Chapter III

Li\(^+\) TRANSPORT PROPERTIES OF HIGH Li\(^+\) CONDUCTIVE 
CUBIC PHASE TELLURIUM SUBSTITUTED Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) 
LITHIUM GARNETS

3.1. INTRODUCTION

Succeeding the initial results of high Li\(^+\) conduction in the Al incorporated 
Li\(_7\)La\(_3\)Zr\(_2\)O\(_{12}\) (LLZ) there has been significant interest in the synthesis, structural and 
electrical conductivity of high Li\(^+\) conductive cubic phase LLZ [1-9]. Searching for 
proper dopants for the stabilization of LLZ in high Li\(^+\) conductive cubic phase has 
become an important topic in recent times. The results reported in literatures on doping 
with LLZ indicated a reduction in sintering temperature with La\(^{3+}\) site doping [10, 11] 
and improved conductivity by doping the Zr\(^{4+}\) site [4, 12, 13]. Partial substitution of Zr\(^{4+}\) 
by cations such as Ta, Nb, Y, Sr, Sb, Te, Ce, W, In and Ge [1-4, 8-17] is more efficient 
way to stabilize LLZ in high Li\(^+\) conductive cubic phase. Doping of high valance cation 
results in decreasing lithium content in LLZ and thus enhances the Li\(^+\) conductivity by 
creating more lithium vacancies [18]. Thus searching for proper dopants has become an 
important topic in understanding the stabilization of LLZ in cubic phase and enhancing 
its Li\(^+\) conduction properties.

The Li\(^+\) conduction in a high Li\(^+\) conductive cubic phase lithium garnet is mainly 
dependent upon the concentration of lithium and nature of distribution of lithium atoms 
among tetrahedral and octahedral sites. Based on neutron diffraction studies, Xie et al. 
predicted that optimum Li\(^+\) concentration required to achieve the maximized Li\(^+\) 
conductivity in Li\(_x\)A\(_3\)B\(_2\)O\(_{12}\) garnet is around \(x = 6.4 \pm 0.1\) and \(x = 7.5\) is the upper limit
that can be tolerated in $\text{Li}_x\text{A}_3\text{B}_2\text{O}_{12}$ garnet [19]. The maximized $\text{Li}^+$ conductivity observed in LLZ might be originated from the diffusion of $\text{Li}^+$ between two distorted octahedral sites ($96h-96h$) and as well as three dimensional distorted octahedral-tetrahedral-distorted octahedral ($96h-24d-96h$) diffusion path.

For further understanding of the $\text{Li}^+$ dynamics in lithium garnets and the effect of substitution of six valent Tellurium ($\text{Te}^{6+}$) for $\text{Zr}^{4+}$ on structure and $\text{Li}^+$ transport properties of LLZ a systematic investigations has been carried out in the present work on $\text{Li}_{7-2x}\text{La}_3\text{Zr}_{2-x}\text{Te}_x\text{O}_{12}$ ($x = 0.125$ and $0.25$) lithium garnets.

### 3.2. EXPERIMENTAL SECTION

#### 3.2.1. Synthesis of $\text{Li}_{7-2x}\text{La}_3\text{Zr}_{2-x}\text{Te}_x\text{O}_{12}$ ($x = 0.125$ and $0.25$)

Lithium garnets with nominal compositions of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}$ and $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}$ were prepared from the stoichiometric amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ (Sigma-Aldrich, $>99\%$), $\text{La}_2\text{O}_3$ (Merck, $>99\%$ pre dried at $900\ ^\circ\text{C}$ for $24$ hours), $\text{ZrO}_2$ (Acros, $98\%$) and $\text{TeO}_2$ (Himedia, $97\%$) by conventional solid-state reaction technique. The powders were ball milled using zirconia balls in 2-propanol for $6$ hours using a Pulverisette7, Fritsch, Germany. After the evaporation of solvent, the powders were heated at $750\ ^\circ\text{C}$ for $6$ hours and then cooled down to room temperature. The obtained powders were ball milled again for another $6$ hours using zirconia balls in 2-propanol. After the evaporation of the solvents the powders were pressed into pellets. The pellets were covered with the same mother powder to reduce possible lithium loss and heated in
a closed alumina crucible from room temperature to 1100 °C and held at this temperature for 15 hours.

