INVESTIGATION ON Li⁺ CONDUCTIVITY AND PHASE STABILITY OF YTTRIUM SUBSTITUTED Li₇La₃Zr₂O₁₂ FOR LITHIUM-AIR BATTERY APPLICATION

5.1. INTRODUCTION

Many efforts have been devoted to realize a solid electrolyte with high Li⁺ conductivity and excellent chemical stability against metallic lithium, which helps to improve the performance of present Li⁺ batteries and also thereby to introduce new types of high energy density lithium metal based batteries such as Li-air batteries (11,140 Whkg⁻¹ excluding oxygen weight and 5,200 Whkg⁻¹ including oxygen weight) [1].

Unlike conventional zinc-air batteries, the Li-air batteries cannot be operated with aqueous electrolytes without protection for the lithium metal due to the strong reaction between lithium metal and water. Hence a water-stable Li⁺ conductive electrolyte membrane is usually used to separate the metallic lithium negative electrode from the aqueous electrolyte. Unfortunately the well known water stable lithium titanium aluminium phosphate (LTAP) electrolyte membrane is not stable in contact with lithium metal, hence a separator soaked with the organic electrolyte between the lithium metal and the solid electrolyte membrane is used, resulting in a dual-electrolyte Li-air battery [2].

Advanced Li-air battery architecture demands a high Li⁺ conductive solid electrolyte membrane that is electrochemically stable against metallic lithium and aqueous electrolyte. Particularly, garnet structured Li₇La₃Zr₂O₁₂ (LLZ) has been widely
considered in recent times for such applications because of its high Li$^+$ conductivity and good stability against lithium metal [3-6]. In addition to the high total (bulk + grain-boundary) Li$^+$ conductivity and electrochemical stability against lithium metal, the dense microstructure is also an essential factor for the successful application of LLZ as solid electrolyte membrane in Li$^+$ and Li-air battery applications. The dense LLZ solid electrolyte membrane is expected to prevent the catholyte from reacting with metallic lithium and also to suppress lithium dendrite penetration.

The results on doping with LLZ indicated a reduction in sintering temperature with La$^{3+}$ site doping and improved conductivity by doping the Zr$^{4+}$ site (Nb$^{5+}$ or Ta$^{5+}$). Although the conductivity has been improved by stabilizing the cubic phase relatively at lower sintering temperature with the Ta$^{5+}$ doping for Zr$^{4+}$ in LLZ, the density of the prepared pellet was found to be relatively poor with large amount of pores compared to dense LLZ. Hence, it is very important to explore new possible sintering agent as dopant to realize the stabilization of high Li$^+$ conductive cubic phase LLZ with dense microstructure. Y$_2$O$_3$ is also a well known sintering agent and hence the small doping of Y$^{3+}$ for La$^{3+}$ in LLZ may help to increase the density by reducing the grain-boundary resistance. The feasibility of utilizing the lithium garnet in aqueous Li-air battery also demands a detailed understanding of its structural and chemical evolutions in aqueous solutions with variable pH.

Hence in the present work, systematic investigation has been carried out on the microstructure, Li$^+$ conduction behaviour and phase stability of Li$_7$La$_{3-x}$Y$_x$Zr$_2$O$_{12}$ ($x = 0.125, 0.25$ and $0.50$) prepared by conventional solid-state reaction technique.
5.2. EXPERIMENTAL SECTION

5.2.1. Synthesis of Li$_7$La$_{3-x}$Y$_x$Zr$_2$O$_{12}$ ($x = 0.125, 0.25$ and $0.50$)

Lithium garnets with nominal compositions Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ were prepared by conventional solid-state reaction technique. Appropriate amount of LiOH.H$_2$O (Sigma-Aldrich, 99.9%; 10 wt.% excess was added to compensate the loss of lithium by volatilization at elevated temperature), La$_2$O$_3$ (Sigma-Aldrich, >99% pre dried at 900 °C for 24 hours), Y$_2$O$_3$ (Sigma-Aldrich, >99%) and ZrO$_2$ (Sigma-Aldrich, 99%) were ball milled using zirconia balls in 2-propanol for about 6 hours. After the evaporation of solvents, the mixtures were annealed at 750 °C for 6 hours to decompose the salts and cooled down to room temperature. The resultant powders were ball milled again and pressed into pellets. Then the pellets were transferred into the closed alumina crucible and covered with the same mother powder to avoid the possible lithium loss and sintered to the optimized condition at 1200 °C for 18 hours.

