STRUCTURAL STABILITY OF TETRAGONAL AND HIGH Li⁺ CONDUCTIVE CUBIC PHASE Li₇La₃Zr₂O₁₂ LITHIUM GARNETS

2.1. INTRODUCTION

Solid-state fast lithium ion (Li⁺) conductors have attracted much attention in recent times owing to their potential application in electrochemical energy storage devices particularly in developing high performance all-solid-state lithium batteries. Solid Li⁺ conducting electrolytes are believed to be superior to the presently used organic liquid electrolytes in terms of safety issues such as dendrite formation, flammability and leakage problem [1, 2]. Solid electrolyte with high Li⁺ conductivity, low electronic conductivity and wide electrochemical window is strongly required for the development of safe, high power and high capacity all-solid-state lithium secondary battery for heavy duty application like electric vehicle (EV). So far, many inorganic solid electrolytes with different crystal structures including perovskite titanates Li₃ₓLa(2/3-x)TiO₃ (0<x<0.16) [3–5], NASICON (sodium superionic conductor) Li₁.₃Ti₁.₇Al₀.₃(PO₄)₃ [6–8], LISICON (lithium superionic conductor) Li₁₄ZnGe₄O₁₆ [9, 10] and lithium ‘stuffed’ garnets [11–19] have been explored. Among these, garnet-like structural compounds reported by Weppner et al. received considerable attention in recent times for potential application as electrolytes in all-solid-state lithium batteries [11–19].

Lithium stuffed oxide with the nominal formula Li₇La₃Zr₂O₁₂ (LLZ) reported by Murugan et al. has been widely studied because of its high total (bulk + grain-boundary) Li⁺ conductivity (σ_Li⁺ > 10⁻⁴ S cm⁻¹) at room temperature [20, 21]. LLZ exist in three kinds of crystal phases, namely tetragonal phase belonging to the space group I₄₁/acd...
(No. 142) [22], high Li\(^+\) conductive cubic phase belonging to the space group \(Ia\bar{3}d\) (No. 230) [20, 21, 23] and low temperature cubic phase [24]. The Li\(^+\) conductivity of the tetragonal and low temperature cubic phases is two orders of magnitude lower than that of high Li\(^+\) conductive cubic phase [20-22, 24]. LLZ in tetragonal phase (\(I4_1/acd\)) is an ordered structure with lithium on tetrahedral 8\(a\) site and octahedral 16\(f\) and 32\(g\) sites [22]. LLZ in high Li\(^+\) conductive cubic phase (\(Ia\bar{3}d\)) is disordered with lithium on tetrahedral 24\(d\) and octahedral 96\(h\) sites [23]. The low temperature cubic phase arises due to either CO\(_2\) absorption or hydration mechanism in tetragonal phase [17, 18].

Among these three phases of LLZ, the high conductive cubic phase (space group \(Ia\bar{3}d\)) is the most preferred owing to its high Li\(^+\) conductivity with excellent chemical and electrochemical compatibility against lithium metal and potential electrodes [20, 21, 25]. Tetragonal phase LLZ was found to be sensitive to ambient conditions, especially when exposed to humid conditions [26]. In addition to the high Li\(^+\) conductivity, the chemical stability of electrolyte under ambient atmosphere and in aqueous solutions should be also important in particular for Li-air and Li-water battery applications.

The ion exchange properties of various solid Li\(^+\) electrolytes have been explored, particularly, the substitution of protons (H\(^+\)) for Li\(^+\) to understand the lithium occupation in the structure. Boulant et al. demonstrated the ion-exchange ability in perovskite, La\(_{(2/3)-x}\)Li\(_{3x}\)TiO\(_3\), using H\(_2\)O as an exchange medium [27]. Bohnke et. al. reported the Li\(^+\)/H\(^+\) exchange property of La\(_{(2/3)-x}\)Li\(_{3x}\)TiO\(_3\) in water and in humid atmosphere [28]. The Li\(^+\)/H\(^+\) exchange reaction has been reported recently for several lithium garnets [29-32].
Galven et al. reported that the Li\(^+\)/H\(^+\) exchange probability depends upon the concentration of lithium in lithium garnets [29]. The Li\(^+\)/H\(^+\) exchange occurs only for the lithium stuffed garnets Li\(_x\)A\(_3\)B\(_2\)O\(_{12}\) with \(x > 3\) (in which A and B refers to 8- and 6-coordinated cation sites, respectively) i.e. lithium concentration greater than permitted by conventional garnet [29].

While extensive studies have focused on the relationship between chemical composition and ionic conductivity, the stability of the LLZ in aqueous solutions is rarely reported. As the best candidate among the known garnet-type electrolytes, it is necessary to understand the stability of high Li\(^+\) conductive LLZ in aqueous solutions for future applications in Li-air batteries. Hence systematic investigation on the structural stability of tetragonal and high Li\(^+\) conductive cubic phase LLZ against solution of benzoic acid and ethanol, distilled water and humid atmosphere were carried out.

2.2. EXPERIMENTAL SECTION

2.2.1. Synthesis of Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) (LLZ) using solid-state reaction technique

LiOH.H\(_2\)O (Sigma-Aldrich, 99.9%; 15 wt.% excess lithium reactant was added to compensate the lithium loss during high temperature sintering), La\(_2\)O\(_3\) (Sigma-Aldrich, >99% pre dried at 900 °C for 24 hours) and ZrO\(_2\) (Sigma-Aldrich, 98%) were used as the starting material for the preparation of Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) (LLZ) by conventional solid-state reaction technique. The appropriate amounts of the reactants were ball milled with 2-propanol using zirconia balls for 6 hours in a Pulverisette 7, Fritsch, Germany. After the evaporation of the solvent, the mixtures were heated in an open alumina crucible and
maintained at 850 °C for 6 hours. The resultant powders were ball milled again using zirconsia balls for 6 hours. After the evaporation of the solvent the powders were pressed into pellets. The pellets were covered with the powder of the same composition to reduce possible lithium loss during high temperature sintering of 900 °C for 20 hours and 1225 °C for 30 hours in a closed alumina crucible.

