Lithium ion (Li\textsuperscript{+}) batteries have strong advantages over the other types of rechargeable batteries. Inorganic solid fast Li\textsuperscript{+} conductor based batteries are expected to overcome limitations over the safety concerns of currently available organic polymer electrolyte based Li\textsuperscript{+} batteries. The main features required for the successful solid electrolytes are high Li\textsuperscript{+} conductivity, negligible electronic conductivity and wide electrochemical window. So far many efforts have been devoted to realize a solid electrolyte with high Li\textsuperscript{+} conductivity and excellent chemical stability against metallic lithium, which helps to improve the present Li\textsuperscript{+} batteries and thereby to introduce new types of lithium metal based batteries such as all-solid-state lithium and Li-air batteries.

Among the metal-air batteries, the superior energy density of Li-air battery (11,140 Whkg\textsuperscript{-1} excluding oxygen weight and 5,200 Whkg\textsuperscript{-1} including oxygen weight) makes it as a promising candidate for future electric vehicles (EVs) application. Unlike conventional zinc-air batteries, the Li-air batteries cannot be operated with aqueous electrolytes without the protection of the lithium metal due to the strong reaction between lithium metal and water. Hence a water-stable Li\textsuperscript{+} solid electrolyte is usually used to separate the lithium negative electrode from the aqueous electrolyte. Since the most commonly used water stable lithium titanium aluminium phosphate (LTAP) electrolyte membrane is not stable in contact with lithium metal, a separator soaked with the organic electrolyte between the lithium metal and the solid electrolyte membrane (LTAP) is necessary, resulting into a dual-electrolyte Li-air cell battery. However the advanced Li-air battery architecture requires lithium metal negative electrode, porous carbon
positive electrode, aqueous electrolyte and a high Li\textsuperscript{+} conductive solid electrolyte membrane that is electrochemically stable against metallic lithium and aqueous electrolyte. Moreover, the solid electrolyte membrane should be dense to prevent the catholyte from reacting with metallic lithium and also to suppress lithium dendrite penetration.

Recently, garnet-like structural compounds has received considerable attention for potential application as electrolytes in all-solid-state lithium batteries. Particularly, garnet structured Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZ) has been widely studied because of its high Li\textsuperscript{+} conductivity ($\sigma_{\text{Li}} > 10^{-4}$ Scm\textsuperscript{-1} at room temperature) and good stability against lithium metal. The garnet structured LLZ exists in three phases: high Li\textsuperscript{+} conductive cubic, low temperature cubic and tetragonal. The stoichiometric Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZ) stabilizes in tetragonal phase. Al contamination from the alumina crucible is the key aspect in stabilizing the high Li\textsuperscript{+} conductive cubic phase. The low temperature cubic phase arises due to either CO\textsubscript{2} absorption or hydration mechanism. The Li\textsuperscript{+} conductivity of the high Li\textsuperscript{+} conductive cubic phase is two orders of magnitude higher than that of tetragonal and low temperature cubic phases. The Li\textsuperscript{+} conductivity of cubic Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} depends highly on synthesis conditions, sintering temperature and nature of the crucible used.

The main focus of this thesis is to develop high Li\textsuperscript{+} conductive cubic phase lithium garnets with dense microstructure for all-solid-state Li\textsuperscript{+} battery application and to develop lithium garnets that are stable against aqueous solution for Li-air battery applications. The role of La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} pyrochlore in the formation of LLZ and the effect of lithium concentration in the stabilization of high Li\textsuperscript{+} conductive cubic phase LLZ
through solid-state reaction method have been investigated in detail. An attempt has been made to enhance the total (bulk + grain-boundary) \( \text{Li}^+ \) conductivity of LLZ by partial substitution of hexavalent Te for a tetravalent Zr i.e., with nominal compositions \( \text{Li}_{7-2x}\text{La}_3\text{Zr}_{2-x}\text{Te}_x\text{O}_{12} \) (\( x = 0.125 \) and 0.25). High \( \text{Li}^+ \) conductive cubic phase Sn based lithium garnets are successfully prepared by partially substituting Ta for Sn in \( \text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12} \) through solid-state reaction technique. The structural stability of tetragonal phase \( \text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12} \) against distilled water, acidic medium (under reflux) and under humid conditions are also investigated. The chemical stability and \( \text{Li}^+ \) conductivity have been enhanced successfully by partial substitution of \( \text{Y}^{3+} \) for \( \text{La}^{3+} \) in \( \text{Li}_7\text{La}_{3-x}\text{Y}_x\text{Zr}_2\text{O}_{12} \) garnet.