5.2.2. Characterization

The sintered pellets were ground into powder and were characterized at room temperature by powder X-ray diffraction (PXRD) (X’pert PRO PANalytical) with Cu-K$_\alpha$ radiation of $\lambda = 1.5418$ Å with a step of 0.025° in 2θ range from 10° to 80°. Confocal micro-Raman spectra (Renishaw in via reflex spectrometer) were recorded at room temperature in the range 50-1000 cm$^{-1}$ with a 50 mW internal Ar$^+$ laser source of excitation wavelength 514 nm.
The surface morphology of the sintered pellets was characterized by field-emission scanning electron microscope (SU8000 Family Ultra-High Resolution FE-SEM). The density of the sintered pellets was measured with the Archimedes’ principle at room temperature using deionised water as the immersion medium. Wavelength dispersive X-ray fluorescence spectrometer (WD-XRF), Bruker S4 Pioneer was used to estimate the amount of inclusion of Al$^{3+}$ from the alumina crucible into LLZ.

The electrical conductivity measurements were carried out on the prepared pellets using Li$^+$ blocking Au-electrodes (cured at 600 °C for 1 hour) in the temperature range from 30 °C to 200 °C with the frequency ranges from 5Hz to 20 MHz using a Novocontrol concept 80 broadband dielectric spectrometer (BDS).

Li$^+$ conductivity and phase stability of the Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ pellet sintered at 1200 °C was investigated by immersing the sample under solutions such as 1M LiCl, dist. H$_2$O and 1M LiOH at 30 °C and 50 °C for 2 weeks. The change in the phase and Li$^+$ conductivity of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ pellets after immersed in the solutions of 1M LiCl, dist. H$_2$O and 1M LiOH were investigated by powder X-ray diffraction (PXRD) and Raman spectroscopy and impedance spectroscopy, respectively.

5.3. RESULTS AND DISCUSSION

5.3.1. Powder X-ray diffraction (PXRD)

The PXRD patterns of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ sintered at 1200 °C are shown as Figure 5.1 along with the reported pattern of high Li$^+$ conductive cubic phase LLZ [3, 4]. The presence of sharp diffraction
peaks related to cubic phase and the absence of clear characteristic splitting in the
diffraction peaks related to tetragonal phase in the PXRD patterns of
Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ as shown in Figure 5.1 indicated the stabilization of well crystallized high Li$^+$ conductive cubic phase ($Ia$3$d$) lithium garnets.

The PXRD pattern of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ as shown in Figure 5.1(b) exhibited minor secondary phase of yttrium oxide (YO$_{1.458}$) (JCPDS No.:39-1063; 2θ = 22.77°). At higher doping of Y i.e., Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$, the PXRD pattern exhibited few more additional peaks of YO$_{1.458}$ (JCPDS No.:39-1063; 2θ = 22.77°, 35.15° and 41.61°) as shown in Figure 5.1(c).

The calculated lattice parameter of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ are presented in Table 5.1. The lattice parameter of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ sintered at 1200 °C decreases linearly with increasing Y substitution and obeys Vegard's law [7]. The substitution of smaller Y$^{3+}$ with ionic radius 0.9 Å for the larger La$^{3+}$ with ionic radius 1.16 Å leads to the decrease of lattice parameter with increasing Y concentration in Li$_7$La$_{3-x}$Y$_x$Zr$_2$O$_{12}$ [8].
Figure 5.1. PXRD patterns of (a) Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, (b) Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and (c) Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ sintered at 1200 °C along with the reported pattern of high Li$^+$ conductive cubic phase LLZ [3, 4]. (Impurity phase; *:Y$_{1.458}$)