2.2.2. Li⁺/H⁺ exchange in Li₇La₃Zr₂O₁₂

The pellet sintered at 900 °C was crushed back into powder form for ion-exchange reactions. 1g of Li₇La₃Zr₂O₁₂ in powder form was placed in a round-bottom flask containing a magnetic stir bar, 10 g of benzoic acid (C₆H₅COOH) and 100 mL of ethanol (C₂H₅OH). The solution was heated at 60 °C reflux for one week at first. The above experiment was repeated for longer duration of 4 weeks to investigate the effect of ion exchange reaction in LLZ sintered at 900 °C with time. The pellet sintered at 1225 °C was crushed into powder form and also treated with the solution of benzoic acid and ethanol under reflux at 60 °C for 4 weeks to investigate the ion exchange in LLZ sintered at 1225 °C. The products were washed with ethanol, filtered and dried at 60 °C for further characterization.

The LLZ sample sintered at 900 °C was exposed to humid atmosphere for 1 week and 4 weeks whereas, the LLZ sample sintered at 1225 °C was kept under humid atmosphere for 4 weeks to study the Li⁺/H⁺ exchange.

The Li⁺/H⁺ exchange reaction was also performed by immersing the LLZ sintered at 900 °C for 1 week in a beaker containing distilled water and then the experiment was repeated for longer duration of 4 weeks. The pH of the solution in the beaker was
measured to follow the ion-exchange reaction in water. LLZ sintered at 1225 °C was also immersed in a beaker containing distilled water for 4 weeks. The Li⁺/H⁺ exchanged garnet powders were then recollected for further characterization.

2.2.3. Characterization

Thermogravimetric thermograms (TG) were recorded using SDT Q600 (TA) in air atmosphere with a heating rate of 10 °C/min in the temperature range from room temperature to 1000 °C. The sintered pellets were ground into powder to determine the phase purity by powder X-ray diffraction (PXRD) using X’pert PRO PANalytical X-ray diffractometer with Cu-Kα radiation of λ = 1.5418 Å from 2θ = 10° to 80° with a step size of 0.025°. HITACHI S-3400N scanning electron microscope (SEM) was used to evaluate the surface morphology of the samples. The elemental analyses of the prepared samples were carried out with Bruker S4 Pioneer wavelength dispersive X-ray fluorescence spectrometer (WD-XRF), to estimate the inclusion of Al into the LLZ samples from the alumina crucible. The densities of the sintered pellets at room temperature were obtained using Archimedes’ principle with deionised water as the immersion medium. Room temperature Raman and temperature dependent (30 °C to 200 °C) Raman spectroscopic investigations on the samples in the range 50-1500 cm⁻¹ were performed using a Renishaw in via Reflex spectrometer having a 50 mW internal Ar⁺ laser source at the excitation wavelength of 514 nm. Electrical conductivity measurements of the sintered pellets were performed using Li⁺ blocking Au-electrodes (Au paste cured at 600 °C for 1 hour) in the frequency range 20 Hz to 15 MHz using Wayne Kerr 6500B precision impedance analyzer in the temperature range from room temperature (33 °C) to 200 °C.
2.3. RESULTS AND DISCUSSION

2.3.1. Structural analysis using powder X-ray diffraction (PXRD) and Raman spectroscopy

The PXRD patterns of LLZ sintered at 900 °C and 1225 °C are shown in Figure 2.1 along with the reported patterns of tetragonal phase ($I4_1/acd$) LLZ and high Li$^+$ conductive cubic phase ($Ia\bar{3}d$) phase LLZ [33]. The PXRD pattern of LLZ sintered at 900 °C shown as Figure 2.1(a) indicates the characteristic splitting of diffraction peaks which confirm the formation of tetragonal phase. The tetragonal phase can be identified by peak doublets; the most pronounced is centered at $\theta = 30.5^\circ$.

When the sintering temperature is increased to 1225 °C, the doublet peaks merge into a well defined sharp diffraction peak as shown in Figure 2.1(b), which indicates the stabilization of high Li$^+$ conductive cubic phase LLZ. The PXRD patterns of LLZ sintered at 900 °C and 1225 °C in the $2\theta$ range from 24° to 45° shown as Figure 2.2(a) and (b) clearly revealed the peak splitting for tetragonal phase and sharp peaks for high Li$^+$ conductive cubic phase LLZ, respectively.

The lattice parameters of LLZ sintered at 900 °C was found to be $a = 12.9902(1)$ Å and $c = 12.6817(2)$ Å, which are close to the reported value of tetragonal phase LLZ [22]. The lattice parameter of LLZ sintered at 1225 °C was found to be $12.9651(2)$ Å which is similar to the value reported in the literature for high Li$^+$ conductive cubic phase LLZ [20, 21].
Figure 2.1. PXRD patterns of LLZ sintered at (a) 900 °C and (b) 1225 °C along with the reported patterns of tetragonal phase (I4_1/acd) LLZ and high Li⁺ conductive cubic phase (Ia\tilde{3}d) LLZ [33].
Figure 2.2. PXRD patterns of LLZ sintered at (a) 900 °C and (b) 1225 °C in the 2θ range from 24° to 45° along with the reported patterns of tetragonal phase (I41/acd) LLZ and high Li+ conductive cubic phase (Ia3d) LLZ [33].