### 3.2.2. Characterization

The sintered pellets were ground into powder and were characterized by powder X-ray diffraction (PXRD) (X’pert PRO PANalytical) with Cu-Kα radiation of $\lambda = 1.5418$ Å at room temperature in 2θ range from 10° to 80° with a step of 0.025° to confirm the phase formation. Raman spectra recorded using confocal micro-Raman spectrometer (Renishaw in via reflex spectrometer) with a 50 mW internal Ar+ laser source of excitation wavelength 514 nm.

The microstructure and energy dispersive X-ray (EDX) analysis of the synthesized pellets was studied by means of a Scanning electron microscope (SEM; HITACH S-3400N) equipped with EDX detector. The density of the sintered pellets was measured with the Archimedes’ principle at room temperature using deionised water as the immersion medium.

The electrical conductivity measurements were performed on the prepared pellets using Li+ blocking Au-electrodes (Au paste cured at 600 °C for 1 hour) in the temperature range from -100 to 100 °C with the frequency ranges from 5Hz to 20 MHz using a Novocontrol Concept 80 broadband dielectric spectrometer (BDS).
3.3. RESULTS AND DISCUSSION

3.3.1. Powder X-ray diffraction (PXRD)

The PXRD patterns of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ sintered at 1100 °C are shown as Figure 3.1(a) and (b), respectively, along with the reported pattern of high Li$^+$ conductive cubic phase LLZ [20, 21]. Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ exhibited high Li$^+$ conductive cubic phase with minor secondary phase of Li$_2$ZrO$_3$ ($\theta = 20.21^\circ$ and 26.49°). The recorded PXRD pattern of Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ matches well with that of the reported pattern of high Li$^+$ conductive cubic phase LLZ. Absence of any secondary phase and the sharp diffraction peaks corresponding to the cubic phase confirms the formation of single phase high Li$^+$ conductive cubic phase (Ia$\bar{3}$d) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$.

The lattice parameter of lithium garnets with the nominal composition Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ crystallized in high Li$^+$ conductive cubic phase were found to be 12.9469 Å and 12.9134 Å, respectively. The lattice parameter decreases nearly linearly with increasing Te substitution. The substitution of smaller Te$^{6+}$ with ionic radius 0.56 Å in six coordination for the larger Zr$^{4+}$ with ionic radius 0.72 Å in six coordination together with the simultaneous decrease of the lithium content leads to decrease of the lattice parameter with increasing $x$ in Li$_{7-2x}$La$_3$Zr$_{2-x}$Te$_x$O$_{12}$ [22]. The serious problems with the preparation of LLZ in high Li$^+$ conductive cubic phase by solid-state reaction technique is that it requires high reaction temperature around 1200 °C, long duration of sintering of 36 hours in alumina crucible along with intermittent grinding and repeated heat treatments to obtain dense bodies of the highly
Li⁺ conductive cubic phase ($Ia\bar{3}d$) of LLZ rather than the low conductive tetragonal phase ($I4_1/acd$) LLZ.

Figure 3.1. PXRD patterns of nominal composition (a) Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ sintered at 1100 °C along with the reported pattern of high Li⁺ conductive cubic phase LLZ [20, 21]. (Impurity phase; *: Li$_2$ZrO$_3$).
3.3.2. Raman Spectroscopic Studies

The Raman spectra of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ sintered at 1100 °C are shown as Figure 3.2 along with the standard pattern of high Li$^+$ conductive cubic phase LLZ [23] measured in the range 50-1000 cm$^{-1}$. The Raman spectra of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ appeared to be similar to that of the high Li$^+$ conductive cubic phase with disordered lithium sublattice. Compared to the Raman spectrum of high Li$^+$ conductive cubic phase LLZ the vibrational modes of Te substituted LLZ (Figure 3.2(a) and (b)) appeared to be relatively broad. Broad intense bands at around 374 and 656 cm$^{-1}$ and broad medium intense band at around 254 cm$^{-1}$ were observed in the Raman spectra of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ as shown in Figure 3.2.
Figure 3.2. Raman spectra of (a) Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ sintered at 1100 °C measured in the range 50-1000 cm$^{-1}$ along with reported high Li$^+$ conductive cubic phase LLZ [23].