5.3.2. Raman spectroscopic studies

The Raman spectra of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ sintered at 1200 °C measured in the range 50-1000 cm$^{-1}$ are shown as Figure 5.2 along with the reported high Li$^+$ conductive cubic phase LLZ [9]. The vibrational modes of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ as shown in Figure
5.2(a) and (b), respectively, indicate no appreciable variations in the peak positions, line width and integrated intensity with the difference in the doping amount of Y i.e., \( x = 0.125 \) and 0.5. The Raman spectra for the investigated \( \text{Li}_7\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_2\text{O}_{12} \) and \( \text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12} \) revealed intense broad bands at around 367 and 650 cm\(^{-1}\), medium intense broad bands at around 123, 262 and 524 cm\(^{-1}\) and shoulder bands at around 207 and 418 cm\(^{-1}\) as shown in Figure 5.2, which is similar to that of the reported Raman modes of high Li\(^+\) conductive cubic phase \( \text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12} \) [9]. Although there exist a slight difference in the Raman spectrum of \( \text{Li}_7\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_2\text{O}_{12} \) as shown in Figure 5.2(c) still the major phase is appears to be high Li\(^+\) conductive cubic phase with disordered lithium sub-lattice. The observed slight difference in the vibrational modes of Raman spectrum of \( \text{Li}_7\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_2\text{O}_{12} \) compared to that of the remaining samples might be due to the presence of minor impurity phase as revealed by the PXRD pattern (Figure 5.1(c)). The secondary phase might be resulted due to the excess doping of Y in \( \text{Li}_7\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_2\text{O}_{12} \).
Figure 5.2. Raman spectra of (a) Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, (b) Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and (c) Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ sintered at 1200 °C measured in the range 50-1000 cm$^{-1}$ along with the reported pattern of high Li$^+$ conductive cubic phase LLZ [9].

5.3.3. Microstructural analysis

The FE-SEM images of the fractured surface of Li$_7$La$_3$Zr$_2$O$_{12}$, Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ pellets sintered at 1200 °C and their corresponding magnified images are shown as Figures 5.3 and 5.4, respectively. The FE-SEM image of the sintered LLZ pellet shown as Figure 5.3(a) clearly revealed growth of large grains with clear grain-boundaries. The incorporation of
Y dopant in Li\textsubscript{7}La\textsubscript{3-x}Y\textsubscript{x}Zr\textsubscript{2}O\textsubscript{12} leads to significant changes in the morphology as shown in Figures 5.3(b)-(d). The FE-SEM images of Li\textsubscript{7}La\textsubscript{2.875}Y\textsubscript{0.125}Zr\textsubscript{2}O\textsubscript{12}, Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12} and Li\textsubscript{7}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{2}O\textsubscript{12} exhibited flattened-like morphology. However, in Li\textsubscript{7}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{2}O\textsubscript{12} the secondary phase yttrium oxide may appear over the surface of the sample due to the high concentration of Y doping as shown in Figure 5.3(d).

The magnified FE-SEM images of Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}, Li\textsubscript{7}La\textsubscript{2.875}Y\textsubscript{0.125}Zr\textsubscript{2}O\textsubscript{12}, Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12} and Li\textsubscript{7}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{2}O\textsubscript{12} shown as Figures 5.4(a)-(d), revealed the growth of relatively large grains with better contact with the neighboring grains by addition of Y substitution in LLZ. The magnified FE-SEM images shown as Figures 5.4(b)-(d) also revealed the presence of secondary phase over the surface. The XRF studies indicated the incorporation of 0.72 wt.%, 0.64 wt.% and 0.59 wt.% of Al in the Li\textsubscript{7}La\textsubscript{2.875}Y\textsubscript{0.125}Zr\textsubscript{2}O\textsubscript{12}, Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12} and Li\textsubscript{7}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{2}O\textsubscript{12} samples, respectively. The Y substitution and the inclusion of Al from crucible might have formed an intergranular liquid phase and it lead into significant grain growth. However a detailed high resolution transmission electron microscopic (HRTEM) investigation along with elemental mapping is essential for further understanding on the role of Y in the enhancement of grain growth and density of the pellet.
Figure 5.3. FE-SEM images of the fractured surface of (a) Li$_7$La$_3$Zr$_2$O$_{12}$, (b) Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, (c) Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and (d) Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ pellets sintered at 1200 °C.
Figure 5.4. Magnified FE-SEM images of the fractured surface of (a) Li$_7$La$_3$Zr$_2$O$_{12}$, (b) Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, (c) Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and (d) Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ pellets sintered at 1200 °C.

