EFFECT OF SIMULTANEOUS SUBSTITUTION OF YTTRIUM AND TANTALUM ON THE STABILIZATION OF CUBIC PHASE, MICROSTRUCTURE AND Li⁺ CONDUCTIVITY OF Li₇La₃Zr₂O₁₂ LITHIUM GARNET

4.1. INTRODUCTION

The substitution of super-valent cation Nb⁵⁺ for Zr⁴⁺ in Li₇La₃Zr₂O₁₂ (LLZ) stabilize the high Li⁺ conductive cubic phase relatively at lower temperature [1]. The maximized Li⁺ conductivity of 8 x 10⁻⁴ Scm⁻¹ was observed for the composition Li₀₆₇₅La₃Zr₁₅₇₅Nb₀₂₅O₁₂ in the series Li₀₇₋ₓLa₃Zr₂₋ₓNbₓO₁₂ (x=0-2) [1]. The electrochemical performance of an all-solid-state lithium battery fabricated using LiCoO₂ as positive electrode and Li₀₆₇₅La₃Zr₁₅₇₅Nb₀₂₅O₁₂ as solid electrolyte exhibited good charge-discharge capacities with low interfacial resistance between positive electrode and solid electrolyte [2]. However recent report on the stability of Nb doped LLZ i.e., Li₀₆₇₅₋ₓLa₃Zr₁₅₇₅₋ₓNb₀₂₅₋ₓO₁₂₋ₓ indicated the possible reduction of Nb in contact with lithium metal [3]. The first principles density functional theory (DFT) calculation on the electrochemical stability of lithium garnets Li₅La₃M₂O₁₂ (M = Ti, Zr, Nb, Ta, Sb, Bi; x = 5 or 7) against lithium metal indicated that the Ta containing lithium garnet Li₅La₃Ta₂O₁₂ is more non-reactive with lithium metal compared to that of Li₅La₃Nb₂O₁₂ because of unfavorable thermodynamics [4]. Li et al. indicated that Ta doped LLZ is stable up to measured voltage of 5 V vs. Li⁺/Li [5]. Hence there is a considerable attention in recent times on Ta doped LLZ for potential application as solid electrolyte membrane in all-solid-state lithium batteries.
In addition to the high Li\(^+\) conductivity, the dense microstructure related to grains and grain-boundaries is also a critical issue for the successful application of LLZ as solid electrolyte membrane in all-solid-state lithium and Li-air battery applications. The dense microstructure expected to enhance the total (bulk + grain-boundary) Li\(^+\) conductivity by reducing the grain-boundary resistance and also expected to cordon the dendritic growth during lithium deposition. 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 [6, 7]. The results reported in literatures on doping with LLZ indicated a reduction in sintering temperature with La\(^{3+}\) site doping (Sr\(^{2+}\) or Ce\(^{4+}\)) [8, 9] and improved conductivity by doping the Zr\(^{4+}\) site (Nb\(^{5+}\) or Ta\(^{5+}\)) [1, 5, 10]. However there are only few reports regarding the simultaneous substitution on the La\(^{3+}\) and on the Zr\(^{4+}\) site in LLZ [11, 12]. Therefore, it is vital to explore new possible sintering agent as dopants to realize the stabilization of cubic phase lithium garnets with dense microstructure and high Li\(^+\) conductivity. Y\(_2\)O\(_3\) is also a well known sintering agent and hence the small doping of Y\(^{3+}\) for La\(^{3+}\) in LLZT expected to enhance the density.

Investigations on the ionic conductivity of Li\(_{7-x}\)La\(_3\)Zr\(_{2-x}\)Ta\(_x\)O\(_{12}\) indicated that the maximized Li\(^+\) conductivity was observed for compositions around \(x = 0.5 \pm 0.1\) [5]. Therefore, we have chosen the high Li\(^+\) conductive nominal composition Li\(_{6.6}\)La\(_3\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) (LLZT) for further investigation on the effect of doping Y\(^{3+}\) for La\(^{3+}\) in LLZT ceramics without altering the optimized lithium content of 6.6. In the present
study, systematic investigations have been carried out on \( \text{Li}_{7-x}\text{La}_{3-y}\text{Y}_y\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) \((x = 0.4, y = 0, 0.125, 0.25 \text{ and } 0.5)\) to understand the effect of substitution of \( \text{Y}^{3+} \) for \( \text{La}^{3+} \) and \( \text{Ta}^{5+} \) for \( \text{Zr}^{4+} \) in LLZ on the stabilization of cubic phase, microstructure and \( \text{Li}^+ \) conduction behaviour.