Raman scattering is a very powerful technique for acquiring useful information on the structure of ceramic oxides. Earlier Raman studies on LLZ predicted that the bands between 100 cm\(^{-1}\) and 150 cm\(^{-1}\) corresponds to the vibration of heavy La cation and the band observed around 640 cm\(^{-1}\) correspond to Zr-O bond stretching [34]. For several lithium metal oxide materials and lithium garnets it has been demonstrated that, the
internal modes of LiO$_6$ appear in the range 200-300 cm$^{-1}$, whereas the internal modes of LiO$_4$ occurs in the range 350-500 cm$^{-1}$ [35, 36]. Because of the complex nature of the structure of lithium garnets, considerable mixing between internal modes of LiO$_4$, LiO$_6$ and the other coordinated groups present in the structure are expected and thus the interpretation of Raman spectra of lithium garnets becomes much complicated. Hence it is very difficult to assign the observed Raman bands in the region 200-500 cm$^{-1}$.

The Raman spectra of tetragonal phase ($I4_1/acd$) LLZ, high Li$^+$ conductive cubic phase ($Ia\bar{3}d$) and low temperature cubic phase LLZ reported by our research group [33, 37] in the range 75-1000 cm$^{-1}$ are shown as Figure 2.3(a) - (c), respectively. The characteristic's Raman spectrum of tetragonal ($I4_1/acd$) phase LLZ (Figure 2.3(a)) consist of relatively larger number of Raman modes in the region 200 to 500 cm$^{-1}$ due to the ordered arrangements of lithium on tetrahedral 8a site and octahedral 16f and 32g sites. The characteristic Raman modes for the tetragonal ($I4_1/acd$) phase LLZ are the weak intense band at 209 cm$^{-1}$, strong peak at 248 cm$^{-1}$, medium intense peak at 291 cm$^{-1}$, strong intense peaks at 346, 370, 404 cm$^{-1}$, strong intense band at 646 cm$^{-1}$ and doublets at 108 and 123 cm$^{-1}$ as shown in Figure 2.3(a).
Figure 2.3. Raman spectra of (a) Tetragonal ($I4_1/acd$) phase LLZ (b) High Li$^+$ conductive cubic ($Ia\bar{3}d$) phase LLZ (c) Low temperature cubic phase LLZ [33, 37].

The Raman spectrum of high Li$^+$ conductive cubic ($Ia\bar{3}d$) phase LLZ as shown in Figure 2.3(b) exhibits few broad and fairly overlapping bands in the region 200-500 cm$^{-1}$ which might be due to the static or dynamic disorder of highly mobile Li$^+$ compared to the ordered arrangement in tetragonal phase [37]. The shoulder broad band at 211 cm$^{-1}$, medium intense broad band at 263 cm$^{-1}$, medium strong broad band at 366 cm$^{-1}$, medium
broad shoulder at 417 cm$^{-1}$, strong intense band at 645 cm$^{-1}$, medium intense peak at 122 cm$^{-1}$ and shoulder band at 108 cm$^{-1}$ are the characteristic Raman modes observed for the high Li$^+$ conductive cubic phase ($Ia\bar{3}d$) LLZ. The Raman spectrum in the intermediate-energy region of high temperature cubic ($Ia\bar{3}d$) phase LLZ exhibits broad and fairly overlapping bands associated to degenerate Raman modes, which turn out partly split in tetragonal LLZ phase, due to its lower symmetry. In disordered system, the modifications in crystals local symmetry preventing atoms from vibrating in phase and leads to shift in the vibrational modes accompanied by broadening.

The Raman bands observed in the range 200-500 cm$^{-1}$ (Figure 2.3(b) and (c)) corresponding to the expected internal modes of LiO$_4$ and LiO$_6$ clearly revealed the major difference between the high Li$^+$ conductive cubic phase and low temperature cubic LLZ. The Raman spectrum of the low temperature cubic phase LLZ shown as Figure 2.3(c) revealed strong intense peak at around 307 and 668 cm$^{-1}$, medium intense bands at around 120, 184, 263, 344 and 380 cm$^{-1}$ and a weak bands at around 487 and 534 cm$^{-1}$. The presence of relatively larger number of Raman modes in the region 200 to 500 cm$^{-1}$ for the low temperature cubic phase LLZ might be due to the ordered arrangements of lithium in the crystal lattice. In addition to the above difference in the Raman spectra of the low temperature cubic phase LLZ (Figure 2.3(c)) and high Li$^+$ conductive cubic phase LLZ (Figure 2.3(b)) an appreciable shift in the positions of vibrational stretching mode of ZrO$_6$ octahedral units is observed. The shift of approximately 23 cm$^{-1}$ towards higher wave number for the Zr-O stretching mode and sharpening of the Raman bands in the region of internal modes of LiO$_4$ and LiO$_6$ for the low temperature cubic phase as shown
in Figure 2.3(c) revealed an appreciable modification in the crystal structure of the low temperature cubic and high Li$^+$ conductive cubic phase LLZ. The cubic phase formed at low temperature might be due to the protonation through the Li$^+$/H$^+$ exchange mechanism into the garnet structure. Raman scattering is a very powerful technique for acquiring useful information on the phases of LLZ compared to PXRD technique.

The Raman spectra of LLZ sintered at 900 °C and 1225 °C are shown in Figure 2.4 along with the reported patterns of tetragonal phase ($I4_1/acd$) LLZ and high Li$^+$ conductive cubic phase ($Ia\bar{3}d$) LLZ measured in the range 75-1000 cm$^{-1}$ [33]. The Raman spectrum of LLZ sintered at 900 °C shown in Figure 2.4(a) exhibit the characteristic features of tetragonal phase ($I4_1/acd$) as supported by PXRD pattern. On the other hand, the Raman spectrum of LLZ sintered at 1225 °C (Figure 2.4(b)) exhibit characteristic pattern of high Li$^+$ conductive cubic phase ($Ia\bar{3}d$) LLZ.
Figure 2.4. Raman spectra of LLZ sintered at (a) 900 °C and (b) 1225 °C along with the reported patterns of tetragonal (I4₁/acd) phase LLZ and high Li⁺ conductive cubic (Ia₃d) phase LLZ in the range 75-1000 cm⁻¹ [33].