The density of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ pellets sintered at 1200 °C were determined using Archimedes’ principle by using deionised water as immersion medium. The relative density of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ pellets sintered at 1200 °C are provided in Table 5.1. Among the investigated samples, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ exhibits high relative
density of 96%. FE-SEM images revealed that the doped Y also acted as the sintering aid during the sintering process and thereby helps to enhance the density of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$.

5.3.4. Electrical properties

The impedance (Cole-Cole) plots of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ measured using Li$^+$ blocking Au-electrodes (Au paste cured at 600 °C for 1 hour) at 30 °C are shown as Figure 5.5. The AC impedance plots of Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ sintered at 1200 °C consists of a semicircular arc in the high frequency region and a capacitive tail in the low frequency region. The impedance plots shown in Figure 5.5 could not be well resolved into contributions from bulk and grain-boundary. Hence for experimental and practical reasons of applications we have considered uniformly the total (bulk + grain-boundary) Li$^+$ conductivity, for the presentation of conductivity results over the investigated temperature range.
Figure 5.5. Impedance (Cole-Cole) plots measured at room temperature (30 °C) for (a) Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, (b) Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and (c) Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ pellets sintered at 1200 °C.

The total (bulk + grain-boundary) Li$^+$ conductivity was calculated from the inverse of the resistivity derived from the intercepts of semicircle (close to the tail) with the real axis. The room temperature (30 °C) total (bulk + grain-boundary) Li$^+$ conductivity were estimated to be $2.12 \times 10^{-4}$ S cm$^{-1}$, $3.21 \times 10^{-4}$ S cm$^{-1}$ and $1.33 \times 10^{-4}$ S cm$^{-1}$, respectively, for Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$. The temperature dependence of the total (bulk + grain-boundary) Li$^+$
conductivity was studied in the temperature range from 30 °C to 200 °C in air atmosphere as shown in Figure 5.6. Arrhenius plot for total (bulk + grain-boundary) Li\(^+\) conductivity of Li\(_7\)La\(_{2.875}\)Y\(_{0.125}\)Zr\(_2\)O\(_{12}\), Li\(_7\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_2\)O\(_{12}\) and Li\(_7\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_2\)O\(_{12}\) indicated that the investigated samples are thermally stable without any observable phase changes in the investigated temperature range from 30 °C to 200 °C.

The variation of total (bulk + grain-boundary) Li\(^+\) conductivity measured at 30 °C of Li\(_7\)La\(_{2.875}\)Y\(_{0.125}\)Zr\(_2\)O\(_{12}\), Li\(_7\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_2\)O\(_{12}\) and Li\(_7\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_2\)O\(_{12}\) revealed that the increase of Li\(^+\) conductivity with an increase of \(x\) in Li\(_7\)La\(_{3-x}\)Y\(_x\)Zr\(_2\)O\(_{12}\) and reaches a maximized value of 3.21 x 10\(^{-4}\) S cm\(^{-1}\) for Li\(_7\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_2\)O\(_{12}\) and then decreases with further increase of \(x\), i.e., for Li\(_7\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_2\)O\(_{12}\). On the other hand the activation energy decreases with an increase of Y dopant and reaches the minimum value of 0.31eV for Li\(_7\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_2\)O\(_{12}\) and then increases with the further increase of Y dopant, i.e., for Li\(_7\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_2\)O\(_{12}\) as shown in Table 5.1.
Figure 5.6. Arrhenius plots for total (bulk + grain-boundary) Li$^+$ conductivity of (a) Li$_7$La$_{2.875}$Y$_{0.125}$Zr$_2$O$_{12}$, (b) Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and (c) Li$_7$La$_{2.5}$Y$_{0.5}$Zr$_2$O$_{12}$ in the temperature range from 30 °C to 200 °C.
Table 5.1. Lattice parameter, total (bulk + grain-boundary) Li\textsuperscript{+} conductivity, activation energy (in the temperature range from 30 °C to 200 °C) and relative density of Li\textsubscript{7}La\textsubscript{2.875}Y\textsubscript{0.125}Zr\textsubscript{2}O\textsubscript{12}, Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12} and Li\textsubscript{7}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{2}O\textsubscript{12} sintered at 1200 °C.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Lattice parameter (Å)</th>
<th>$\sigma_{\text{total}}$ 30 °C (Scm$^{-1}$)</th>
<th>$E_a$ (eV)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li\textsubscript{7}La\textsubscript{2.875}Y\textsubscript{0.125}Zr\textsubscript{2}O\textsubscript{12}</td>
<td>a = 12.9705</td>
<td>2.12 x 10$^{-4}$</td>
<td>0.33</td>
<td>90</td>
</tr>
<tr>
<td>Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12}</td>
<td>a = 12.9674</td>
<td>3.21 x 10$^{-4}$</td>
<td>0.31</td>
<td>96</td>
</tr>
<tr>
<td>Li\textsubscript{7}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{2}O\textsubscript{12}</td>
<td>a = 12.9603</td>
<td>1.33 x 10$^{-4}$</td>
<td>0.34</td>
<td>83</td>
</tr>
</tbody>
</table>

