Higher Conductivity Li-Garnets by a Multi-Element Doping Strategy

Tong, Xia; Thangadurai, Venkataraman; Wachsman, Eric

American Chemical Society

http://hdl.handle.net/1880/51582
journal article

Downloaded from PRISM: https://prism.ucalgary.ca
Higher Conductivity Li-Garnets by a Multi-Element Doping Strategy

Xia Tong¹, Venkataraman Thangadurai¹, * and Eric D. Wachsman²

¹ Department of Chemistry, University of Calgary, 2500 University Dr. NW, Calgary, Alberta, T2N 1N4
² University of Maryland Energy Research Center, University of Maryland, Maryland, USA, 20742

*For correspondence (vthangad@ucalgary.ca) Phone: 1 403 210 8649; Fax: 1 403 210 9649
ABSTRACT: Highly conductive Li$_7$La$_7$Zr$_2$O$_{12}$ (LLZ) garnet-type solid electrolytes were further optimized to improve Li-ion conduction by La$^{3+}$-sites substitution with Ba$^{2+}$, and Zr$^{4+}$-sites substitution with Ta$^{5+}$ and Nb$^{5+}$. Garnet structured metal oxides of the nominal chemical compositions Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$O$_{12}$, Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (x = 0, 0.1, 0.2 and 0.3) and the parent LLZ, as a reference, were prepared via conventional solid-state reaction to investigate the effect of multi-element doping on ionic conductivity. The phase formation, morphology, and Li ion conductivity were characterized using powder X-ray diffraction (PRXD), scanning electron microscopy, and AC impedance spectroscopy methods, respectively. In addition, solid-state $^{27}$Al and $^7$Li MAS NMR was used to study the effect of “Al-doping” on the investigated multi-element doped Li-stuffed garnet metal oxides. All the prepared samples obtained the cubic garnet-type structure (space group: $Ia3d$; No. 230) at 1150 °C, similar to that of cubic LLZ. Except for Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$, all the members show Al-content by Al MAS NMR. However, it was not possible to detect Al-based impurity phases using PXRD in any of the investigated garnets. Among the samples investigated in this work, “Al-free,” Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ demonstrated a bulk Li ion conductivity of 0.7 mS cm$^{-1}$ at 25 °C, with apparent activation energy of 0.26 eV, significantly higher than the reference “Al-doped” parent LLZ.

KEYWORDS: Li-stuffed garnets; Powder X-ray analysis, AC impedance analysis, Li ion conductivity; Doping chemistry, Conductivity optimization
1. INTRODUCTION

Lithium ion secondary (rechargeable) batteries are one of the most promising electrical energy storage technologies\textsuperscript{1-4}. However, safety and energy density issues remain that can be addressed by thermally stable highly Li-ion conducting ceramic electrolytes. Several solid state Li ion conductors based on rock-salt, perovskite, Na-superionic conducting phosphates, Na-beta-alumina and Li- super ionic conducting germanium oxides structures have been investigated\textsuperscript{1, 5, 6}. Very recently, a garnet-type structure metal oxide of the chemical formula Li\textsubscript{5}La\textsubscript{3}M\textsubscript{2}O\textsubscript{12} (M = Nb, Ta) was reported as a fast Li ion conductor.\textsuperscript{1} These Li-garnets have been considered the most promising electrolyte to replace current organic polymer-based Li ion electrolytes due to their desirable chemical and electrochemical stabilities and electrical transport properties. Subsequently, Li\textsubscript{5}La\textsubscript{3}M\textsubscript{2}O\textsubscript{12} has been doped with several metal ions at La and M (Nb/Ta) sites to further optimize the Li ion conductivity for all-solid-state Li ion batteries\textsuperscript{7-28}.