The temperature dependent Raman spectra of LLZ sintered at 900 °C in tetragonal (I4₁/acd) phase LLZ and LLZ sintered at 1225 °C in high Li⁺ conductive cubic (Ia₃d) phase are shown as Figure 2.5(a) and (b), respectively. Temperature dependent Raman spectra of tetragonal phase (I4₁/acd) LLZ (Figure 2.5(a)) exhibit tetragonal to cubic phase transition at around 120 °C. The absence of any major changes in the spectral profile of
high Li\textsuperscript{+} conductive cubic phase ($Ia\bar{3}d$) LLZ sintered at 1225 °C (Figure 2.5(b)) indicated the absence of any phase transition in the investigated temperature range (30 °C to 200 °C), which clearly confirms the better thermal stability of the high Li\textsuperscript{+} conductive cubic phase ($Ia\bar{3}d$) LLZ sintered at 1225 °C.

**Figure 2.5.** Temperature dependent Raman spectra measured in the temperature range from 30 °C to 200 °C for LLZ measured in the range 75-1000 cm\textsuperscript{-1} sintered at (a) 900 °C in tetragonal phase ($I4_1/acd$) LLZ and (b) 1225 °C in high Li\textsuperscript{+} conductive cubic phase ($Ia\bar{3}d$) LLZ.
2.3.2. Microstructural analysis

The SEM images of the fractured surface of LLZ pellet sintered at 900 °C and 1225 °C are shown as Figures 2.6(a) and (b), respectively. SEM image of the fractured surface of LLZ pellet sintered at 900 °C revealed that the grains are not in good contact with the neighbouring grains. At this sintering temperature the density of the pellet was found to be poor. The SEM image (Figure 2.6(b)) of the pellet sintered at 1225 °C revealed dramatic improvement in density compared to the sample sintered at 900 °C (Figure 2.6(a)). The SEM image of the LLZ pellet sintered at 1225 °C shown as Figure 2.6(b) exhibited flattened like morphology with dense microstructure.

Figure 2.6. SEM images of the fractured surfaces of LLZ pellet sintered at (a) 900 °C and (b) 1225 °C, respectively.

The relative density of LLZ pellet sintered at 900 °C and 1225 °C were estimated using Archimedes’ principle with deionized water as the immersion medium.
Chapter II

The experimental density of the pellets were derived from the equation given below

\[ \rho_{\text{experimental}} = \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{water}}} \times \rho_{\text{water}} \]  \hspace{1cm} (2.1)

where

- \( W_{\text{air}} \) is the weight of the sample in air (g)
- \( W_{\text{water}} \) is the weight of the sample in deionised water (g)
- \( \rho_{\text{water}} \) is the density of deionised water (g/cm\(^3\)).

The theoretical unit cell density \( \rho_{\text{theoretical}} \) can be estimated from powder X-ray diffraction (PXRD) by

\[ \rho_{\text{theoretical}} = \frac{MZ}{VA} \]  \hspace{1cm} (2.2)

where \( M \) is the molecular weight of the investigated garnet sample, \( Z \) is the number of formula units per unit cell (\( Z = 8 \)), \( V \) is the unit cell volume (\( V = a^3 \), where \( a \) is cubic lattice constant) and \( A \) is Avogadro’s number (\( A = 6.022 \times 10^{23} \text{ mol}^{-1} \)).

Relative density can be calculated using the formula

\[ \text{Relative density in } \% = \frac{\rho_{\text{experimental}}}{\rho_{\text{theoretical}}} \times 100 \]  \hspace{1cm} (2.3)

The estimated relative density of LLZ pellets sintered at 900 °C and 1225 °C are given in Table 2.1. The XRF studies on the LLZ sintered at 900 °C indicated the absence of Al. However, at high sintering temperature around 1225 °C the inclusion of Al from alumina crucible was found to be 0.97 wt%.
2.3.3. Impedance analysis

Typical room temperature (33 °C) AC impedance (Cole-Cole) plots of LLZ pellets sintered at 900 °C and 1225 °C are given in Figure 2.7(a) and (b), respectively. The real and imaginary parts of impedance (Z′(Ω) and Z″(Ω)) were multiplied by a factor of A/t (where A and t are surface area and thickness of the pellet, respectively) and are plotted in Figure 2.7 as Z′(Ωcm) vs. Z″(Ωcm) for the purpose of the comparison of the samples with different geometrical sizes. The total (bulk + grain-boundary) Li⁺ conductivity was calculated from the inverse of the resistivity derived from the intercepts of the low frequency semicircle (close to the tail) with the real axis. The AC impedance plot of LLZ pellet sintered at 900 °C (Figure 2.7(a)) could be resolved into two semicircles. In the semicircle, the region near the origin can be attributed to the bulk resistance of LLZ, while the semicircle in the low-frequency range correlated with the grain-boundary resistance. The room temperature (33 °C) experimental impedance data points of LLZ pellet sintered at 900 °C was fitted with an equivalent circuit consisting of two parallel combination of resistances (R) and constant phase elements (CPEs) representing the electrical bulk and grain-boundary contribution (RbCPEb)(RgbCPEGb) (where R is the resistance and CPE is the constant phase element and the subscript b and gb refers to the bulk and grain-boundary contribution, respectively).

