High conductive yttrium doped $Li_7La_3Zr_2O_{12}$ cubic lithium garnet

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ABSTRACT

An attempt has been made in this work to increase the bulk and total conductivity of $Li_7La_3Zr_2O_{12}$ (LLZ) with partial substitution of trivalent Y for a tetravalent Zr using yttria-stabilized ZrO_2 (3% YSZ) as reactant. The small doping of Y for Zr helps to increase the bulk and total conductivity to 9.56×10^{-4} and $8.10 \times 10^{-4} Scm^{-1}$, respectively, at 25 °C. The presence of small amount of Y helped to get well sintered pellet relatively at lower temperature with lower sintering time compared to LLZ, which helps to improve the overall conductivity.

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1. Introduction

Solid state lithium ionic conductors (SSLIC's) have recently had drawn much attention due to their possible potential application in the field of clean and safe energy storage systems such as high density all-solid-state rechargeable (secondary) batteries, powerful supercapacitors as well as in other advanced solid-state electrochemical devices.

A solid electrolyte with high lithium-ion conductivity, low electronic conductivity, and wide electrochemical window is strongly required for the development of safe high power and high capacity all-solid-state lithium secondary battery. In the last few years, a series of garnet-like structural compounds have been investigated as a novel family of fast lithium ion conductors by Weppner and his group [1–10]. Among them, $Li_6BaLa_2Ta_2O_{12}$ (LBLT) and $Li_7La_3Zr_2O_{12}$ (LLZ) have been paid much attention because of their stable nature against Li metal [3,5,11–14].

An attempt has been made in this work to increase the bulk and total conductivity of LLZ with partial substitution of trivalent Y for a tetravalent Zr using yttria stabilized ZrO_2 (3% YSZ) as reactant and also by a suitable sintering process.

2. Experimental

Required stoichiometric amounts of high purity chemicals, LiOH (pre-dried at 200 °C for 6 h) (10 wt.% excess was added to compensate for the loss of lithium during annealing), La_2O_3 (pre-dried at 900 °C for 24 h) and 3% Y stabilized ZrO_2 were ball-milled using zirconia balls for about 6 h in 2-propanol initially and after heat treatments at 900 and 1100 °C for 12 h in air using alumina crucibles. Subsequently, the reaction products were pressed into pellets and sintered at 1200 °C for 16 h while the samples were covered with the same mother powder.

A sintered pellet was crushed into powder for X-ray diffraction measurement. Structural characterization of resulting compounds was performed by X-ray powder diffraction (XRPD) analysis with a X'Pert Pro PANalytical (Philips) using CuK_α radiation at room temperature in the 2 theta ranges from 10° to 90°. The surface morphology of powders was characterized by scanning electron microscope (SEM) (HITACH S-3400 N).

Electrical conductivity measurements of the prepared pellets were performed in open air using Li-ion blocking Au-electrodes (Au paste cured at 700 °C for 1 h) in the temperature range from room temperature to 350 °C using a LCR meter (HP 4280A). Prior to each impedance measurement, the samples were equilibrated for 1 h at constant temperature. For each sample, the impedance measurements were made for the heating and cooling cycle.

3. Results and discussion

Fig. 1 shows the measured powder XRPD pattern of the expected composition $Li_{7.06}La_3Y_{0.06}Zr_{1.94}O_{12}$ (LLYZ) along with the reported XRPD pattern of $Li_7La_3Zr_2O_{12}$ (LLZ) [5]. We could index the diffraction pattern for a cubic cell (space group $Ia 3d$) with a lattice constant of $a = 12.9672$ Å, which is slightly smaller than that of $a = 12.9682$ reported for cubic LLZ [5].