4.2. EXPERIMENTAL SECTION

4.2.1. Synthesis of \( \text{Li}_{7-x}\text{La}_{3-y}\text{Y}_y\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) \((x = 0.4, y = 0, 0.125, 0.25 \text{ and } 0.5)\)

Conventional solid-state reaction procedure was employed for the preparation of compounds having nominal compositions \( \text{Li}_{7-x}\text{La}_{3-y}\text{Y}_y\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) \((x = 0.4, y = 0, 0.125, 0.25 \text{ and } 0.5)\) i.e., \( \text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \), \( \text{Li}_{6.6}\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \), \( \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) and \( \text{Li}_{6.6}\text{La}_{2.8}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) using stoichiometric amounts of high purity chemicals \( \text{LiNO}_3 \) (Sigma-Aldrich, >99%; 15 wt.% excess was added to compensate the loss of lithium during sintering), \( \text{La}_2\text{O}_3 \) (Merck, >99%; pre dried at 900 °C for 24 hours), \( \text{ZrO}_2 \) (Acros, 98%), \( \text{Y}_2\text{O}_3 \) (Sigma-Aldrich, 98%) and \( \text{Ta}_2\text{O}_5 \) (Alfa-aesar, 99%). The precursors were ball milled with zirconia balls in 2-propanol for about 6 hours using a Pulverisette 7, Fritsch, Germany. After the evaporation of the solvents at room temperature, the mixtures were heated from room temperature to 750 °C in an open alumina crucible and held at this temperature for 6 hours and then cooled down to room temperature. The resultant powders were ball milled again for 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 sintered at 750 °C for 12 hours and 1200 °C for 18 hours using alumina crucible.
Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) in high Li$^+$ conductive cubic [13, 14] and tetragonal phase [15] were also prepared at elevated temperature through solid-state reaction with procedure described earlier for the purpose of comparison.

4.2.2. Characterization

The sintered pellets were crushed into powder for powder X-ray diffraction (PXRD) and Raman measurements. The phase purity and crystal structure of the prepared samples were examined by powder X-ray diffraction (PXRD) using X’pert PRO PANalytical X-ray diffractometer with Cu-K$_\alpha$ radiation of $\lambda = 1.5418$ Å from $\theta = 10^\circ$ to $80^\circ$ with a step width of 0.025°. Confocal micro-Raman spectra have been recorded at room temperature in the range 50-4000 cm$^{-1}$ using a Renishaw inVia Reflex spectrometer with a 50 mW internal Ar$^+$ laser source of excitation wavelength 514 nm. Fourier transform infrared (FTIR) spectra were recorded with Thermo Nicolet 6700 using KBr pellet technique.

Thermogravimetric analysis (TGA) was performed with a SDT Q600 (TA) under air flow with a heating rate of 10 °C/min. A field-emission scanning electron microscope SU8000 Family Ultra-High Resolution (FE-SEM) equipped with energy dispersive X-ray detector (EDX) was used to obtain microstructure of the fractured surface of the pellet. The elemental analysis for the prepared samples were carried out using wavelength dispersive X-ray fluorescence spectrometer (WD-XRF), Bruker S4 Pioneer to estimate the amount of inclusion of Al$^{3+}$ from the alumina crucible. The relative densities of the
sintered pellets at room temperature were obtained with the Archimedes’ principle using deionised water as the immersion medium.

Electrical conductivity measurements of the prepared pellets were performed using Li\(^+\) blocking Au-electrodes (Au paste cured at 600 °C for 1 hour) in the temperature range from 27 °C to 200 °C using a Novocontrol concept 80 broadband dielectric spectrometer (BDS) in the frequency range from 5 Hz to 20 MHz.

### 4.3. RESULTS AND DISCUSSION

#### 4.3.1. Powder X-ray diffraction (PXRD)

Figure 4.1 shows the powder X-ray diffraction (PXRD) patterns of Li\(_{6.6}\)La\(_{3}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.875}\)Y\(_{0.125}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) and Li\(_{6.6}\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) sintered at 750 °C along with the patterns of tetragonal (I\(_{4}/\text{acd}\)) LLZ and high Li\(^+\) conductive cubic (I\(_{a\tilde{3}d}\)) phase LLZ. The presence of all the diffraction peaks corresponding to that of cubic phase and absence of clear splitting of the diffraction peaks corresponding to that of characteristic tetragonal phase in the case of the measured PXRD patterns of Li\(_{6.6}\)La\(_{3}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.875}\)Y\(_{0.125}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) and Li\(_{6.6}\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) as shown in Figure 4.1(a) - (d), respectively, indicates the possibility of stabilization of cubic-like garnet phase even at lower sintering temperature at around 750 °C.
Chapter IV