**ORGANISATION OF THE THESIS**

The first chapter deals with a brief introduction about working principle of present \( \text{Li}^+ \) batteries, its advantages, disadvantages and the need for all-solid-state lithium secondary battery and Li-air battery for high energy density applications. It also gives a brief review on the status of Li-air batteries. The challenges for the successful fabrication of all-solid-state lithium rechargeable battery and Li-air battery and their expected advancements are discussed in this chapter.

There is great debate regarding synthesis, chemical composition, structure and stabilization of high \( \text{Li}^+ \) conductive cubic phase LLZ (\( \text{Ia}\bar{3}d \)). Review of literature on the preparation of LLZ through wet chemical method indicated the formation of pyrochlore
La$_2$Zr$_2$O$_7$ initially at lower temperature then the subsequent reaction of La$_2$Zr$_2$O$_7$ with unreacted/amorphous phase Li$_7$LaO$_5$ to attain the LLZ phase.

The aim of the research work presented in Chapter II is to study the role of La$_2$Zr$_2$O$_7$ (LZ) pyrochlore phase in the formation of LLZ and the effect of lithium concentration in the stabilization of high Li$^+$ conductive cubic phase LLZ. Systematic investigation have been carried out on direct solid-state reaction of LZ pyrochlore with lithium-lanthanum oxides Li$_7$LaO$_5$ (LL) and lithium-aluminium-lanthanum oxides Li$_{6.28}$Al$_{0.24}$LaO$_5$ (LAL) to understand the role of LZ pyrochlore in the formation of tetragonal and high Li$^+$ conductive cubic phase Li$_7$La$_5$Zr$_2$O$_{12}$ (LLZ). Powder X-ray diffraction (PXRD) and Raman spectroscopy studies indicated that LLZ (prepared using LZ+LL) and Li$_{6.28}$Al$_{0.24}$La$_5$Zr$_2$O$_{12}$ (LALZ) (prepared using LZ+LAL) stabilized into tetragonal phase at the sintering temperature of 950 °C and into high Li$^+$ conductive cubic phase only by sintering the samples at 1200 °C. However, Li$_{6.28}$Al$_{0.24}$La$_5$Zr$_2$O$_{12}$ (LALZ-cs) prepared from the reactants LiOH, H$_2$O, La$_2$O$_3$, Al$_2$O$_3$ and ZrO$_2$ stabilized into high Li$^+$ conductive cubic phase by sintering the sample at relatively lower temperature of about 950 °C. Lithium evaporation in LLZ during the heating process to 1200 °C might have accelerated the incorporation of Al from the alumina crucible in the crystal lattice and stabilized it into high Li$^+$ conductive cubic phase. The sintering temperature of 950 °C might not have sufficient for the doping of Al in the lithium site in the crystal lattice in the case of LALZ. Among the investigated samples, the lithium deficient and Al doped LALZ-cs sintered at 1200 °C prepared by conventional solid-state reaction from
the reactants exhibits maximised relative density (93%) and total (bulk + grain-boundary) Li$^+$ conductivity of $4.43 \times 10^{-4}$ Scm$^{-1}$ at 30 °C with activation energy of 0.37 eV.

An attempt has been made to improve the total (bulk + grain-boundary) Li$^+$ conductivity of Li$_7$La$_3$Zr$_2$O$_{12}$ lithium garnet by reducing the grain-boundary resistance with partial substitution of Te$^{6+}$ for Zr$^{4+}$ in Li$_{7-2x}$La$_3$Zr$_{2-x}$Te$_x$O$_{12}$ ($x = 0.125$ and 0.25) by conventional solid-state reaction technique and the results are presented as Chapter III. PXRD and 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$_{12}$ lithium garnets sintered at 1100 °C indicated the stabilization of phase pure high Li$^+$ conductive cubic phase ($\bar{I}a\bar{d}3d$). Among the investigated compositions Li$_{6.5}$La$_3$Zr$_{1.75}$Te$_{0.25}$O$_{12}$ exhibits the maximized total (bulk + grain-boundary) Li$^+$ conductivity of $1.02 \times 10^{-3}$ Scm$^{-1}$ at 30 °C.

In order to understand the Li$^+$ transport properties of the investigated samples a detailed complex modulus spectra analysis have been carried out. The overlap of the normalized modulus spectra obtained for both the investigated samples indicates that the distribution of relaxation process is independent of temperature. Also 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 suitable doping in Li$_7$La$_3$Zr$_2$O$_{12}$.