A typical impedance plot obtained at 25 °C for LLYZ is shown in Fig. 2. The impedance plot could be well resolved into bulk, grain boundary and electrode resistances. The Arrhenius plots for the bulk and total (bulk + grain-boundary) electrical conductivity of LLYZ and comparison with the total conductivity of LLZ are shown in

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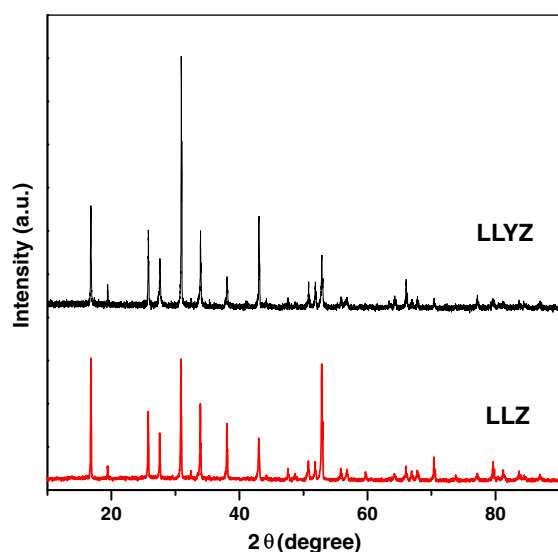*E-mail addresses:* moranamurugan@pec.edu, moranamurugan@yahoo.com (R. Murugan).

Fig. 1. X-ray powder diffraction (XRPD) pattern of $Li_{7.06}La_3Y_{0.06}Zr_{1.94}O_{12}$ (LLYZ) together with the reported XRPD pattern of $Li_7La_3Zr_2O_{12}$ (LLZ) [5].

Fig. 3. Arrhenius plots for the bulk and total (bulk + grain-boundary) electrical conductivity of LLYZ obtained in consecutive heating and cooling cycle compared with the total conductivity of LLZ [5].

Fig. 3. The grain-boundary resistance contribution to the total (bulk + grain-boundary) resistance at 25 and 50 °C for the LLYZ sample were estimated to be around 17 and 16%, respectively. LLYZ sample exhibit the bulk and total (bulk + grain-boundary) Li$^+$-ion conductivity of 9.56×10^{-4} Scm^{-1} and 8.10×10^{-4} Scm^{-1}, respectively, at 25 °C. The activation energies obtained for both bulk and total conductivity of the LLYZ are 0.29 eV and 0.26 eV, respectively, and slightly smaller than that of LLZ, 0.34 eV and 0.31 eV, respectively [5].

In spite of numerous X-ray and neutron diffraction studies on lithium garnets still there is debate in description of the crystallographic sites of Li$^+$ [15–17]. The difficulty in determination of Li$^+$ site occupancies of lithium stuffed cubic garnets leads to confusion among the researcher in understanding the transport behaviour. Disordered arrangement of Li$^+$ across tetrahedral and octahedral sites is prime factor for the observed high conductive in cubic LLZ. The complete ordering of Li$^+$ across all of the octahedra and one third of the tetrahedra in the tetragonally distorted garnet LLZ leads to two orders of lower ionic conductivity compared to the cubic phase [13]. Although the investigations indicated that tetrahedral vacancies provide potential hopping sites for
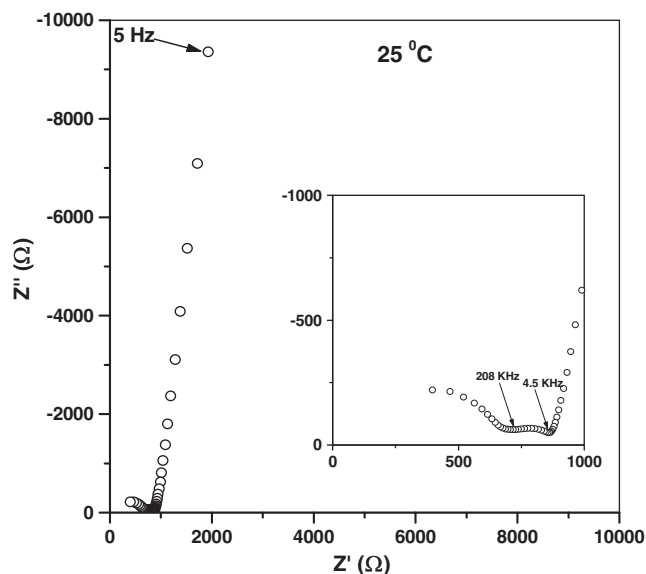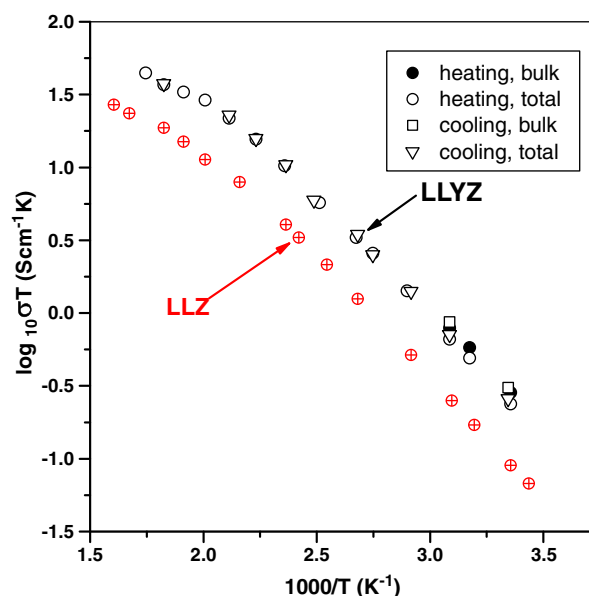
lithium conductivity in lithium stuffed garnets still the optimum number of Li$^+$ required to get the maximum conductivity in these systems by keeping the optimal vacancies in tetrahedral sites is not completely understood.