Figure 4.1. PXRD patterns of (a) Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C along with the patterns of tetragonal LLZ and high Li$^+$ conductive cubic phase LLZ.
The PXRD patterns of Li\(_{6.6}\)La\(_3\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.875}\)Y\(_{0.125}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) and Li\(_{6.6}\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) sintered at 1200 °C along with the patterns of tetragonal LLZ and high Li\(^{+}\) conductive cubic phase LLZ are shown as Figure 4.2. The PXRD patterns of Li\(_{6.6}\)La\(_3\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.875}\)Y\(_{0.125}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) and Li\(_{6.6}\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) shown in Figure 4.2 (a)-(d), respectively, confirm the garnet-like structure with high Li\(^{+}\) conductive phase, which could be evidenced by sharp diffraction peaks without splitting. Lithium garnet prepared with the nominal composition Li\(_{6.6}\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) exhibits weak impurity peaks corresponding to Ta\(_2\)O\(_5\) and TaO\(_2\). The cubic lattice parameter of Li\(_{6.6}\)La\(_3\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.875}\)Y\(_{0.125}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\), Li\(_{6.6}\)La\(_{2.75}\)Y\(_{0.25}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) and Li\(_{6.6}\)La\(_{2.5}\)Y\(_{0.5}\)Zr\(_{1.6}\)Ta\(_{0.4}\)O\(_{12}\) sintered at 1200 °C were found to be 12.9484(2) Å, 12.9371(2) Å, 12.9214(1) Å and 12.9041(3) Å, respectively. The cubic lattice parameter decreases nearly linearly with increasing Y substitution, since the ionic size of Y\(^{3+}\) (0.9 Å) is smaller than that of La\(^{3+}\) (1.16 Å) [16].
Figure 4.2. PXRD patterns of (a) Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 1200 °C along with the patterns of tetragonal LLZ and high Li$^+$ conductive cubic phase LLZ. (Impurity phase; #: Ta$_2$O$_5$ and +: TaO$_2$).
The selected PXRD patterns ($2\theta = 24^\circ$ to $45^\circ$) of Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C and 1200 °C shown as Figure 4.3 do not exhibit major change in the pattern but exhibit slightly broadened diffraction peaks along with clear shift in peak positions towards the lower diffraction angle for the samples sintered at 750 °C compared to that of samples sintered at 1200 °C. The shift in the diffraction peaks towards the lower diffraction angle suggesting an increase in the lattice parameter for the samples sintered at 750 °C. The cubic lattice parameter of Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C were found to be 12.9594(2) Å, 12.9572(4) Å, 12.9506(5) Å and 12.9479(3) Å, respectively.
Figure 4.3. PXRD patterns of Li$_{7-x}$La$_3$Y$_x$Zr$_{2-y}$Ta$_y$O$_{12}$ ($x = 0.4, y = 0, 0.125, 0.25$ and $0.5$) sintered at 750 °C (red colour) and 1200 °C (blue colour) in the 2θ range 24° to 45°.

4.3.2. Raman spectroscopic studies

Raman scattering is a very powerful technique for acquiring useful information on the structure of ceramic oxides. The Raman spectra of Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$,
Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.25}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C and 1200 °C along with the tetragonal LLZ and high Li$^+$ conductive cubic phase LLZ are shown as Figures 4.4 and 4.5, respectively. Although the PXRD patterns of Li$_{6.6}$La$_{2}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C and 1200 °C shown as Figures 4.1 and 4.2 did not exhibit major change in the pattern like their dramatic difference of corresponding Raman spectra shown as Figures 4.4 and 4.5.

The Raman bands observed in the range 200-500 cm$^{-1}$ (Figures 4.4 and 4.5) corresponding to the expected internal modes of LiO$_4$ and LiO$_6$ clearly revealed the major difference between the samples sintered at 750 °C and 1200 °C. The Raman spectra of Li$_{6.6}$La$_{2}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C measured in the range 200-500 cm$^{-1}$ revealed at least six bands with a maximum intense band at around 295 cm$^{-1}$, medium intense bands at around 255, 342, 371 and 462 cm$^{-1}$ and a weak band at around 206 cm$^{-1}$. The Raman spectra of Li$_{6.6}$La$_{2}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 1200 °C measured in the range 200-500 cm$^{-1}$ revealed a broad intense band at around 377 cm$^{-1}$, broad medium intense band at around 260 cm$^{-1}$ and shoulder band at around 420 cm$^{-1}$. The close observation between the Raman spectra shown in Figures 4.4 and 4.5 revealed that the phase stabilized at around 750 °C for the Li$_{7-x}$La$_{3}$Y$_{x}$Zr$_{2-x}$Ta$_{3}$O$_{12}$ ($x = 0.4$, $y = 0$, 0.125, 0.25 and 0.5) sample is different from that of both the tetragonal ($I4_1/acd$) and high Li$^+$ conductive cubic phase ($Ia\tilde{3}d$).
In addition to the above difference in the Raman spectra of Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_2$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C and 1200 °C an appreciable shift in the positions of vibrational stretching modes of ZrO$_6$ and TaO$_6$ octahedral units was observed as shown in Figure 4.6. The Raman spectrum of Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ exhibits shift of Zr-O stretching mode from 684 to 656 cm$^{-1}$ and Ta-O stretching mode from 773 to 743 cm$^{-1}$ while sintering temperature increased from 750 °C to 1200 °C. Similar shift in the Zr-O and Ta-O stretching mode was observed for the remaining samples as shown in Figure 4.6. The shift of approximately 30 cm$^{-1}$ towards lower wave number observed for the Zr-O and Ta-O stretching modes and broadening of the Raman bands in the intermediate energy range clearly revealed an appreciable modifications in the crystal structure for the Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ samples while sintering temperature increased from 750 °C to 1200 °C.
Figure 4.4. Raman spectra of (a) Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C measured in the range 50-1000 cm$^{-1}$ along with the patterns of tetragonal LLZ and high Li$^+$ conductive cubic phase LLZ.
Chapter IV