3.3.3. Microstructural analysis

The SEM images of fractured surfaces of the Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ pellets sintered at 1100 °C are shown as Figures 3.3(a) and (b), respectively. The Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ pellet revealed well-crystallized large grains with good contact between the grains compared to that of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$. Increase in the concentration of Te in LLZ produce dramatic changes in the microstructure with
grain growth and increase in density as shown in Figure 3.3(b). A glass like phase covering over the grains was observed in the SEM image of Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$. Energy dispersive X-ray detector (EDX) analysis indicated the incorporation of Al$^{3+}$ from the Al$_2$O$_3$ crucible during sintering process as 0.295 and 0.185 wt.% in Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$, respectively.

Figure 3.3. SEM images of the fractured surface of (a) Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ pellets sintered at 1100 °C.
The minimum amount of Al\(^{3+}\) necessary to stabilize the high Li\(^{+}\) conductive cubic phase was estimated to be around 0.9 wt.% in LLZ. The presence of Al\(^{3+}\) content lesser than the 0.9 wt.% in the investigated samples indicated that the stabilization of cubic phase is not merely by the inclusion of Al\(^{3+}\) alone. Although the EDX analysis indicated the incorporation of Al\(^{3+}\), further detailed neutron diffraction and \(^{27}\)Al magic angle nuclear magnetic resonance (MAS NMR) are essential to understand the kind of Al\(^{3+}\) distribution on the different sites of crystal lattice and transmission electron microscopy (TEM) studies for the identification of kind of Al\(^{3+}\) incorporated phase at the grain-boundary and its role in the ionic conductivity of the investigated samples. The density of Li\(_{6.75}\)La\(_3\)Zr\(_{1.875}\)Te\(_{0.125}\)O\(_{12}\) and Li\(_{6.5}\)La\(_3\)Zr\(_{1.75}\)Te\(_{0.25}\)O\(_{12}\) pellets sintered at 1100 °C were determined using Archimedes’ principle by using deionised water as the immersion medium. The relative density of Li\(_{6.75}\)La\(_3\)Zr\(_{1.875}\)Te\(_{0.125}\)O\(_{12}\) and Li\(_{6.5}\)La\(_3\)Zr\(_{1.75}\)Te\(_{0.25}\)O\(_{12}\) exhibited 90% and 94%, respectively.

3.3.4. Electrical properties

3.3.4.1. Impedance analysis

In order to understand the effect of Te substitution in LLZ on the Li\(^{+}\) conductivity systematic impedance measurements was performed on the prepared pellets in the temperature interval from -100 °C to 100 °C. The impedance (Cole-Cole) plots measured at -50 °C, 0 °C and 30 °C for the composition of Li\(_{6.75}\)La\(_3\)Zr\(_{1.875}\)Te\(_{0.125}\)O\(_{12}\) and Li\(_{6.5}\)La\(_3\)Zr\(_{1.75}\)Te\(_{0.25}\)O\(_{12}\) sintered at 1100 °C are shown as Figures 3.4(a) and (b), respectively. The high frequency portion of the impedance plot measured at 0 °C and
30 °C were magnified for clarity and given as inset in Figures 3.4(a) and (b), respectively. The appearance of a capacitive tail for the investigated samples at the low frequency side in the case of the applied ionically blocking Au electrode as shown in Figures 3.4(a) and (b) is an indication that the investigated material is ionically conducting in nature. The lack of clear two semicircles in the higher frequency part of the impedance plots in Figures 3.4(a) and (b) indicated that the bulk and grain-boundary resistance could not be well resolved. We have considered uniformly the total (bulk + grain-boundary) Li\(^+\) conductivity for the presentation of conductivity results over the investigated temperature range.
Figure 3.4. (a) AC impedance (Cole-Cole) plots of $\text{Li}_{6.75}\text{La}_{3}\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}$ measured at -50 °C, 0 °C and 30 °C. The impedance plot in the high frequency region measured at 0 °C and 30 °C are shown as inset.
Figure 3.4. (b) AC impedance (Cole-Cole) plots of Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ measured at -50 °C, 0 °C and 30 °C. The impedance plot in the high frequency region measured at 0 °C and 30 °C are shown as inset.