The first report on cubic LLZ by Murugan et al. primarily focussed on Li$^+$ conductivity, chemical stability against molten lithium and high densification [5]. Al_2O_3 addition as sintering additive to avoid the formation of $La_2Zr_2O_7$ impurity phase at high calcinations temperature in the preparation of LLZ solid electrolyte was reported [18]. LLZ with high total Li$^+$ conductivity of 6.8×10^{-4} Scm^{-1} was reported recently by the inclusion of appropriate amounts of Al and Si from the crucible and bowl of pulverizer, respectively [14]. The formation of amorphous Li–Al–Si–O with nano-crystalline $LiAlSiO_4$ at the grain boundaries facilitated the Li$^+$ transfer between the LLZ particles, resulting in the decrease of the grain boundary resistance and then increasing the total Li$^+$ conductivity of LLZ [14]. Although the recent studies revealed the presence of Al^{3+} in the grains it is not known whether the included Al^{3+} occupies the Li$^+$ sites or an interstitial sites [14,17]. If the Al^{3+} replaces some of the Li$^+$ which may lead to Li$^+$ extraction from the bulk (via charge compensation for the above substitution) in to the grain boundary region for the formation of favourable Li$^+$ conducting thin layer and hence the simultaneous increased numbers of empty structural sites could permit increased Li$^+$ mobility and thus conductivity. However detailed further studies are essential to understand the incorporation of Al^{3+} into the LLZ lattice/interstitial sites, its role in stabilization of the cubic structure and enhancement of conductivity, which is progress in our laboratory.