Figure 2.7(b) shows the AC impedance plot of LLZ pellet sintered at 1225 °C. The separate contribution from the grain and grain-boundary could not be distinguished, since only one semicircle was observed instead of two. The tail at the low frequency region was due to the effect of interface between the sample and the ionically blocking...
Au electrodes. Hence, the corresponding impedance plot was fitted with the suitable equivalent circuit using individual resistance (R) and constant phase element (CPE) representing the bulk + grain-boundary and electrode response, respectively, (RCPE) and (CPE_{el}) shown as Figure 2.7(b).

The room temperature (33 °C) total (bulk + grain-boundary) Li^+ conductivity of the LLZ pellets sintered at 900 °C and 1225 °C are given in Table 2.1. The room temperature total (bulk + grain-boundary) Li^+ conductivity was found to be 3.43 x 10^{-7} Scm^{-1} for the tetragonal phase LLZ, while the obtained value for high Li^+ conductive cubic phase was 3.8 x 10^{-4} Scm^{-1}, almost three orders of magnitude higher than the former.

![Figure 2.7](image_url)

**Figure 2.7.** Typical room temperature (33 °C) AC impedance (Cole-Cole) plots of LLZ pellets sintered at (a) 900 °C and (b) 1225 °C measured using Li^+ blocking Au electrodes.
The Arrhenius plots (temperature range 33 °C to 200 °C) for the total (bulk + grain-boundary) Li$^+$ conductivity of LLZ pellets sintered at 900 °C and 1225 °C are shown in Figure 2.8. The activation energies ($E_a$) for the total (bulk + grain-boundary) Li$^+$ conductivity of LLZ were determined from the Arrhenius plot by the equation

$$\sigma T = A \exp\left(\frac{-E_a}{kT}\right)$$  \hspace{1cm} (2.4)

where $A$ is the pre-exponential parameter, $k$ is Boltzmann’s constant and $T$ is the absolute temperature. $E_a$ is the activation energy which can be determined from the slope of log ($\sigma T$) vs. 1000/T plot. Activation energy was calculated to be 0.61 eV and 0.32 eV for tetragonal and cubic phase LLZ, respectively.

**Table 2.1.** Compound, sintering temperature, phase, room temperature (33 °C) total (bulk + grain-boundary) Li$^+$ conductivity, activation energy (in the temperature range 33 °C to 200 °C) and relative density of LLZ pellet.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sintering Temperature</th>
<th>Phase</th>
<th>$\sigma_{\text{total}}$ (Scm$^{-1}$) at 33 °C</th>
<th>Activation Energy $E_a$ (eV)</th>
<th>Relative density %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLZ</td>
<td>900 °C</td>
<td>Tetragonal ($I4_1/acd$)</td>
<td>$3.43 \times 10^{-7}$</td>
<td>0.61</td>
<td>79</td>
</tr>
<tr>
<td>LLZ</td>
<td>1225 °C</td>
<td>Cubic ($Ia\bar{3}d$)</td>
<td>$3.8 \times 10^{-4}$</td>
<td>0.32</td>
<td>93</td>
</tr>
</tbody>
</table>
Figure 2.8. Arrhenius plots for the total (bulk + grain-boundary) Li\(^+\) conductivity of LLZ pellet sintered at (a) 900 °C and (b) 1225 °C measured in the temperature range from 33°C to 200 °C.

2.3.4. Stability of tetragonal phase LLZ

Tetragonal phase Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) (LLZ) lithium garnet was found to be very sensitive to humid conditions, especially when exposed to moisture [34]. Investigation on the phase transition of tetragonal phase LLZ by Wang et al. revealed the tetragonal to cubic phase transition around 100-150 °C and cubic to tetragonal phase transition around 800-900 °C [38]. In order to understand the structural stability of tetragonal and high Li\(^+\) conductive cubic phase LLZ, systematic investigation has been carried out and discussed
by means of proton-exchange under humid atmosphere, distilled water and with solution of benzoic acid and ethanol.

To investigate the reaction between tetragonal phase LLZ and distilled water, freshly prepared tetragonal phase LLZ powder was added to the distilled water (pH = 7) and stirred at room temperature. The pH was measured as a function of time. The pH value increases after the powder was added into distilled water as shown in Figure 2.9. After 20 minutes, the pH became very high (pH > 11). The increase in pH suggests a proton exchange reaction occurs between distilled water and tetragonal phase LLZ. The ion-exchange reaction involves replacement of Li$^+$ by H$^+$ in the garnet-type structure, leaving LiOH to form as a byproduct. The increase in pH may be attributed to the LiOH formation.

![Figure 2.9](image.png)

**Figure 2.9.** Plot of pH value as a function of time for tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$ in distilled water. The pH at 0 min was measured before LLZ was added into water.
There are several possible mechanisms like physical absorption, hydration, proton exchange for lithium and carbonation due to the reaction between LLZ with H₂O and CO₂.

LLZ may react with water as described by the following reactions [39].

\[
\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} + x\cdot \text{H}_2\text{O} \rightarrow \text{Li}_{7-x}\text{H}_x\text{La}_3\text{Zr}_2\text{O}_{12} + x\cdot \text{LiOH} \quad (2.5)
\]

\[
2\text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} \quad (2.6)
\]

LLZ under CO₂ exposure leads to the formation of Li₂CO₃ along with the extra vacancy at the lithium site.

\[
\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} + x\cdot \text{CO}_2 \rightarrow \text{Li}_{7-2x}\text{La}_3\text{Zr}_2\text{O}_{12-x} + x\cdot \text{Li}_2\text{CO}_3 \quad (2.7)
\]

Another possible reaction is that the La₂O₃ raw material used in the preparation might have initially reacted with water to form LaOH and/or LaOOH. Then LaOOH might have reacted with atmospheric CO₂ to form lanthanum oxycarbonate La₂O₂CO₃.