In 2007, Murugan et al. synthesized cubic garnet-type Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} (LLZ), by replacing elemental Li reducible Nb\textsuperscript{V} with stable Zr\textsuperscript{IV} in Li\textsubscript{5}La\textsubscript{3}Nb\textsubscript{2}O\textsubscript{12}, demonstrating excellent chemical stability against reaction with Li metal, electrochemical stability up to 6V vs. Li, and the highest total Li ion conductivity of $\sim$10\textsuperscript{-4} Scm\textsuperscript{-1} at room temperature\textsuperscript{7}. However, reproducibility of highly conducting cubic LLZ remains challenging in the literature due to Li volatilization and contamination of Al from the alumina crucibles during sintering, and incomplete knowledge of the Li\textsubscript{2}O-La\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} phase diagram\textsuperscript{1, 25}. It has been confirmed that a trace amount (ppm level) of Al doping is critical for the stabilization of highly Li ion conducting cubic LLZ (space group: \textit{Ia\bar{3}d}; No. 230)\textsuperscript{25}. LLZ is known to crystallize into both cubic and tetragonal crystal structures. Li ions in the tetragonal structure (space group: \textit{I4}_1/acd; No. 142) are ordered at the tetrahedral 8\textit{a} sites and octahedral 16\textit{f} and 32\textit{g} sites. Whereas, in the cubic structure (space group: \textit{Ia\bar{3}d}; No. 230) the Li ions are disordered at the tetrahedral 24\textit{d} Li(1) and octahedral 48\textit{g} and 96\textit{h} Li(2) sites\textsuperscript{8}. 
Since 2007, a major effort has focused on obtaining the high temperature cubic phase, which exhibits ~2 orders of magnitude higher conductivity than the lower temperature tetragonal polymorph\(^9\), at temperatures lower than 1230 °C. To achieve this it is necessary to investigate substitutional chemistry, which may stabilize the cubic garnet structure through a reduction in Li content and/or increased Li vacancy concentration. A variety of compositional variations have been investigated, including Li\(_{7-x}\)La\(_{3-y}\)AxZr\(_{2-x}\)M\(_x\)O\(_{12}\) (A = K, Ca, Sr, Ba, Y; M = Ga, Al, Si, Bi, Sb, Nb, Ta) in order to vary the lattice constant and Li-ion population\(^{10-18}\). The doping results have shown a reduction in sintering temperature by La sites doping with alkaline earth ions, and improved conductivity by doping the Zr(IV)-sites with Ta(V) or Nb(V)\(^{19-21}\). Doping with higher-valence cations increases the Li-ion vacancy concentration and significantly reduces the degree by local ordering\(^{21,26}\). Yet the results seem to vary widely depending on synthesis conditions, and no clear consensus has emerged as to how doping affects the structure/ionic-conductivity relationship.

The room temperature stability of cubic Zr-based LLZ garnet was demonstrated to improve with partial substitution of Zr with dopants\(^{22,23}\). Moreover, it has been commonly believed that Al-doping, from use of alumina crucibles, introduced vacancies or formed Li ion conducting phases in the Li\(_2\)O-Al\(_2\)O\(_3\) system leading to stabilization of the highly conducting cubic LLZ\(^{23,24}\). On a charge neutrality basis, Al substitution for Li (Al\(^{3+}\) = 3Li\(^+\)) leads to a reduction in Li content and an increase in Li-site vacancies, which strongly affects phase stability\(^{25}\). However, the possibility for achieving high total Li ion conductivity in Ba, Ta or Nb substituted LLZ without the help of Al substitution has not yet been investigated.

Here, for the first time, we substitute Ba\(^{2+}\) for La\(^{3+}\)-sites and Ta\(^{5+}\) and Nb\(^{5+}\) for Zr\(^{4+}\)-sites in LLZ to further improve conductivity and also decrease the final sintering temperature requirement to obtain highly Li ion conducting cubic garnet. Ta\(^{5+}\) and Nb\(^{5+}\) were selected because they prefer to occupy
octahedral coordinated sites, like Zr$^{4+}$ in the garnet structured compounds. We report cubic garnets of the nominal chemical formula $\text{Li}_{6.65}\text{La}_{2.75}\text{Ba}_{0.25}\text{Zr}_{1.4}\text{Ta}_{0.5}\text{Nb}_{0.1}\text{O}_{12}$ and $\text{Li}_{6.4}\text{La}_{3}\text{Zr}_{1.4}\text{Ta}_{0.6-x}\text{Nb}_{x}\text{O}_{12}$ ($x = 0, 0.1, 0.2$ and $0.3$) with bulk Li-ion conductivity of $0.5$ mS cm$^{-1}$ and $0.7$ mS cm$^{-1}$ at $25$ °C, respectively. Further, solid state $^{27}$Al MAS NMR indicates “Al-free” $\text{Li}_{6.4}\text{La}_{3}\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ cubic garnet was obtained at $1150$ °C, which is $80$ °C lower than the temperature required to obtain the highly conducting cubic parent LLZ containing Al impurities$^{25}$.