Figure 4.5. Raman spectra of (a) Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 1200 °C measured in the range 50-1000 cm$^{-1}$ along with the patterns of tetragonal LLZ and high Li$^+$ conductive cubic phase LLZ.
Figure 4.6. Raman spectra of Li$_{7-x}$La$_{3-y}$Y$_y$Zr$_{2-x}$Ta$_x$O$_{12}$ ($x = 0.4$, $y = 0$, 0.125, 0.25 and 0.5) sintered at 750 °C (red colour) and 1200 °C (blue colour) along with the patterns of high Li$^+$ conductive cubic phase LLZ (black colour) measured in the range 600–900 cm$^{-1}$ showing an appreciable shift in the positions of vibrational stretching modes of ZrO$_6$ and TaO$_6$ octahedral units.
Investigation on the structural stability 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 [17]. Tetragonal phase or lithium deficient lithium garnets were reported to be sensitive to humid conditions [18]. The formation of a low temperature cubic phase well below the usual tetragonal to cubic transition temperature is found to depend upon hydration mechanisms [18]. The nature of the high and low temperature cubic garnets are totally different: the one found above the phase transition (tetragonal to cubic) at higher temperature does not involve any major change in the stoichiometry, whereas the cubic phase formed at low temperature might be due to the effect of the insertion of water molecules and the protonation through the Li⁺/H⁺ exchange mechanism into the garnet structure.

Thermogravimetric (TG), Raman and FTIR measurements for samples sintered at 750 °C were carried out to investigate the hydration effect in these samples. Raman spectra revealed the presence of OH stretching vibration around 3537 cm⁻¹ shown as Figure 4.7. Similarly the FTIR spectra (Figure 4.8) revealed the presence of OH stretching vibration at around 3567 cm⁻¹. TG thermograms of all these samples indicated the onset of major weight loss around 300 °C and ends at 450 °C shown in Figure 4.9. In addition to this an additional small weight loss in the temperature range 200-300 °C is observed for the Li₇₋ₓLaₓ₃₋₉YₓZr₂₋ₓTaₓO₁₂ (x = 0.4, y = 0) sample only. The major weight loss observed at around 300-450 °C in TG might be due to the release of crystalline water and not from the surface adsorbed water. The water vapour from the atmosphere might enter into the lattice and replaced the Li⁺ by protons to form O-H bonds [19]. An increase
in the cell parameter observed for the Li\textsubscript{6.6}La\textsubscript{3}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12}, Li\textsubscript{6.6}La\textsubscript{2.875}Y\textsubscript{0.125}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12}, Li\textsubscript{6.6}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12} and Li\textsubscript{6.6}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12} sintered at 750 °C compared to that of 1200 °C might be due to the replacement of Li-O bonds by O-H⋯O hydrogen bonds [20]. The changes in the Raman spectra revealed that the cubic-like phase observed for the Li\textsubscript{6.6}La\textsubscript{3}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12}, Li\textsubscript{6.6}La\textsubscript{2.875}Y\textsubscript{0.125}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12}, Li\textsubscript{6.6}La\textsubscript{2.75}Y\textsubscript{0.25}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12} and Li\textsubscript{6.6}La\textsubscript{2.5}Y\textsubscript{0.5}Zr\textsubscript{1.6}Ta\textsubscript{0.4}O\textsubscript{12} samples sintered at 750 °C is different from \textit{Ia\overline{3}d} space group cubic phase. However further detailed temperature dependent Raman, neutron and nuclear magnetic resonance (NMR) investigations are essential for unambiguous of the structure of the low temperature cubic phase.
Figure 4.7. Raman spectra of (a) Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C measured in the range 50-4000 cm$^{-1}$. The appearance of band at around 3537 cm$^{-1}$ gives an evidence for the presence of OH stretching vibration.
Figure 4.8. FTIR spectra of (a) Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C measured in the range 500-4000 cm$^{-1}$. The appearance of band at around 3567 cm$^{-1}$ gives an evidence for the presence of OH stretching vibration.
4.3.3. Microstructural analysis

Dense polycrystalline ceramic electrolyte with large size grain is highly desired for device application. High porosity in solid electrolytes may cause a high grain-boundary resistance as well as mechanical failure. Particularly for all-solid-state lithium battery application solid electrolytes with dense microstructure is very much essential to avoid dendritic growth during lithium deposition. FE-SEM images of...
fractured surface of \( \text{Li}_{6.6}\text{La}_{3}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \), \( \text{Li}_{6.6}\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \), \( \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) and \( \text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) pellets sintered at 1200 °C are shown in Figures 4.10(a)-(h), respectively. The magnified FE-SEM images of these pellets are shown as Figures 4.10(e)-(h), respectively. The cross sectional FE-SEM image performed on larger area (20 µm) of the \( \text{Li}_{6.6}\text{La}_{3}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) and \( \text{Y} \) substituted relatively dense \( \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) pellets are provided as Figure 4.11.