In addition to the high total (bulk + grain-boundary) Li\textsuperscript{+} conductivity the dense microstructure is also an indispensable factor for the successful application of LLZ as solid electrolyte membrane in all-solid-state lithium and Li-air battery applications. Among the investigated samples Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12} exhibits the maximized room temperature (30 °C) total (bulk + grain-boundary) Li\textsuperscript{+} conductivity of 3.21 x 10$^{-4}$ Scm$^{-1}$ and maximized relative density of 96%. Hence the Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12} has been chosen in this work to explore the phase and Li\textsuperscript{+} conductivity stability of this composition for the possible application as solid electrolyte membrane in Li-air battery.

5.3.5. Investigation on stability of Li\textsubscript{7}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{2}O\textsubscript{12}

The understanding of stability of the high Li\textsuperscript{+} conductive solid electrolytes in different solutions with various pH is essential for possible application as a protective layer for lithium metal electrode and aqueous electrolytes. Garnet-type Li\textsuperscript{+} conducting
solid electrolyte LLZ is chemically stable against molten lithium [3, 4]. Shimonishi et al. reported that cubic LLZ was stable in saturated 1M LiCl aqueous solution with respect to structure and electrical conductivity [10]. However, there are only few reports on studies of stability of garnet-type Li\(^+\) conducting solid electrolyte in different aqueous solution. In this work an attempt has been made to study the stability of high Li\(^+\) conductive \(\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}\) solid electrolyte in the solutions of 1M LiCl, dist. H\(_2\)O and 1M LiOH as depicted in Figure 5.7.

![Figure 5.7](image)

**Figure 5.7.** \(\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}\) pellets in 1M LiCl, dist. H\(_2\)O and 1M LiOH solutions for 2 weeks at 30 °C and 50 °C.