2. EXPERIMENTAL SECTION

2.1 Synthesis of Li-stuffed garnets Conventional solid-state synthesis was performed to prepare the desired Li-stuffed garnet-oxides. LiOH (EMD Chemicals, pre-dried at $200$°C for 6h), $\text{La}_2\text{O}_3$ (99.9%, Alfa Aesar, pre-dried at $900$°C for 24h), $\text{ZrO}_2$ (99%, Alfa Aesar), $\text{Ta}_2\text{O}_5$ (99.85%, Alfa Aesar), $\text{Nb}_2\text{O}_5$ (99.5%, Alfa Aesar) and $\text{BaCO}_3$ (BDH Chemicals) were used for the synthesis of $\text{Li}_{6.65}\text{La}_{2.75}\text{Ba}_{0.25}\text{Zr}_{1.4}\text{Ta}_{0.5}\text{Nb}_{0.1}\text{O}_{12}$ and $\text{Li}_{6.4}\text{La}_{3}\text{Zr}_{1.4}\text{Ta}_{0.6-x}\text{Nb}_{x}\text{O}_{12}$ ($x = 0, 0.1, 0.2$ and $0.3$). To compensate for volatile lithium loss during calcining/sintering, 10 wt.% excess LiOH was added to the starting materials.$^{26}$ The starting materials were ball milled (Pulverisette, Fritsch, Germany) in a zirconia grinding bowl with zirconia balls for 12 h in 2-propanol at 200 rpm. The resultant powders were dried at $200$°C and then calcined at $750$°C for 6h in air. After calcination another ball milling step was performed using the same parameters. The powdered material was uni-axially pressed to a pellet at 30 MPa and the pellet subsequently compacted further to a pressure of 200 MPa with an isostatic press. The resulting pellet was covered in powder of the same composition and sintered in air at $900$°C for 6h and $1150$°C for 12h in an $\text{Al}_2\text{O}_3$ crucible, covered with an $\text{Al}_2\text{O}_3$ lid. Synthesis and processing of the garnet samples are shown in scheme 1.
In order to compare with undoped Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ), it was prepared by solid-state reaction using requirement amounts of LiOH (EMD Chemicals, pre-dried at 200°C for 6h), La$_2$O$_3$ (99.9%, Alfa Aesar, pre-dried at 900°C for 24h), and ZrO$_2$ (99%, Alfa Aesar). The precursor powders were ball milled in a zirconia bowl with zirconia balls for 12 h in 2-propanol with 200 rpm. The powders were dried at 900°C for 4h in air. After this calcination step, another ball milling step was performed using the same parameters. The powdered material was initially uni-axially pressed to a pellet at 30 MPa and subsequently, the pellet was compacted further with a pressure of 200 MPa by isostatic press. The resulting pellet was covered in powder of the same composition and sintered in air at 1175°C for 12h in an Al$_2$O$_3$ crucible and covered with an Al$_2$O$_3$ lid. To compensate lithium loss due to a volatile species, 10 wt.% excess of LiOH was added to the starting materials.
2.2. Characterization. Phase formation was analyzed by powder X-ray diffraction (PXRD) (Bruker D8 Advance powder X-ray diffractometer Cu Kα, 40 kV, 40 mA) from two theta (2θ) 10° to 80° at a scan rate of 0.05° s⁻¹. Cross-sectional microstructures of the garnet pellets Li₆.₆₅La₂.₇₅Ba₀.₂₅Zr₁.₄Ta₀.₅Nb₀.₁O₁₂ and Li₆.₄La₃Zr₁.₄Ta₀.₆₋ₓNbₓO₁₂ (x = 0, 0.1, 0.2 and 0.3) were obtained using a Philips XL 30 l scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDX). ²⁷Al and ⁷Li magic angle spinning nuclear magnetic resonance (MAS NMR) (AMS 300, Bruker, at spinning rate 5 kHz) was performed for the undoped Li₇La₃Zr₂O₁₂, Li₆.₆₅La₂.₇₅Ba₀.₂₅Zr₁.₄Ta₀.₅Nb₀.₁O₁₂ and Li₆.₄La₃Zr₁.₄Ta₀.₆₋ₓNbₓO₁₂ (x = 0, 0.1, 0.2 and 0.3) powders. The chemical shift values of Al and Li were expressed against solid Al(NO₃)₃ (VWR) and LiCl (99.95%, Alfa Aesar), respectively. A Solartron SI 1260 impedance and gain-phase analyzer in the frequency range of 0.1Hz to 1 MHz at an AC amplitude of 100 mV was used to measure the Li ion conductivity of the garnet pellets in air. Li ion blocking Au (painted Au paste and cured at 700 °C for 1h in air) was used as current collectors for the measurements. Zview software was used to analyze the impedance spectra.