FE-SEM images of \( \text{Li}_{6.6}\text{La}_{3}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) (Figures 4.10(a) and (e) and Figure 4.11(a)) reveal the absence of well crystallized grains and appearance of pores in between the grains, which leads to poor density. Significant change in microstructure has been observed by introduction of yttrium as dopant as shown in Figures 4.10((b)-(d), (f)-(h)) and Figure 4.11. At low yttrium concentration, the FE-SEM images of \( \text{Li}_{6.6}\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) as shown in Figures 4.10(b) and (f) reveal growth of grains and better contact with the neighbouring grains, but certain amount of pores can be observed in between the grains. FE-SEM images of \( \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) shown in Figure 4.10(c) and (g) and Figure 4.11(b) reveal well crystallized large grains, large contact area of the grains with the neighbouring grains, reduction in the size of pores at the grain-boundaries and absence of any visible secondary phase. Good connection between the grains and absence of secondary phase in the grain-boundary expected to reduce the grain-boundary resistance. Further increase of \( \text{Y} \) dopant leads to segregation of secondary phase between the grains of \( \text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) as shown in Figure 4.10(d) and (h). FE-SEM investigations on the investigated samples indicated that the \( \text{Y} \) dopant also act as the sintering aid during the preparation process by improving the better
connection between grains. The maximized relative density of 95% was observed for the 
$\text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ sample as given in Table 4.1. The theoretical, experimental 
and relative density of Y and Ta doped LLZ with different Y contents are provided as 
Table 4.1.

**Table 4.1.** Theoretical, experimental and relative density of $\text{Li}_{7-x}\text{La}_{3-y}\text{Y}_{x}\text{Zr}_{2-x}\text{Ta}_{x}\text{O}_{12}$ 
($x = 0.4, y = 0, 0.125, 0.25$ and $0.5$) sintered at $1200$ °C.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>$\rho_{\text{theoretical}}$ (g cm$^{-3}$)</th>
<th>$\rho_{\text{experimental}}$ (g cm$^{-3}$)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}<em>{6.6}\text{La}</em>{3}\text{Zr}<em>{1.6}\text{Ta}</em>{0.4}\text{O}_{12}$</td>
<td>5.34</td>
<td>4.44</td>
<td>83</td>
</tr>
<tr>
<td>$\text{Li}<em>{6.6}\text{La}</em>{2.875}\text{Y}<em>{0.125}\text{Zr}</em>{1.6}\text{Ta}<em>{0.4}\text{O}</em>{12}$</td>
<td>5.32</td>
<td>4.53</td>
<td>85</td>
</tr>
<tr>
<td>$\text{Li}<em>{6.6}\text{La}</em>{2.75}\text{Y}<em>{0.25}\text{Zr}</em>{1.6}\text{Ta}<em>{0.4}\text{O}</em>{12}$</td>
<td>5.30</td>
<td>5.04</td>
<td>95</td>
</tr>
<tr>
<td>$\text{Li}<em>{6.6}\text{La}</em>{2.5}\text{Y}<em>{0.5}\text{Zr}</em>{1.6}\text{Ta}<em>{0.4}\text{O}</em>{12}$</td>
<td>5.24</td>
<td>4.72</td>
<td>90</td>
</tr>
</tbody>
</table>
Figure 4.10. FE-SEM images of the fractured surface of (a) Li$\textsubscript{6.6}$La$\textsubscript{3}$Zr$\textsubscript{1.6}$Ta$\textsubscript{0.4}$O$\textsubscript{12}$, (b) Li$\textsubscript{6.6}$La$\textsubscript{2.875}$Y$\textsubscript{0.125}$Zr$\textsubscript{1.6}$Ta$\textsubscript{0.4}$O$\textsubscript{12}$, (c) Li$\textsubscript{6.6}$La$\textsubscript{2.75}$Y$\textsubscript{0.25}$Zr$\textsubscript{1.6}$Ta$\textsubscript{0.4}$O$\textsubscript{12}$ and (d) Li$\textsubscript{6.6}$La$\textsubscript{2.5}$Y$\textsubscript{0.5}$Zr$\textsubscript{1.6}$Ta$\textsubscript{0.4}$O$\textsubscript{12}$ pellets sintered at 1200 °C and (e-h) represent the magnified FE-SEM images of the respective samples.
Figure 4.11. Comparison of FE-SEM images of the fractured surface of (a) Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (b) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ pellets sintered at 1200 °C.