Arrhenius plot for total (bulk + grain-boundary) Li$^+$ conductivity of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ samples sintered at 1100 °C shown in Figure 3.5 indicated that there is no appreciable shift in the conductivity and this implies that the investigated samples are thermally stable without any phase transition in the measured temperature range from -100 °C to 100 °C.
Figure 3.5. Arrhenius plots for total (bulk + grain-boundary) Li$^+$ conductivity of (a) Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ in the temperature interval from -100 ºC to 100 ºC.

The activation energy ($E_a$) was estimated from the slope of the log$\sigma$T versus 1000/T. The activation energy obtained for total (bulk + grain-boundary) Li$^+$ conductivity of Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ in the temperature range from -100 ºC to 100 ºC is 0.37 eV, which is comparable to that of 0.31 eV (18 ºC to 300 ºC) of Li$_7$La$_3$Zr$_2$O$_{12}$ [20, 21]. The total (bulk + grain-boundary) Li$^+$ conductivity measured at various temperatures derived from the intercepts of semicircles (close to the tail) with the real axis and activation energies derived from Arrhenius plots for the total (bulk + grain-boundary) Li$^+$
conductivity (in the temperature range from -100 °C to 100 °C) of the investigated samples sintered at 1100 °C are tabulated in Table 3.1. Earlier investigations on Li\(^+\) conductivity of cubic Li\(_{7-x}\)La\(_3\)Zr\(_{2-x}\)Ta\(_x\)O\(_{12}\) and Li\(_{7-x}\)La\(_3\)Hf\(_{2-x}\)Ta\(_x\)O\(_{12}\) indicated that the maximum conductivity for the composition around \(x = 0.4 \pm 0.1\) [1, 13, 24]. In the present investigation the maximized room temperature (30 °C) total (bulk + grain-boundary) Li\(^+\) conductivity of \(1.02 \times 10^{-3}\) Scm\(^{-1}\) was achieved for the composition Li\(_{6.5}\)La\(_3\)Zr\(_{1.75}\)Te\(_{0.25}\)O\(_{12}\) sintered at 1100 °C.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Total (bulk + grain-boundary) Li(^+) conductivity (Scm(^{-1})) sintered at 1100 °C</th>
<th>(E_a) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-100 °C</td>
<td>-50 °C</td>
</tr>
<tr>
<td>Li(<em>{6.75})La(<em>3)Zr(</em>{1.875})Te(</em>{0.125})O(_{12})</td>
<td>6.02 x 10(^{-9})</td>
<td>1.91 x 10(^{-6})</td>
</tr>
<tr>
<td>Li(<em>{6.5})La(<em>3)Zr(</em>{1.75})Te(</em>{0.25})O(_{12})</td>
<td>9.37 x 10(^{-9})</td>
<td>4.09 x 10(^{-6})</td>
</tr>
</tbody>
</table>

3.3.4.2. AC conductivity behavior

The AC conductivity spectra of many solids, including glasses, polymers, crystals and semiconductors, were found to obey the following Jonscher’s universal power law [25],
\[
\sigma'(\omega) = \sigma_{dc} + A\omega^n
\]  \hspace{1cm} (3.1)

where \(\sigma_{dc}\) is frequency-independent conductivity, \(A\) is pre-factor that depends on temperature and composition and it is defined as \(A = (\sigma_{dc}/\omega_p^n)\), \(\omega_p\) is the hopping frequency of the charge carriers and \(n\) is the dimensionless frequency exponent which lies in the range 0\(<n<1\). The above equation is rewritten as,

\[
\sigma'(\omega) = \sigma_{dc}\left[1 + \left(\frac{\omega}{\omega_p}\right)^n\right]
\]  \hspace{1cm} (3.2)

\(\omega\) is angular frequency.