3. RESULTS AND DISCUSSION

3.1 Structural properties. Figure 1 shows the PXRD patterns for all the as-prepared garnets calcined at 1150 °C in air. The XRD reveals stabilization of a cubic garnet-type structure in the space group Ia₃d for Li₆.₆₅La₂.₇₅Ba₀.₂₅Zr₁.₄Ta₀.₅Nb₀.₁O₁₂ and Li₆.₄La₃Zr₁.₄Ta₀.₆₋ₓNbₓO₁₂ (x = 0, 0.1, 0.2 and 0.3), and is similar to that of the un-doped LLZ cubic structure (space group: Ia₃d; No. 230)²⁹. The stimulated cubic LLZ phase is shown for comparison in Figure 1. However, Li₆.₆₅La₂.₇₅Ba₀.₂₅Zr₁.₄Ta₀.₅Nb₀.₁O₁₂ exhibits a small amount of La₂Zr₂O₇ pyrochlore impurity in addition to the main cubic garnet structure under similar preparation condition³⁰ (Figure 1).
3.2 SEM and EDX Analysis. High porosity in solid electrolytes may cause high grain boundary resistance as well as mechanical failure. Moreover, a dense microstructure is very critical to avoid dendritic growth during lithium deposition. The cross-sectional morphology of the sintered garnets are shown in Figure 2. The grains were well connected after sintering at 1150°C. However, pores with an average size of several microns still existed. This might be due to the evaporation of lithium compounds and subsequent shrinkage during grain growth. In the case of Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$, larger pores and smaller particles could be clearly observed, indicating poor sintering. EDX analysis confirmed the presence of 0.12wt % ~ 0.31wt.% Al for all the Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (x = 0.1, 0.2, 0.3) and Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ garnets, except for Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$. It should be noted that only Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ did not show any signal due to Al in MAS NMR, while all other members show characteristic peaks due to Al in octahedral sites. The minimum amount of Al$^{3+}$ necessary to stabilize the LLZ sample in the cubic phase was estimated to be around 0.9 wt.%$^8$. The presence of Al$^{3+}$ content less than the 0.9 wt.% in the investigated samples, especially Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ without Al incorporated, indicates that the stabilization of the cubic phase in this work is not merely by the inclusion of Al$^{3+}$. A recent study also confirmed the cubic phase stabilization of LLZ through Ta doping without Al$^{3+}$. $^{11,31}$

3.3 $^{27}$Al and $^7$Li MAS NMR. NMR is a complementary technique for the investigation of structural features and ionic motion in an ion conductor. $^7$Li MAS NMR spectra for Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$, Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (x = 0, 0.1, 0.2 and 0.3) and parent LLZ (Figure 2A) show a single resonance at 1.3 ppm (before doping LLZ), which gradually shifts to 2.1 ppm (after doping). This is likely due to dopant effects on Li-Li interactions in the crystalline solids. $^7$Li NMR resonances may also be affected by homo-nuclear dipolar interactions. Li ion mobility is directly related to peak shape and a narrow peak generally indicates a high Li ion mobility$^4$, $^{27}$. As the
preparation process involves the use of alumina crucibles, $^{27}$Al MAS NMR was used to determine
presence of potential Al-based impurity phases and the data is shown in Figure 2B. No obvious Al-based
impurity phases were seen in the PXRD (Figure 1).

