionic conductivity $\sigma_b$ enhancement from $1.61 \times 10^{-5}$ S/cm to $2.16 \times 10^{-5}$ S/cm; $\sigma_{gb}$ decrease from $3.07 \times 10^{-6}$ S/cm to $2.21 \times 10^{-6}$ S/cm which was potentially due to the enhanced re-distribution of gallium atoms at the grain boundaries after extended sintering time leading to the higher resistance in the boundary areas.

Future work of LLZO

The improvement of the ionic conductivity of LLZO requires additional attention. Although high bulk ionic conductivity of the pellets up to $9.08 \times 10^{-4}$ S/cm has been obtained in this work and total ionic conductivity is low as $5.81 \times 10^{-5}$ S/cm, these values are still relatively low when compared with commercial liquid electrolytes such as ethylene carbonate/dimethyl carbonate 1M LiPF$_6$ ($\sim 10^{-2}$ S/cm) [77]. There is still room for the advancement on several crucial aspects of this materials system such as enlarging the grain size to decrease the resistance between the grains, using other dopants or techniques to help the sintering process targeting dense pellets or films.
Furthermore, the construction of full solid-state lithium ion batteries based on the previous studies of Ga-doped LLZO electrolytes should be another important research direction to promote the practical use of all solid-state lithium ion batteries. The high lithium ionic conductivity of Ga-LLZO at room temperature will reduce the internal resistance of the batteries, leading to the enhancement of the energy output. Therefore, materials such as LiCoO₂, LiNi₁/₃Mn₁/₃Co₁/₃O₄, or LiFePO₄ can be employed as cathode materials, while anode materials like LiC₆ and even lithium metal can be pursued due to the enhanced chemical stability of LLZO against lithium metal.
6.2 Ga-doped BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$

Gallium, working as the secondary substitution strategy also has been employed to lower the sintering temperature and enhance the densification of the perovskite type of BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ in this thesis work. Powders of BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$, BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$ and BaZr$_{0.8}$Ga$_{0.2}$O$_{3-\delta}$ were synthesized via a solid-state reaction. A single phase perovskite structure has been verified by X-ray diffraction with a small shift of peak position correlated with gallium content.

Pellets were sintered at 1500°C and 1550°C for 10 hours. The relative density of the BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$, BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$ and BaZr$_{0.8}$Ga$_{0.2}$O$_{3-\delta}$ pellets sintered at 1500°C were 75.92%, 86.33%, and 92.56%, which was measured by the Archimedes method using deionized water with respect to theoretical density of BaZrO$_3$ (6.21 g/cm$^3$)[82]. Although gallium was doped in to the lattice of BZY helping improve sinterability, this improved processing resulted in a degradation of ionic conductivity. The order of conductivity is BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$, BaZr$_{0.8}$Y$_{0.1}$Ga$_{0.1}$O$_{3-\delta}$, and then BaZr$_{0.8}$Ga$_{0.2}$O$_{3-\delta}$, when compared with at the same measuring temperature range from 400°C ~600°C.
CHAPTER 7. REFERENCES