The above equation 3.2 is called framework of Almond - West conductivity formalism [26, 27]. Many solids, including glasses, polymers and crystals, show deviation from the Jonscher power law when frequency exceeds \(\omega_p\) by several orders of magnitude [28-30].

Figures 3.6(a) and (b) shows the frequency dependent conductivity in the temperature interval from -100 °C to 0 °C of \(\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}\) and \(\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}\), respectively. Two clear dispersion regions were found in the frequency dependent conductivity of \(\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}\) and \(\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}\) presented as Figures 3.6(a) and (b), respectively. The dispersion processes are related to ion transport in the bulk and grain-boundaries of the ceramics. The lower frequency part corresponds to the relaxation processes in grain-boundaries, and the \(\text{Li}^+\) blocking character of the electrode. The long range conductivity process through the sample is indicated by the presence of a plateau corresponding to the dc conductivity of the \(\text{Li}^+\). At
high frequency the conductivity displays a dispersive behavior attributed to the relaxation processes in grains as generally observed in ionic conductors. The processes are thermally activated and dispersion regions shift towards higher frequencies as temperature increases.

In Figures 3.6(a) and (b) the different symbols represent the experimental AC conductivity data measured at different temperatures and the continuous lines represent data fitted to equation (3.2). In the fitting \( \sigma_{dc} \), \( \omega_p \), and \( n \) values are varied to get the best fit, and the parameters obtained by Levenberg-Marquard nonlinear least-squares fitting are given in Table 3.2 and 3.3 for Li\(_{6.75}\)La\(_3\)Zr\(_{1.875}\)Te\(_{0.125}\)O\(_{12}\) and Li\(_{6.5}\)La\(_3\)Zr\(_{1.75}\)Te\(_{0.25}\)O\(_{12}\), respectively. Increase in the \( \sigma_{dc} \) and the \( \omega_p \) with temperature is due to the increase in the thermally activated drift mobility of ions according to hopping conduction mechanism.
Figure 3.6. Frequency dependent conductivity measured in the temperature interval from -100 °C to 0 °C of (a) Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$. The solid lines are best fit to the Almond-West conductivity formalism [26].
**Table 3.2.** Parameters derived from the fits of AC conductivity measurements for Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$.

<table>
<thead>
<tr>
<th>Temp ( ºC)</th>
<th>$\sigma_{dc}$ (Scm$^{-1}$)</th>
<th>A (Scm$^{-1}$rad$^{-n}$)</th>
<th>n</th>
<th>$\omega_p$ (rad s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100</td>
<td>$6.22 \times 10^{-09}$</td>
<td>$2.37 \times 10^{-11}$</td>
<td>0.54</td>
<td>$3.02 \times 10^4$</td>
</tr>
<tr>
<td>-90</td>
<td>$1.65 \times 10^{-08}$</td>
<td>$4.51 \times 10^{-11}$</td>
<td>0.53</td>
<td>$6.86 \times 10^4$</td>
</tr>
<tr>
<td>-80</td>
<td>$7.25 \times 10^{-08}$</td>
<td>$8.72 \times 10^{-11}$</td>
<td>0.53</td>
<td>$3.23 \times 10^5$</td>
</tr>
<tr>
<td>-70</td>
<td>$1.92 \times 10^{-07}$</td>
<td>$1.12 \times 10^{-10}$</td>
<td>0.54</td>
<td>$9.79 \times 10^5$</td>
</tr>
<tr>
<td>-60</td>
<td>$8.65 \times 10^{-07}$</td>
<td>$5.67 \times 10^{-10}$</td>
<td>0.49</td>
<td>$3.13 \times 10^6$</td>
</tr>
<tr>
<td>-50</td>
<td>$2.10 \times 10^{-06}$</td>
<td>$6.00 \times 10^{-10}$</td>
<td>0.52</td>
<td>$6.54 \times 10^6$</td>
</tr>
<tr>
<td>-40</td>
<td>$4.20 \times 10^{-06}$</td>
<td>$8.29 \times 10^{-10}$</td>
<td>0.51</td>
<td>$1.84 \times 10^7$</td>
</tr>
<tr>
<td>-30</td>
<td>$9.04 \times 10^{-06}$</td>
<td>$1.06 \times 10^{-09}$</td>
<td>0.52</td>
<td>$3.62 \times 10^7$</td>
</tr>
<tr>
<td>-20</td>
<td>$2.00 \times 10^{-05}$</td>
<td>$2.08 \times 10^{-09}$</td>
<td>0.51</td>
<td>$6.48 \times 10^7$</td>
</tr>
<tr>
<td>0</td>
<td>$8.20 \times 10^{-05}$</td>
<td>$4.88 \times 10^{-09}$</td>
<td>0.49</td>
<td>$4.19 \times 10^8$</td>
</tr>
</tbody>
</table>
Table 3.3. Parameters derived from the fits of AC conductivity measurements for \( \text{Li}_{6.5}\text{La}_{3}\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12} \).