The PXRD patterns of \(\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}\) (sintered at 1200 °C) immersed in the solutions of 1M LiCl (pH = 6), dist. H\(_2\)O (pH = 7) and 1M LiOH (pH = 14) for 2 weeks at 30 °C and 50 °C along with that of the pristine \(\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}\) are shown as Figures 5.8 and 5.9, respectively. The PXRD pattern shown as Figure 5.8 (a), (b) and (c) exhibited the similar diffraction peaks compared to that of the pristine
Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and no significant changes were observed for the samples after immersed in the investigated solutions at 30 °C. The PXRD pattern shown as Figure 5.9 (a) and (b) exhibited the similar diffraction peaks compared to that of the pristine Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and no significant changes were observed for the samples after immersed in the investigated solutions at 50 °C. A close examination of the sample immersed in 1M LiOH and maintained at 50 °C for 2 weeks exhibits small amount of impurity phase La$_2$Zr$_2$O$_7$ (2θ = 28.53°) as shown in Figure 5.9 (c). Lattice parameters of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in the solution of 1M LiCl, dist. H$_2$O and 1M LiOH at 30 °C and 50 °C for 2 weeks are shown in Table 5.2. There is no appreciable variation in the lattice parameter of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ sample after immersed in 1M LiCl and dist. H$_2$O. However slight variation in lattice parameter due to the presence of secondary phase was observed for the sample Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in the solution of 1M LiOH at 50 °C for 2 weeks.
Table 5.2. Comparison of lattice parameter of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in 1M LiCl, dist.H$_2$O water and 1M LiOH solutions at 30 °C and 50 °C for 2 weeks.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 30 °C</td>
</tr>
<tr>
<td>Li$<em>7$La$</em>{2.75}$Y$_{0.25}$Zr$<em>2$O$</em>{12}$ immersed in 1M LiCl for 2 weeks</td>
<td>a = 12.9674</td>
</tr>
<tr>
<td>Li$<em>7$La$</em>{2.75}$Y$_{0.25}$Zr$<em>2$O$</em>{12}$ immersed in dist. H$_2$O for 2 weeks</td>
<td>a = 12.9674</td>
</tr>
<tr>
<td>Li$<em>7$La$</em>{2.75}$Y$_{0.25}$Zr$<em>2$O$</em>{12}$ immersed in 1M LiOH for 2 weeks</td>
<td>a = 12.9674</td>
</tr>
</tbody>
</table>
Figure 5.8. PXRD patterns of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in (a) 1M LiCl, (b) dist. H$_2$O and (c) 1M LiOH solutions at 30 °C for 2 weeks along with the pristine Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$. 
Figure 5.9. PXRD patterns of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in (a) 1M LiCl, (b) dist. H$_2$O and (c) 1M LiOH solutions at 50 °C for 2 weeks along with the pristine Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$. (Impurity phase; *:La$_2$Zr$_2$O$_7$)
Figures 5.10 and 5.11 show the Raman spectra of Li$_{7}$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ sintered at 1200 °C after immersed in the solutions of 1M LiCl, dist. H$_2$O and 1M LiOH for 2 weeks, respectively, at 30 °C and 50 °C along with that of the pristine Li$_{7}$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$. The absence of major change in the peak positions, integrated intensity and width of the Raman modes as shown in Figures 5.10 and 5.11 indicated that the garnet structured Li$_{7}$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ cubic phase is structurally stable with 1M LiCl, dist. H$_2$O and 1M LiOH aqueous solution.
Figure 5.10. Raman spectra of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in (a) 1M LiCl, (b) dist. H$_2$O and (c) 1M LiOH solutions at 30 °C for 2 weeks measured in the range 50-1000 cm$^{-1}$ along with pristine Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$. 
Figure 5.11. Raman spectra of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in (a) 1M LiCl, (b) dist. H$_2$O and (c) 1M LiOH solutions at 50 °C for 2 weeks measured in the range 50-1000 cm$^{-1}$ along with pristine Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$. 
The present investigations indicated that the stability of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ pellet in aqueous solutions is dependent on the pH of the solutions. The PXRD and Raman investigations indicated that Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ is structurally stable for longer period of time in 1M LiCl and dist. H$_2$O (with pH less than 10) even at 50 °C.