Table 4.2. Lattice parameter and total (bulk + grain-boundary) Li$^+$ conductivity of Li$_{7-x}$La$_{3-y}$Y$_y$Zr$_{2-x}$Ta$_x$O$_{12}$ ($x = 0.4$, $y = 0$, 0.125, 0.25 and 0.5) samples sintered at 750 °C.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Lattice Parameter, $a$ (Å)</th>
<th>$\sigma_{\text{total}}$ 27 °C (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{6.6}$La$</em>{3}$Zr$<em>{1.6}$Ta$</em>{0.4}$O$_{12}$</td>
<td>12.9594(2)</td>
<td>9.08 x 10$^8$</td>
</tr>
<tr>
<td>Li$<em>{6.6}$La$</em>{2.875}$Y$<em>{0.125}$Zr$</em>{1.6}$Ta$<em>{0.4}$O$</em>{12}$</td>
<td>12.9572(4)</td>
<td>2.31 x 10$^7$</td>
</tr>
<tr>
<td>Li$<em>{6.6}$La$</em>{2.75}$Y$<em>{0.25}$Zr$</em>{1.6}$Ta$<em>{0.4}$O$</em>{12}$</td>
<td>12.9506(5)</td>
<td>6.05 x 10$^7$</td>
</tr>
<tr>
<td>Li$<em>{6.6}$La$</em>{2.5}$Y$<em>{0.5}$Zr$</em>{1.6}$Ta$<em>{0.4}$O$</em>{12}$</td>
<td>12.9479(3)</td>
<td>3.26 x 10$^8$</td>
</tr>
</tbody>
</table>
EDX mapping for $\text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ and $\text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ pellets sintered at 1200 °C have been given as Figures 4.12 and 4.13, respectively. The elemental mapping for the $\text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ shown as Figure 4.12 revealed the uniform distribution of La, Y, Zr, Al and Ta throughout the grains and also indicated the absence of any secondary phase at the grain-boundary. EDX mapping for the Y rich sample $\text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ (Figure 4.13) indicated the possible segregation of Y containing secondary phase at the grain-boundary.

*Figure 4.12.* FE-SEM image and EDX mapping of $\text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ pellets sintered at 1200 °C.
Studies on, zirconium containing lithium garnets revealed that unintentional incorporation of $\text{Al}^{3+}$ from the crucibles helps to stabilize the high $\text{Li}^+$ conductive cubic
phase. The XRF and EDX studies on the investigated lithium garnets sintered at 750 °C indicated the absence of Al$^{3+}$ in these samples. However, the XRF and EDX studies indicated the inclusion of Al$^{3+}$ from alumina crucible during the preparation of the investigated lithium garnets at high sintering temperature around 1200 °C. The amount of Al$^{3+}$ content present in the Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 1200 °C was estimated to be 0.66 wt.%, 0.57 wt.%, 0.36 wt.% and 0.25 wt.%, respectively. The minimum amount of Al$^{3+}$ necessary to stabilize LLZ sample in cubic phase was estimated to be around 0.9 wt.% [21]. The presence of Al$^{3+}$ content lesser than the 0.9 wt.% in the investigated samples indicated that the stabilization of cubic phase in this work is not merely by the inclusion of Al$^{3+}$ alone. Recent report also confirmed the stabilization of LLZ in cubic phase through Ta doping without Al$^{3+}$ [22].

4.3.4. Electrical properties

Typical AC impedance (Cole-Cole) plots measured at room temperature (27 °C) for Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 750 °C are shown as Figure 4.14. The total (bulk + grain-boundary) Li$^+$ conductivity values of all the investigated samples were in the order of $10^{-7}$ to $10^{-8}$ Scm$^{-1}$ (Table 4.2).
Figure 4.14. Typical AC impedance (Cole-Cole) plots measured at room temperature (27 °C) for Li$_{7-x}$La$_{3+y}$Y$_{y}$Zr$_{2-x}$Ta$_x$O$_{12}$ ($x = 0.4$, $y = 0$, 0.125, 0.25 and 0.5) pellets sintered at 750 °C using Li$^+$ blocking Au electrodes. The impedance plot in the high frequency region is shown as insert.
Table 4.3. Lattice parameter, bulk and total (bulk + grain-boundary) Li$^+$ conductivity, and activation energy for total (bulk + grain-boundary) Li$^+$ conductivity (in the temperature range 27 °C to 200 °C) of Li$_{7-x}$La$_{3-x}$Y$_x$Zr$_{2-x}$Ta$_x$O$_{12}$ ($x = 0.4$, $y = 0$, 0.125, 0.25 and 0.5) sintered at 1200 °C.