<table>
<thead>
<tr>
<th>Temp ( ºC)</th>
<th>( \sigma_{dc} ) (S( \text{cm}^{-1} ))</th>
<th>A (S( \text{cm}^{-1} ) rad(^{-n} ))</th>
<th>n</th>
<th>( \omega_p ) (rad s(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100</td>
<td>9.99 x 10(^{-09} )</td>
<td>3.44 x 10(^{-11} )</td>
<td>0.54</td>
<td>3.64 x 10(^{4} )</td>
</tr>
<tr>
<td>-90</td>
<td>7.50 x 10(^{-08} )</td>
<td>9.42 x 10(^{-11} )</td>
<td>0.57</td>
<td>1.23 x 10(^{5} )</td>
</tr>
<tr>
<td>-80</td>
<td>2.00 x 10(^{-07} )</td>
<td>1.82 x 10(^{-10} )</td>
<td>0.55</td>
<td>3.38 x 10(^{5} )</td>
</tr>
<tr>
<td>-70</td>
<td>5.92 x 10(^{-07} )</td>
<td>2.92 x 10(^{-10} )</td>
<td>0.55</td>
<td>1.03 x 10(^{6} )</td>
</tr>
<tr>
<td>-60</td>
<td>1.55 x 10(^{-06} )</td>
<td>3.12 x 10(^{-10} )</td>
<td>0.58</td>
<td>2.36 x 10(^{6} )</td>
</tr>
<tr>
<td>-50</td>
<td>4.51 x 10(^{-06} )</td>
<td>8.92 x 10(^{-10} )</td>
<td>0.55</td>
<td>5.43 x 10(^{6} )</td>
</tr>
<tr>
<td>-40</td>
<td>1.01 x 10(^{-05} )</td>
<td>1.08 x 10(^{-09} )</td>
<td>0.56</td>
<td>1.23 x 10(^{7} )</td>
</tr>
<tr>
<td>-30</td>
<td>2.00 x 10(^{-05} )</td>
<td>3.95 x 10(^{-09} )</td>
<td>0.50</td>
<td>2.56 x 10(^{7} )</td>
</tr>
<tr>
<td>-20</td>
<td>4.00 x 10(^{-05} )</td>
<td>4.99 x 10(^{-09} )</td>
<td>0.50</td>
<td>6.43 x 10(^{7} )</td>
</tr>
<tr>
<td>0</td>
<td>2.10 x 10(^{-04} )</td>
<td>9.99 x 10(^{-09} )</td>
<td>0.51</td>
<td>2.99 x 10(^{8} )</td>
</tr>
</tbody>
</table>
Figures 3.7 and 3.8 show the plots of $\log(\sigma_{dc}T)$ versus $1000/T$ and $\log(\omega_p)$ versus $1000/T$, respectively, for $\text{Li}_6.75\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}$ and $\text{Li}_6.5\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}$. This temperature dependency is found to obey the Arrhenius equation,