\[
\text{La}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{LaOOH} \quad (2.8)
\]

\[
2\text{LaOOH} + \text{CO}_2 \rightarrow \text{La}_2\text{O}_2\text{CO}_3 + \text{H}_2\text{O} \quad (2.9)
\]

The reaction of the LLZ powder with humid atmosphere (CO₂) and with H₂O can then be

\[
\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} + x/2\cdot \text{H}_2\text{O} + x/2\cdot \text{CO}_2 \rightarrow \text{Li}_{7-x/2}\text{H}_{x/2}\text{La}_3\text{Zr}_2\text{O}_{12} + x/2\cdot \text{Li}_2\text{CO}_3 \quad (2.10)
\]
Figure 2.10(b) - (d), respectively, represents the TG thermograms of freshly prepared tetragonal phase LLZ, tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 1 week. Among all the investigated samples freshly prepared tetragonal LLZ exhibits a minimum weight loss of around 2.5% in the entire investigated temperature range of 30 °C -1000 °C.

The minimal weight loss observed initially below 100 °C in TG (Figure 2.10) corresponds to the elimination of adsorbed water on the surface of the powder. It is interesting to note that, there was a noticeable weight gain around 100 °C -300 °C for all the samples except for tetragonal LLZ phase treated with the solution of benzoic acid and ethanol. The observed weight gain can be attributed to the uptake of CO$_2$/H$_2$O. The earlier TG analysis showed that the preferred temperature range for the CO$_2$ absorption process of LLZ is around 100 °C -200 °C [40]. The extraction process of CO$_2$ was observed around 450 °C -600 °C.

The TGA result of tetragonal LLZ treated with the solution of benzoic acid and ethanol (Figure 2.10(b)) exhibit a major single step weight loss of 5.93% in the interval 300 °C-600 °C. The weight loss is associated with the proton departure. The single step major weight loss suggests the bonding natures of the protons are similar to the Li$^+$. The absence of weight gain in the range 100 °C - 300 °C (Figure 2.10(b)) indicates that there is no reaction between the sample and atmospheric CO$_2$.

It is interesting to note that the freshly prepared tetragonal phase LLZ exhibit maximum weight gain in 100 °C-200 °C compared to that of the remaining samples. This
weight gain might be due to the large intake of CO\(_2\) from the atmosphere. Among the investigated samples the maximum weight loss was observed for the tetragonal phase LLZ exposed to humid condition. This maximum weight loss might be correlated to departure of large amount proton as H\(_2\)O along with the CO\(_2\).

![Graph](image)

**Figure 2.10.** TG thermograms of (a) freshly prepared tetragonal phase LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 1 week.

PXRD patterns of freshly prepared tetragonal phase LLZ, tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 1 week along with the reported patterns of high Li\(^+\)
conductive cubic ($Ia\bar{3}d$) phase LLZ and tetragonal ($I4_1/acd$) phase LLZ are shown as Figure 2.11 and their corresponding Raman spectra are shown as Figure 2.12. The room temperature PXRD pattern of tetragonal phase LLZ immersed in distilled water and exposed to humid atmosphere for 1 week shown as Figure 2.11(c) and (d) indicates the presence of all the diffraction peaks corresponding to that of tetragonal phase. The Raman spectra of the corresponding samples shown in Figure 2.12(c) and (d) also revealed the tetragonal phase. The PXRD pattern (Figure 2.11(b)) and Raman spectrum (Figure 2.12(b)) of tetragonal phase LLZ treated with the solution of benzoic acid and ethanol exhibit a cubic-like garnet phase. The observed cubic-like phase is different from that of high Li$^+$ conductive cubic ($Ia\bar{3}d$) phase LLZ. The lattice parameter of tetragonal phase LLZ treated with the solution of benzoic acid and ethanol increased to 13.0105 Å after ion exchange. The increase in lattice parameter owed to the replacement of Li-O bonds by O–H···O hydrogen bonds [29] through Li$^+$/H$^+$ exchange.
Figure 2.11. PXRD patterns of (a) freshly prepared tetragonal LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 1 week along with the reported patterns of high Li$^+$ conductive cubic ($I\bar{a}3d$) phase LLZ and tetragonal ($I4_1/acd$) phase LLZ [33].
Figure 2.12. Raman spectra of (a) freshly prepared tetragonal phase LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 1 week along with the reported patterns of high Li$^+$ conductive cubic ($Ia\overline{3}d$) phase LLZ and tetragonal ($I4_1/acd$) phase LLZ [33].

SEM images of the fractured surface of freshly prepared tetragonal phase LLZ, tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 1 week are shown as Figure 2.13(a) - (d), respectively. SEM image of the fractured surface of freshly prepared tetragonal
LLZ exhibited relatively small and distribution of uniform sized grains. SEM images (Figure 2.13(b) - (d)) of the fractured surface of tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 1 week exhibited a slight increase in the grain size. SEM image of tetragonal phase LLZ (Figure 2.13(c)) immersed in the distilled water revealed clear surface without any impurity phase over the surface. SEM image of tetragonal phase LLZ (Figure 2.13(d)) exposed to humid atmosphere revealed the presence of secondary phase over the sample surface which might be due to reaction of atmospheric CO$_2$. 
Figure 2.13. SEM images of the fractured surface of (a) freshly prepared tetragonal phase LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 1 week.

Figure 2.14(a) – (d) represents the TG thermograms of freshly prepared tetragonal phase LLZ, tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, distilled water and exposed to humid atmosphere for 4 weeks, respectively. Similar TG profile was observed for all the investigated samples as observed for 1 week treatment ((Figure 2.10). However, there is a slight increase in the weight loss for tetragonal phase LLZ immersed in distilled water and exposed to humid atmosphere for 4 weeks. This
indicates that the reaction time has an effect on the extent of ion exchange in reaction with distilled water and exposed to humid atmosphere. However, no major change in the weight loss observed for the tetragonal phase LLZ treated with the solution of benzoic acid and ethanol for 1 week and 4 weeks and hence indicated no major change in Li\(^+\)/H\(^+\) exchange with time.