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Lattice Parameter, $a$ (Å)</th>
<th>$\sigma_{\text{bulk}}$ $27$ °C (Scm$^{-1}$)</th>
<th>$\sigma_{\text{total}}$ $27$ °C (Scm$^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_{6.6}$La$<em>3$Zr$<em>1.6$Ta$</em>{0.4}$O$</em>{12}$</td>
<td>12.9484(2)</td>
<td>3.13 x 10$^{-4}$</td>
<td>3.04 x 10$^{-4}$</td>
<td>0.38</td>
</tr>
<tr>
<td>Li$<em>{6.6}$La$</em>{2.875}$Y$<em>{0.125}$Zr$</em>{1.6}$Ta$<em>{0.4}$O$</em>{12}$</td>
<td>12.9371(2)</td>
<td>-</td>
<td>3.17 x 10$^{-4}$</td>
<td>0.35</td>
</tr>
<tr>
<td>Li$<em>{6.6}$La$</em>{2.75}$Y$<em>{0.25}$Zr$</em>{1.6}$Ta$<em>{0.4}$O$</em>{12}$</td>
<td>12.9214(1)</td>
<td>-</td>
<td>4.36 x 10$^{-4}$</td>
<td>0.34</td>
</tr>
<tr>
<td>Li$<em>{6.6}$La$</em>{2.5}$Y$<em>{0.5}$Zr$</em>{1.6}$Ta$<em>{0.4}$O$</em>{12}$</td>
<td>12.9041(3)</td>
<td>3.00 x 10$^{-4}$</td>
<td>2.26 x 10$^{-4}$</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Typical AC impedance (Cole-Cole) plots measured at room temperature (27 °C) for Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 1200 °C are shown in Figures 4.15(a) - (d), respectively. The AC impedance data of Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ (Figure 4.15(a)) was fitted with a suitable equivalent circuit using individual resistances and constant phase elements (CPEs) representing the electrical bulk, grain-boundary and electrode response, respectively, ($R_b$CPE$_b$) ($R_{gb}$CPE$_{gb}$) (CPE$_{el}$) (where R is the resistance and CPE is the constant phase element and the subscript b, gb and el refers to the bulk, grain-boundary and electrode contribution, respectively). The bulk and total (bulk + grain-boundary) Li$^+$ conductivity of Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ was estimated to be 3.13 x 10$^{-4}$ Scm$^{-1}$ and
3.04 x 10^{-4} \text{ S cm}^{-1}, \text{ respectively. The AC impedance (Cole-Cole) plots for the } \text{Li}_{6.6}\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \text{ and Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \text{ shown as Figures 4.15(b) and (c), respectively, revealed that the bulk and grain-boundary contribution could not be resolved clearly which in turn indicates negligible grain-boundary resistance in that samples. Hence, the corresponding impedance plot were fitted with the suitable equivalent circuit using individual resistances and constant phase element (CPE) representing the total resistance and electrode response, respectively, (RCPE) (CPE_{el}). The total (bulk + grain-boundary) Li\text{\textsuperscript{+}} conductivity for Li_{6.6}\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \text{ and Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \text{ were estimated to be } 3.17 \times 10^{-4} \text{ S cm}^{-1} \text{ and } 4.36 \times 10^{-4} \text{ S cm}^{-1}, \text{ respectively. The experimental impedance data points of Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \text{ was fitted with a suitable equivalent circuit using individual resistances and constant phase elements (CPEs) representing the electrical bulk, grain-boundary and electrode response, respectively, (R_{b}CPE_{b}) (R_{gb}CPE_{gb}) (CPE_{el}) (Figure 4.15(d)). The bulk and total (bulk + grain-boundary) Li\text{\textsuperscript{+}} conductivity of Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \text{ was estimated to be } 3 \times 10^{-4} \text{ S cm}^{-1} \text{ and } 2.26 \times 10^{-4} \text{ S cm}^{-1}, \text{ respectively.}
Figure 4.15. Typical AC impedance (Cole-Cole) plots measured at room temperature (27 °C) for (a) Li$_{6.6}$La$_{3}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ pellets sintered at 1200 °C using Li$^+$ blocking Au electrodes. Open circle are the experimental data and the solid lines are the fitted curves with an equivalent circuit model. The two semi-circles (dotted line) below the fitting curve in Figure 4.15(d) illustrate the separation of bulk and grain-boundary contributions, respectively.
Arrhenius plots for the total (bulk + grain-boundary) Li$^+$ conductivity of garnet structured electrolytes Li$_6$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ are shown in Figure 4.16(a) - (d), respectively. Arrhenius plots shown in Figure 4.16 indicated that the investigated samples are thermally stable without any phase transition since there is no appreciable shift in conductivity in the temperature range from 27 °C to 200 °C. The activation energy ($E_a$) was estimated from the slope of log($\sigma T$) vs. 1000/T.