$$
\sigma_{dc}T = \sigma_0 \exp\left(\frac{-E_\sigma}{k_B T}\right)
$$

(3.3)

$$
\omega_p = \omega_0 \exp\left(\frac{-E_p}{k_B T}\right)
$$

(3.4)

where $\sigma_0$ is the dc conductivity pre-exponential factor, $E_\sigma$ is the dc conductivity activation energy for mobile ions, $k_B$ is the Boltzmann’s constant, $\omega_0$ is the pre-exponential of the conductivity relaxation frequency and $E_p$ is the activation energy for the conductivity relaxation frequency. The activation energy for dc conductivity ($E_\sigma$) is found to be close to the activation energy of hopping frequency ($E_p$).
Figure 3.7. Arrhenius plots of $\log_{10}(\sigma_{dc}T)$ versus $1000/T$ for (a) $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}$ and (b) $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}$. 
3.3.4.3. Modulus spectra analysis

Complex modulus formalism is an important tool to derive information related to charge transport processes. The complex electric modulus ($M^*$) has been calculated from the complex impedance ($Z^*$) data using the relation

$$M^*(\omega) = 1/\varepsilon^*(\omega) = i\omega C_0 Z^* = M'(\omega) + iM''(\omega)$$

$$= M_\infty \left[1 - \int_0^\infty \exp(-i\omega t) \left(\frac{d\phi(t)}{dt}\right) dt\right]$$  \hspace{1cm} (3.5)
where $\varepsilon^* (\omega)$ is the complex permittivity, $C_0$ is the geometrical capacitance $= \varepsilon_0 A/t$ ($\varepsilon_0$ = permittivity of free space, $A$ = area of the electrode and $t$ = thickness), $M'$ = real part of the electric modulus, $M'' = \text{imaginary part of the electric modulus}$, $M_\infty = 1/\varepsilon_\infty$ ($\varepsilon_\infty$ is the high frequency asymptotic value of the real part of the dielectric permittivity) and the relaxation function $\varphi(t)$ gives the time evolution of the electric field within the material.

Figures 3.9(a) and (b) shows the imaginary part of the electric modulus ($M''$) with $\log(f)$ of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}$ and $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}$ measured at different temperatures in the temperature range from $-100$ °C to $0$ °C. The frequency dependence of imaginary part of the electric modulus ($M''$) measured at different temperatures ($-100$ °C to $0$ °C) of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}$ and $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}$ shown in Figures 3.9(a) and (b) indicated visibly resolved peaks at unique frequency. The appearance of peak in modulus spectra provides a clear signal of conductivity relaxation. The low frequency wing below peak maximum ($M''_{\text{max}}$) represents the range in which the charge carriers are mobile at long distances; i.e., ions can perform successful hopping from one site to the neighboring site. On the other hand, at frequencies above peak maximum, the carriers are confined to potential wells and are mobile at short distances.

The position of the peaks ($M''_{\text{max}}$) in Figures 3.9(a) and (b) shifts towards higher frequencies as temperature is increased. This behavior suggests that the relaxation rate for this process increases with increasing temperature in which hopping mechanism of charge carriers dominates intrinsically. The peak frequency $f_m$ represents the most probable conductivity relaxation frequency from the relation $f_m \tau_m = 1$, where $\tau_m$ is the...
characteristic relaxation time represents the time scale of the transition from the long-range to short-range mobility.

**Figure 3.9.** Plot of imaginary part of modulus ($M''$) versus log($f$) of (a) Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$. 
A better information on the bulk conduction properties may be obtained from Arrhenius plots of frequency \((f_m)\) at the modulus peak maximum \(M''_\text{max}\) [31]. The activation energy \((E_a)\) was calculated from,

\[
f_mT = f_0 \exp\left(\frac{-E_a}{k_B T}\right)
\]

(3.6)

where \(f_0\) is the pre-exponential parameter of the relaxation frequency. The Arrhenius plots of \(\log(f_mT)\) versus \(1000/T\) obtained from the temperature range -100 °C to 0 °C for \(\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}\) and \(\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}\) are shown in Figure 3.10. The similarity in the activation energy derived from the slope of \(\log(f_mT)\) versus \(1000/T\) and \(\log(\sigma T)\) versus \(1000/T\) suggests the long-range translational motion of \(\text{Li}^+\).