Our studies on cubic LLZ indicated that the incorporation of a major viscosity and devitrification agent Al_2O_3 from the crucible helps to form favourable lithium ion conducting thin layer in the grain boundary regions through Li_2O-ZrO_2-Al_2O_3 eutectic. Here in the present work energy dispersive X-ray (EDX) analysis indicated the inclusion of 1.6 wt.% of Al_2O_3 from the crucible. Y_2O_3 is also a well known sintering agent and with the small doping of Y for Zr in LLZ really helps to increase the bulk conductivity and total conductivity of 9.56×10^{-4} and 8.10×10^{-4} Scm^{-1}, respectively for LLYZ, compared to 7.74×10^{-4} and 5.11×10^{-4} Scm^{-1} for LLZ, respectively, at 25 °C [5]. Typical cross sectional scanning electron microscope (SEM) image of the LLYZ pellet shown in Fig. 4 revealed that the
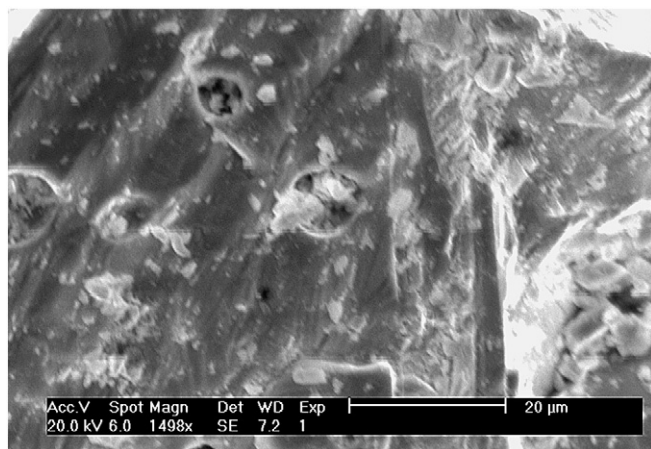

Fig. 2. Ac impedance plot obtained at 25 °C for LLYZ sample. The impedance plot in the high frequency region is shown as inset.

Fig. 4. Scanning electron microscope (SEM) image of LLYZ.

pellet was sintered very well. Although the SEM image indicated the existence of few small voids no grain boundary was observed.

New chemical compositions $Li_6La_3ZrTaO_{12}$ with garnet-like structure with reasonable ionic conduction as members of the $Li_5La_3M_2O_{12}$ series was isolated for the first time by our research group [11,12]. Our studies on $Li_6La_3ZrTaO_{12}$ indicated that substitution of Ta for Zr in LLZ helped the formation of single cubic phase at relatively low temperature of 950 °C [11,12]. The $Li_6La_3ZrTaO_{12}$ sample exhibits appreciable grain-boundary resistance contributions of about 36% to the total (bulk + grain-boundary) resistance at measured temperature of 25 °C because of poor sintering at around 950 °C [11,12]. However further studies on partial substitution of Ta for Zr in LLZ and sintering at relatively high temperature indicated the appreciable reduction in the grain boundary resistance. Similarly here in the present work the presence of Y helped to get high conductive and dense pellet relatively at lower temperature with lower sintering time compared to LLZ. The LLYZ was found to be stable against molten lithium.

Lithium garnet-type oxides $Li_{7-x}La_3(Zr_{2-x}Nb_x)O_{12}$ ($x = 0$–2) with maximum conductivity of approximately around 8×10^{-4} Scm^{-1} at 25 °C for $x = 0.25$ was reported [19]. Lithium stuffed garnets synthesized with Nb indicated the chemical instability against molten lithium [1]. Hence the chemically stable LLYZ with better conductivity suggested that LLYZ may be a promising solid electrolyte for all solid state lithium battery application.

4. Conclusions

Partial substitution of trivalent Y for a tetravalent Zr in LLZ with the expected composition of $Li_{7.06}La_3Y_{0.06}Zr_{1.94}O_{12}$ (LLYZ) with garnet-like structure was prepared using yttria stabilized ZrO_2 (3% YSZ) as reactant. The small doping of Y for Zr in LLZ helps to increase the bulk and total conductivity of 9.56×10^{-4} and 8.10×10^{-4} Scm^{-1}, respectively, at 25 °C. The present study indicated the suitable and optimal amount of dopant for Zr in LLZ and with optimal lithium concentration the total conductivity of cubic lithium stuffed zirconium containing garnet may be increased in the order of 10^{-3} Scm^{-1} at room temperature. The high lithium ion conductivity, good thermal and chemical stability, and ease of preparation of dense LLYZ suggest that this zirconium and partial yttrium-containing lithium garnet may be a promising solid ceramic electrolyte for all-solid state lithium rechargeable batteries, as well as other ionic devices.

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