Figure 4.16. Arrhenius plots of (a) Li$_{6.6}$La$_3$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (b) Li$_{6.6}$La$_{2.875}$Y$_{0.125}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$, (c) Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ and (d) Li$_{6.6}$La$_{2.5}$Y$_{0.5}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ measured in the temperature range from 27 °C to 200 °C.
The variation of total Li\(^{+}\) conductivity measured at 27 °C indicated that the total (bulk + grain-boundary) Li\(^{+}\) conductivity increased initially with an increase of Y dopant and reaches a maximized value of 4.36 \times 10^{-4} \text{ Scm}^{-1} for \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} then decreases with further increase of Y dopant i.e., for \text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}. In contrast, the activation energy (measured in temperature range from 27 °C to 200 °C) initially decreases with an increase of Y dopant and reaches a minimum of 0.34 eV for \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} and then increases with the further increase of Y dopant i.e., for \text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}. The enhancement in total (bulk + grain-boundary) Li\(^{+}\) conductivity in \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} might be related to dense microstructure as reflected in the FE-SEM image and density measurement. The decrease in the total (bulk + grain-boundary) Li\(^{+}\) conductivity for the lithium garnet with nominal composition \text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} might be due to the formation of secondary phase as revealed by FE-SEM/EDX images.

The lattice parameter, bulk and total (bulk + grain-boundary) Li\(^{+}\) conductivity measured at room temperature (27 °C) and activation energies derived from Arrhenius plots for total (bulk + grain-boundary) Li\(^{+}\) conductivity (in the temperature range from 27 °C to 200 °C) for the samples sintered at 1200 °C are tabulated in Table 4.3.

The results obtained in this work indicated that the optimal Y substitution helps to reduce the grain-boundary resistance in a major way and also helps to reduce the bulk resistance slightly. AC impedance analysis on the investigated samples indicated that \text{Li}_{6.6}\text{La}_{2.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} (Figure 4.15(a)) and \text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} (Figure 4.15(d)) have detectable grain-boundary resistances. However \text{Li}_{6.6}\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}
(Figure 4.15(b)) and \( \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) (Figure 4.15(c)) do not exhibit any resolvable grain-boundary resistance. When the Y substitution is lower it helps to reduce the grain-boundary resistance but larger doping of Y (greater than \( y = 0.25 \) in \( \text{Li}_{7-x}\text{La}_{3-y}\text{Y}_y\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) (\( x = 0.4 \)) leads to segregation of Y containing secondary phases in to the grain-boundary and increases the grain-boundary resistance. The AC impedance, FE-SEM/EDX and density studies indicated that the optimal amount of yttrium incorporation in LLZT (i.e., \( \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \)) helps to enhance the total (bulk + grain-boundary) \( \text{Li}^+ \) conductivity along with the dense microstructure.

### 4.4. CONCLUSION

Garnet structured solid electrolytes \( \text{Li}_{6.6}\text{La}_{3}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \), \( \text{Li}_{6.6}\text{La}_{2.875}\text{Y}_{0.125}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \), \( \text{Li}_{6.6}\text{La}_{2.75}\text{Y}_{0.25}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) and \( \text{Li}_{6.6}\text{La}_{2.5}\text{Y}_{0.5}\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12} \) were prepared by conventional solid-state reaction method. Raman spectra revealed that the cubic phase stabilized at around 750 °C for the \( \text{Li}_{7-x}\text{La}_{3-y}\text{Y}_y\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12} \) (\( x = 0.4, y = 0, 0.125, 0.25 \) and 0.5) sample is different from that of the high \( \text{Li}^+ \) conductive cubic phase (\( Ia\bar{3}d \)) and the transition to high \( \text{Li}^+ \) conductive cubic phase with distorted lithium sub-lattice (\( Ia\bar{3}d \)) was observed for the samples sintered at elevated temperature around 1200 °C. Thermogravimetric (TG), Raman and FTIR studies indicated that the cubic phase exhibited by the investigated lithium garnets sintered at 750 °C might be driven by the insertion of water vapour from the humid atmosphere. The water vapour from the atmosphere might enter into the lattice and replaced the lithium ions by protons to form O-H bonds. FE-SEM images revealed that the lithium garnet with
nominal composition Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ is relatively dense and the grains are in good contact with each other. This could be due to the better sinterability of the garnets with the yttrium doping. Among the investigated lithium garnets Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ sintered at 1200 °C exhibits maximized room temperature total (bulk + grain-boundary) Li$^+$ conductivity of 4.36 x 10$^{-4}$ Scm$^{-1}$. The present study indicated the possibility of enhancement in the density and total Li$^+$ conductivity of LLZ through suitable and optimal amount of dopant for La and Zr along with optimal lithium concentration. The observation of high total (bulk + grain-boundary) Li$^+$ conduction and relatively dense microstructure suggest that this lithium garnet Li$_{6.6}$La$_{2.75}$Y$_{0.25}$Zr$_{1.6}$Ta$_{0.4}$O$_{12}$ may be a promising solid ceramic electrolyte for all-solid-state lithium rechargeable batteries.
REFERENCES


Chapter IV

2046.