**Figure 3.10.** Arrhenius plots of \(\log_{10}(f_{\text{max}} T)\) versus 1000/\(T\) in the temperature interval from -100 to 0 °C of (a) \(\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.875}\text{Te}_{0.125}\text{O}_{12}\) and (b) \(\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}\).
The modulus scaling behavior gives an insight into the dielectric process occurring inside the material. We have scaled $M''$ by $M''_{\text{max}}$ and each frequency by $f_{\text{max}}$, where $f_{\text{max}}$ corresponds to the frequencies of the peak positions in $M''_{\text{max}}$ versus log $f$ plots. Figures 3.11 shows the normalized imaginary part of the modulus ($M''/M''_{\text{max}}$) versus normalized log($ff_{\text{max}}$) measured at various temperatures of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_0.125$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_0.25$O$_{12}$, respectively.

The low frequency side of the peak in $M''/M''_{\text{max}}$ versus log($ff_{\text{max}}$) curve represents the range of frequencies in which the charge carriers can cover a longer distance by successfully hopping from one site to another site. The high frequency side of $M''/M''_{\text{max}}$ versus log($ff_{\text{max}}$) curve represents the range of frequencies in which the charge carriers are spatially confined to their potential wells and therefore can make only localized motions inside the well. The region where the peak occurs is an indication of the transition from the long-range to the short-range mobility with increase in frequency [32]. The overlapping of all the peaks of different temperatures indicates that all dynamic processes occurring at different time scales exhibit the same activation energy and that the distribution of relaxation process is independent of temperature [33].
Figure 3.11. Modulus scaling behavior of (a) Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and (b) Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$.
The full width at half maximum (FWHM) value derived from the master modulus curve of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ were found to be 1.574 and 1.531 decade, respectively. The FWHM for the master modulus curve of the Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ are wider than the width of a typical Debye peak (1.14 decade) suggesting the presence of non-Debye type conductivity relaxation phenomena.

3.4. CONCLUSION

Te substituted Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ lithium garnets were successfully synthesized by conventional solid-state reaction technique. The PXRD indicated that the selected compositional range was found to crystallize in the high Li$^+$ conductive cubic phase at around 1100 °C. The AC conductivity behaviour of Li$_{6.75}$La$_3$Zr$_{1.875}$Te$_{0.125}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ has been investigated over a wide temperature range. Among the investigated compositions Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ exhibited a maximum total Li$^+$ conductivity of $1.02 \times 10^{-3}$ Scm$^{-1}$ at 30 °C. The FWHM for master modulus curve of Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ was found to be least among the investigated lithium garnets. The overlap of the normalized modulus spectra obtained for different temperatures indicated that the distribution of relaxation process is independent of temperature. The present studies supports the earlier prediction of optimum Li$^+$ concentration required for maximized room temperature Li$^+$ conductivity in Li$_{7-x}$La$_3$Zr$_{2-x}$M$_x$O$_{12}$ is around $x = 0.4 \pm 0.1$. The present studies revealed the stabilization of the high Li$^+$ conductive cubic garnet phase relatively at lower sintering temperature.
along with an enhancement in Li\(^{+}\) conductivity with lithium content lesser than 7 by Te doping in Li\(_{7}\)La\(_{3}\)Zr\(_{2}\)O\(_{12}\). The six valent dopant Te\(^{6+}\) for Zr\(^{4+}\) is more effective in enhancing the Li\(^{+}\) conductivity of LLZ than the pentavalent dopants Ta\(^{5+}\)/Nb\(^{5+}\)/Sb\(^{5+}\).

In addition to the high Li\(^{+}\) conductivity, the stability against potential electrodes and lithium metal is also a critical issue for the successful application of this Te substituted LLZ as solid electrolyte membrane in all-solid-state lithium battery application. Hence further studies are essential to determine its reaction stability against potential electrodes and lithium metal.
REFERENCES


Chapter III