Figures 5.12 and 5.13 shows the room temperature impedance profile of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in the solutions of 1M LiCl, dist. H$_2$O and 1M LiOH for 2 weeks at 30 °C and 50 °C, respectively. The room temperature impedance profile of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ after immersed in the investigated solutions at 30 °C for 2 weeks (Figures 5.12 (a)-(C)) indicated no remarkable change in Li$^+$ conductivity i.e., it is in the same order (10$^{-4}$ S cm$^{-1}$) when compared to that of pristine Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$. Similarly there is no significant change in the impedance profile of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ after immersed in 1M LiCl and dist. H$_2$O at 50 °C for 2 weeks (Figure 5.13 (a) and (b)), which indicated that the high Li$^+$ conductive cubic phase solid electrolyte Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ is stable and do not react with the solution of 1M LiCl and dist. H$_2$O. However, Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ after immersed in 1M LiOH at 50 °C exhibited appreciable variation in the impedance profile as shown Figure 5.13 (c). The degradation in the Li$^+$ conductivity might be due to the formation of secondary phase at the grain-boundary as a result of the reaction between Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ and 1M LiOH aqueous solution at 50 °C.
Figure 5.12. Room temperature impedance (Cole-Cole) plots of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ immersed in (a) 1M LiCl, (b) dist. H$_2$O and (c) 1M LiOH solutions at 30 °C for 2 weeks.
Figure 5.13. Room temperature impedance (Cole-Cole) plots of \( \text{Li}_7 \text{La}_{2.75} \text{Y}_{0.25} \text{Zr}_2 \text{O}_{12} \) immersed in (a) 1M LiCl, (b) dist. H\(_2\)O and (c) 1M LiOH solutions at 50 °C for 2 weeks.
Earlier reports indicated the Li⁺/H⁺ exchange reaction in several lithium garnets. Li⁺/H⁺ exchange rate depends on the pH of the solutions and if it is intense it may lead to a structural transformation or even decomposition and consequently it may degrade the Li⁺ conductivity. However in the present investigation Li₇La₂.₇₅Y₀.₂₅Zr₂O₁₂ preserved its high Li⁺ conductive cubic structure (Ia₃d) against 1M LiCl and dist. H₂O and hence it demonstrates no degradation in Li⁺ conductivity. The appearance of impurity phase and the degradation of Li⁺ conductivity in 1M LiOH suggest that Li₇La₂.₇₅Y₀.₂₅Zr₂O₁₂ cannot be used in strong alkaline medium at elevated temperature for longer period of time.

The high Li⁺ conductivity, good thermal and chemical stability and ease of preparation of dense Li₇La₂.₇₅Y₀.₂₅Zr₂O₁₂ suggest that this lanthanum and partial yttrium-containing lithium garnet may be a promising solid ceramic electrolyte for all-solid-state lithium rechargeable batteries. Moreover it can be used as a protective layer for lithium metal electrode in Li-air batteries with 1M LiCl and dist. H₂O solutions because of its excellent structural stability. The model Li-air battery architecture with lithium garnet shown as Figure 5.14 could be expected to deliver a high specific energy density.

![Figure 5.14. Model Li-air battery architecture with garnet structured solid electrolyte.](image-url)
5.4. CONCLUSION

$Y^{3+}$ doped lithium garnets $\text{Li}_7\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_2\text{O}_{12}$, $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_2\text{O}_{12}$ were synthesized by conventional solid-state reaction technique. The PXRD and Raman spectra revealed the stabilization of high $\text{Li}^+$ conductive cubic-like garnet structure for the entire investigated compositions sintered at 1200 °C. FE-SEM images indicate strong stitching between the grains and practically no porosity for the $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ pellet. Among the investigated compounds $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ sintered at 1200 °C exhibited a maximized room temperature total (bulk + grain-boundary) $\text{Li}^+$ conductivity of $3.21 \times 10^{-4}$ S cm$^{-1}$ along with improved relative density of 96%.

The stability of high $\text{Li}^+$ conductive solid electrolyte in aqueous solutions is very much essential for possible application as a protective layer for the lithium electrode in Li-air battery. Hence the high $\text{Li}^+$ conductive and dense $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ has been chosen in this work to explore its phase and $\text{Li}^+$ conductivity stability for the possible application as solid electrolyte membrane in aqueous Li-air battery. This preliminary investigation on the stability of $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ in the solutions of 1M LiCl and dist. $\text{H}_2\text{O}$ at 30 °C and 50 °C indicated that the $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ was found to be stable in 1M LiCl and dist. $\text{H}_2\text{O}$. The appearance of impurity phase and the degradation of $\text{Li}^+$ conductivity in 1M LiOH suggest that $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ cannot be used in strong alkaline medium at elevated temperature for longer period of time.

The high $\text{Li}^+$ conductivity, relative density and good thermal stability of $\text{Li}_7\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_2\text{O}_{12}$ suggest that this lithium garnet may be a promising solid ceramic
electrolyte for all-solid-state lithium rechargeable batteries. Moreover it can be used as a protective layer for lithium metal electrode in Li-air batteries with because of its excellent structural stability.
REFERENCES