In Chapter IV systematic investigation on synthesis, phase, microstructure and Li$^+$ conducting properties of Li$_7$La$_3$Sn$_2$O$_{12}$ (LLS), Li$_{6.28}$Al$_{0.24}$La$_3$Sn$_2$O$_{12}$ (LALS) and Li$_{7-x}$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ ($x = 0.25$-0.50) (LLST) have been carried out for further understanding of stabilization of high Li$^+$ conductive phase, correlation between structure and
microstructure on bulk and total (bulk + grain-boundary) Li\(^+\) conductivity. An attempt has been made to stabilize high Li\(^+\) conductive cubic phase LLS by substituting Al for Li (i.e., Li\(_{6.28}\)Al\(_{0.24}\)La\(_3\)Sn\(_2\)O\(_{12}\) (LALS)) and substituting Ta for Sn (i.e., Li\(_{7-x}\)La\(_3\)Sn\(_{2-x}\)Ta\(_x\)O\(_{12}\) (\(x = 0.25\) and 0.50) (LLST)) by solid-state reaction technique. Powder X-ray diffraction (PXRD) pattern of LLS sintered at 950 °C was found to be in tetragonal phase \((I4_1/acd)\).

The optimal substitution of Al for Li in LLS did not promote the transformation from tetragonal phase to high Li\(^+\) conductive cubic phase. However the Ta substitution for Sn in LLS transformed it from tetragonal to high Li\(^+\) conductive phase. Among the investigated samples, LLST \((x = 0.50)\) sintered at 1075 °C exhibited maximized total (bulk + grain-boundary) Li\(^+\) conductivity of 2.41 x 10\(^{-4}\) S cm\(^{-1}\) with minimum activation energy of 0.39 eV.

Concurrently the structural stability of tetragonal phase LLS against humid atmosphere, distilled water and treated with solution of benzoic acid and ethanol were carried out to understand the Li\(^+\)/H\(^+\) exchange mechanism. Tetragonal phase LLS lithium garnet was found to be very sensitive to humid atmosphere. The PXRD patterns and Raman spectra of tetragonal phase LLS immersed in humid atmosphere, distilled water and benzoic acid with ethanol medium for 2 weeks indicated the transformation from tetragonal to cubic-like phase. The Raman spectra of tetragonal phase LLS immersed in humid atmosphere, distilled water and benzoic acid with ethanol medium for 2 weeks indicated that the transformed cubic-like phase is slightly different from that of the high Li\(^+\) conductive cubic phase \((Ia\tilde{3}d)\). The present study reveals that the tetragonal phase LLZ \((I4_1/acd)\) undergoes a spontaneous Li\(^+\)/H\(^+\) exchange leading to a possible partially
protonated Li$_{7-x}$H$_x$La$_3$Sn$_2$O$_{12}$ phase while reacting with distilled water, solution of benzoic acid and ethanol, and humid atmosphere.

SEM image of tetragonal phase Li$_7$La$_3$Sn$_2$O$_{12}$ indicates a slight increase in grain size after 2 week of exposure to humid air and immersed in distilled water, whereas the grain size increases dramatically for the sample prepared under reflux due to the maximum replacement of Li$^+$ by means of protons.

Finally an attempt has been made to enhance the stability and Li$^+$ conductivity through partial substitution of Y$^{3+}$ for La$^{3+}$ with nominal compositions Li$_7$La$_{3-x}$Y$_x$Zr$_2$O$_{12}$ ($x = 0.125, 0.25$ and $0.50$) by conventional solid-state reaction technique and the results are presented in Chapter V. PXRD and Raman spectra of Li$_7$La$_{3-x}$Y$_x$Zr$_2$O$_{12}$ ($x = 0.125, 0.25$ and $0.50$) sintered at 1200 °C indicates the formation of high Li$^+$ conductive cubic phase (Im$ar{3}$m). Field-Emission Scanning Electron Microscope (FE-SEM) image indicates strong stitching between the grains and practically no porosity was observed which may help to avoid dendrite formation during charging and discharging cycles. This could be due to the better sinterability of the garnets with the yttrium doping.

Among the investigated compounds Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ sintered at 1200 °C exhibits maximized room temperature total (bulk + grain-boundary) ionic conductivity of $3.21 \times 10^{-4}$ S cm$^{-1}$ along with improved relative density of 96%. Hence the Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ has been chosen in this work to explore the chemical stability of this composition for the possible application as solid electrolyte membrane in Li-air battery. The preliminary investigation on the structural and Li$^+$ conductivity stability of Li$_7$La$_{2.75}$Y$_{0.25}$Zr$_2$O$_{12}$ under various solutions like 1M LiCl, distilled water and 1M LiOH...
at 30 °C and 50 °C indicated that Li₇La₂.₇₅Y₀.₂₅Zr₂O₁₂ is found to be stable in 1M LiCl and dist. H₂O. Hence Li₇La₂.₇₅Y₀.₂₅Zr₂O₁₂ may be a suitable stable protective layer for lithium metal electrode in Li-air batteries.

Chapter VI gives a general summary of the overall research work carried out through this thesis on the lithium garnets and their significance.