![Graph](image.png)

**Figure 2.14.** TG thermograms of (a) freshly prepared tetragonal phase LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 4 weeks.

PXRD patterns of freshly prepared tetragonal phase LLZ, tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 4 weeks are shown as Figure 2.15(a) - (d), respectively. The PXRD pattern of tetragonal phase LLZ treated with the solution of benzoic acid and
ethanol, distilled water and exposed to humid atmosphere for 4 weeks are shown as Figure 2.15(b) - (d), respectively, exhibits a cubic-like phase. Diffraction peaks in the PXRD patterns (Figure 2.15) of the tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, distilled water and exposed to humid atmosphere exhibit broader diffraction peak and slight shifts of the peak positions, indicating the transformation of the tetragonal phase in to cubic-like phase.

Raman spectra of freshly prepared tetragonal phase LLZ, tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 4 weeks are shown as Figure 2.16(a)-(d), respectively, along with the reported patterns of tetragonal (I4₁/acd) phase LLZ, high Li⁺ conductive cubic (Ia₃d) phase LLZ and low temperature cubic phase LLZ. The Raman spectrum of tetragonal LLZ (Figures 2.16(b)) treated with the solution of benzoic acid and ethanol is similar to that of the reported low temperature cubic phase. The Raman spectra of tetragonal LLZ immersed in distilled water and exposed to humid condition for 4 weeks shown as Figures 2.16(c) and (d), respectively, indicated that the transformed cubic phase is slightly different from that of high Li⁺ conductive cubic (Ia₃d) phase and as well as the reported low temperature cubic phase, which might be due to the effect of presence of carbonates in addition to the protonation. However further detailed experimental investigations are essential to confirm this. The non-observable or incomplete phase transition for the tetragonal phase LLZ immersed in distilled water and exposed to humid atmosphere for 1 week is possibly caused by the slow and/or non-homogeneous reaction.
kinetics (Figure 2.12). When the exchange extent is sufficient and homogeneous in 4 weeks, it yields a change in the crystal symmetry as shown in Figure 2.16.

Figure 2.15. PXRD patterns of (a) freshly prepared tetragonal phase LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 4 weeks.
Figure 2.16. Raman spectra of (a) freshly prepared tetragonal phase LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 4 weeks along with the reported patterns of tetragonal ($I4_1/acd$) phase LLZ, high Li$^+$ conductive cubic ($Ia\overline{3}d$) phase LLZ and low temperature cubic phase LLZ [33, 37].
The proton exchange of lithium, first of all, lowers the lithium content in garnet lattice. Secondly, since the protons stay much closer to O atoms than lithium, the introduction of H\(^+\) greatly alters the charge distribution of the oxygen framework [29]. Therefore, the protons in the tetragonal LLZ will disrupt the lithium-ordering and induce the tetragonal-to-cubic phase transition. Tetragonal phase LLZ (\(I4_1/acd\)) undergoes a spontaneous Li\(^+\)/H\(^+\) exchange leading to a possible partially protonated Li\(_{7.3}\)H\(_x\)La\(_3\)Zr\(_2\)O\(_{12}\) phase while reacting with the solution of benzoic acid and ethanol.

SEM images of the fractured surface of freshly prepared tetragonal LLZ, tetragonal phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 4 weeks are shown in Figures 2.17(a) - (d), respectively. SEM image of the fractured surface of tetragonal LLZ pellet (Figure 2.17(a)) revealed that the grains are not in good contact with the neighbouring grains. SEM image of the same fractured surface tetragonal phase LLZ pellet treated with the solution of benzoic acid and ethanol for 4 weeks shown as Figure 2.17(b) exhibited slight increase in the size of grains with minor secondary phase over the surface. SEM image of the fractured surface of tetragonal phase LLZ pellet immersed in distilled water for 4 weeks shown as Figure 2.17(c) exhibited a slight increase in the grain size. The increase in the grain size might be due to the Li\(^+\)/H\(^+\) exchange. The SEM image of tetragonal phase LLZ pellet exposed to humid air for 4 weeks shown as Figure 2.17(d) exhibits appreciable change in microstructure. The change in the microstructure might be due to the reaction of the sample with water vapour and CO\(_2\) in the humid atmosphere, which is clearly visible especially at the grain-boundaries (Figure 2.17(d)). The reaction
between water vapour and LLZ occurs first, which likely weakens the connection between grains, degrading the sintered strength of the sample. It is evident that a reaction layer grew around the grain-boundaries. Since the grain-boundaries are regions of high interfacial energy, they are preferred sites for the onset of any reaction with water vapor. Prolonged exposure of tetragonal phase LLZ pellet in humid air not only altered the surface composition, it also strongly affected the strength of the sintered pellet.

Figure 2.17. SEM images of the fractured surface of (a) freshly prepared tetragonal phase LLZ, tetragonal phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 4 weeks.
2.3.5. Stability of high Li\textsuperscript{+} conductive cubic phase LLZ

The PXRD patterns of freshly prepared high Li\textsuperscript{+} conductive cubic phase LLZ, high Li\textsuperscript{+} conductive cubic phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 4 weeks shown as Figure 2.18(a) - (d), respectively, are similar to that of the high Li\textsuperscript{+} conductive cubic phase lithium garnets. However, the diffraction peaks in the PXRD patterns (Figure 2.18(b) - (d)) are slightly broadened compared to that of high Li\textsuperscript{+} conductive cubic phase LLZ. Raman spectra of freshly prepared cubic phase LLZ, cubic phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 4 weeks are shown as Figure 2.19(a) - (d), respectively. As lithium has a low X-ray scattering factor, Raman spectroscopy is extremely useful to identify lithium containing secondary phases. The Raman spectra of high Li\textsuperscript{+} conductive cubic phase LLZ exposed to humid atmosphere for 4 weeks revealed the presence of minor peaks corresponding to Li\textsubscript{2}CO\textsubscript{3} at 157 cm\textsuperscript{-1} and 380 cm\textsuperscript{-1} as shown in Figure 2.19(d). Therefore, when high Li\textsuperscript{+} conductive cubic phase LLZ was exposed to humid atmosphere it reacts with water vapour and produces partially protanted Li\textsubscript{7-x}H\textsubscript{x}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} along with the LiOH. The LiOH formed on the sample surface might reacted with carbon dioxide present in air to form Li\textsubscript{2}CO\textsubscript{3}. PXRD and Raman spectra of high Li\textsuperscript{+} conductive cubic phase LLZ immersed in distilled water and treated with the solution of benzoic acid and ethanol did not reveal any detectable secondary phases as well as did not reflect any phase transition. PXRD and Raman analysis revealed that the (Ia\texttilde{3}d) structure was
retained for high Li$^+$ conductive cubic LLZ immersed in distilled water and treated with the solution of benzoic acid and ethanol for 4 weeks.

Earlier reports indicated the Li$^+$/$\text{H}^+$ exchange reaction in several lithium garnets. lead in to a structural transformation or even decomposition. However, in the present investigation high Li$^+$ conductive cubic phase LLZ immersed in distilled water and treated with the solution of benzoic acid and ethanol for 4 weeks preserved its high Li$^+$ conductive cubic structure (\(\text{Ia} \bar{3}d\)) and hence it demonstrates its structural stability.
Figure 2.18. PXRD patterns of (a) freshly prepared cubic phase LLZ, cubic phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 4 weeks.
Figure 2.19. Raman spectra of (a) freshly prepared cubic phase LLZ, cubic phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 4 weeks.

SEM images of the fractured surface of freshly prepared cubic phase LLZ, cubic phase LLZ treated with the solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 4 weeks are shown as Figure 2.20(a) - (d), respectively. SEM images of high Li$^+$ conductive cubic phase LLZ treated with the
solution of benzoic acid and ethanol for 4 weeks revealed slight modification on the surface as shown in Figure 2.20(b). SEM images revealed no significant change in the surface morphology for the high Li\(^+\) conductive cubic phase LLZ immersed in distilled water (Figure 2.20(c)) for 4 weeks. However, high Li\(^+\) conductive cubic phase LLZ exposed to humid atmosphere for 4 weeks shown as Figure 2.20(d) exhibited a significant change in surface morphology due to reaction with atmospheric CO\(_2\).

**Figure 2.20.** SEM images of the fractured surface of (a) freshly prepared cubic phase LLZ, cubic phase LLZ (b) treated with the solution of benzoic acid and ethanol, (c) immersed in distilled water and (d) exposed to humid atmosphere for 4 weeks.
2.4. CONCLUSION

Systematic investigation on the structural stability of tetragonal ($I4_1/acd$) and high Li$^+$ conductive cubic phase ($Ia\overline{3}d$) LLZ against solution of benzoic acid and ethanol, distilled water and humid atmosphere were carried out. Powder X-ray diffraction (PXRD) pattern of LLZ synthesized by sintereing at 900 °C was found to crystallize in tetragonal phase ($I4_1/acd$) and the sample sintered at 1225 °C indicates the stabilization of high Li$^+$ conductive cubic phase ($Ia\overline{3}d$). SEM image of LLZ sintered at 900 °C revealed that the grains are not in good contact with the neighbouring grains whereas, the SEM image of the LLZ sintered at 1225 °C are relatively dense and exhibit flattened like morphology.

The structural analysis of tetragonal phase LLZ treated with the solution of benzoic acid and ethanol indicated the transformation to the reported low temperature cubic phase. However tetragonal phase LLZ immersed in distilled water and exposed to humid condition for 4 weeks indicated that the transformation to cubic-like phase but it is different from that of the high Li$^+$ conductive cubic ($Ia\overline{3}d$) phase and as well as the reported low temperature cubic phase, which might be due to the effect of presence of carbonates in addition to the protonation. However further detailed experimental investigations are essential to confirm this.

The SEM image of the fractured surface of tetragonal LLZ pellet treated with solution of benzoic acid and ethanol, immersed in distilled water and exposed to humid atmosphere for 4 weeks exhibited a slight increase in the grain size. The increase in the grain size might be due to the Li$^+/H^+$ exchange. The present study reveals that the tetragonal phase ($I4_1/acd$) LLZ undergoes a spontaneous Li$^+/H^+$ exchange leading to a
possible partially protonated $\text{Li}_{7-x}\text{H}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ phase while reacting with solution of benzoic acid and ethanol, distilled water and humid atmosphere.

The high Li$^+$ conductive cubic phase LLZ immersed in distilled water and treated with the solution of benzoic acid and ethanol for 4 weeks preserved its high Li$^+$ conductive cubic structure ($I_{\alpha \bar{3}d}$) and hence it demonstrates its structural stability. The high Li$^+$ conductivity, dense microstructure, good thermal stability, chemical stability against metallic lithium and structural stability against distilled water and solution of benzoic acid with ethanol observed for the high Li$^+$ conductive cubic structure ($I_{\alpha \bar{3}d}$) suggest that this lithium garnet may be a promising solid ceramic electrolyte for all-solid-state lithium rechargeable batteries and also a protective layer for lithium metal electrode in aqueous Li-air batteries.
REFERENCES


Chapter II