$^{27}$Al MAS NMR chemical shift values can be used to identify the location of Al sites in the metal
oxides. For example, a peak at chemical shift value ($\delta$) in the range 13-17 ppm due to octahedral Al
sites, while peak around 70 ppm attributable to tetrahedral sites$^{20, 28}$. There is only one peak with
chemical shift value in the range 72-76 ppm, which can be assigned “tetrahedral Al” in the
Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.3}$Nb$_{0.3}$O$_{12}$ and Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$. This suggesting that 24d sites Li ions
are partially replaced by Al from the crucible during the synthesis of the Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.3}$Nb$_{0.3}$O$_{12}$ and
Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$. Interestingly, under the similar preparation conditions, the $x = 0.1$
and 0.2 members of Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_{x}$O$_{12}$ and parent LLZ show two $^{27}$Al NMR peaks. The signal at
12ppm shows little intensity, is typical for octahedral co-ordinated Al$^{3+}$ ions. The signal at 12 ppm
suggests that Al occupies the Li2 (96h /48g) sites in the cubic garnet-type $Ia-3d$ structure$^{25}$. The signal at
66-77 ppm clearly indicates the Al sites in the 24d tetrahedral sites in $Ia-3d$ garnet-type structure.
Interestingly, parent LLZ, Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ and Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.4}$Nb$_{0.2}$O$_{12}$ shows NMR peaks
due to both types of Al, indicating that there seem to be no site preference for Al occupation in Li-
stuffed garnet-type compounds. However, it is interesting to mention that no measurable signal can be
observed for Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$. Either there is Al element incorporated in this sample or Al-phase
contained is less then deductible using NMR. For the NMR analysis, the samples pellets were powdered
using pestle and mortar, and these pellets were not in contact with Al crucible. Thus, selection of sample
for NMR studies is seem to be rather important in the Li-stuffed garnets. A small variation in the
sample selection, could lead to a different conclusion in the area of Li-stuffed garnets. It is also
important to mention that diffusion of Al in Li-stuffed garnet will also vary with thickness of the
particles, size of pellets and sintering conduction such as heating and cooling rates and time used during the preparation. We believe that careful systematic work is still needed to fully investigate the role of Al in the stabilization of Li-stuffed cubic garnets.

3.4 Li ion conductivity. Typical ac impedance plots for Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ and Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ ($x = 0, 0.1, 0.2$ and $0.3$) obtained in air using Li ion blocking Au electrodes at 21°C and 53°C are shown in Figure 4. The shape of the impedance plots is typical for fast Li ion conducting solid electrolytes such as Li-garnets. An equivalent circuit, $R_b(R_1Q_1)(R_2Q_2)Q_3$ (where $R$ is the resistance and $Q$ is the constant phase element) can be used to describe the impedance data at 21°C. Solid lines show fits using the equivalent circuit. Table 1 shows the fitted AC impedance data for Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ and Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ ($x = 0.1, 0.2$ and $0.3$) at 21°C. The actual capacitance can be calculated using the expression

$$C = R^{(1-n)}Q_1^{1-n}$$

(1)

The capacitance for the low-frequency regime was determined to be in the order of $\sim 2.5 \times 10^{-6} - 1.9 \times 10^{-5}$ F (due to electrode), while the intermediate / high frequency-regime semicircle shows capacitance in the range of $\sim 1.7 \times 10^{-8} - 1.4 \times 10^{-11}$ F at 21°C and falls within the range for grain-boundary contribution in polycrystalline materials. Table 2 lists the bulk conductivity of investigated Li-based garnets at 25°C and 53°C. The Arrhenius plots of spectra Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ ($0 < x < 0.3$), Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ and undoped Li$_7$La$_3$Zr$_2$O$_{12}$ conductivity are shown in Figure 5.

The apparent activation energies ($E_a$) were estimated from the slope of the log$\sigma$ versus 1000/$T$ plot in the temperature range of 294-693 K. The conductivity activation energies were found to be within the range reported for garnet-type solid electrolytes (Table 2). The data obtained from heating and cooling cycles follow the same line, indicating equilibrium conductivity behaviour. Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ and Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.3}$Nb$_{0.3}$O$_{12}$ show higher conductivity than that of the parent compound Li$_7$La$_3$Zr$_2$O$_{12}$
(LLZ), prepared under comparable conditions. It is important to note that no Al impurity was observed in Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$, while LLZ shows Al impurity phases by MAS NMR.

Among the samples investigated, the Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ exhibits the highest bulk Li ion conductivity of 0.72 mScm$^{-1}$ at 25 °C, and reaches a conductivity of 0.08 Scm$^{-1}$ at 413°C. Room temperature conductivity follows the order: Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ > Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.3}$Nb$_{0.3}$O$_{12}$ > Li$_{6.65}$La$_2.75$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ > (Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.4}$Nb$_{0.2}$O$_{12}$) > Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ > un-doped Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ). For compounds with constant Li content, i.e., Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (x = 0.1, 0.2 and 0.3), the conductivity increases with increasing Nb content. The Ba compound Li$_{6.65}$La$_2.75$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ exhibits bulk ionic conductivity of 5.27×10$^{-4}$ Scm$^{-1}$ at 25°C, which has the highest conductivity in the Ba-based garnets reported so far. Finally, these results demonstrate that higher conductivity can be obtained for cubic garnets without Al-doping. While Al doping helps increase the cubic phase stability, it may not be the best chance to increase Li ion conduction, as indicated in the literature. It must also be mentioned that the room temperature Li ion conductivity of the garnet with single $^{27}$Al MAS NMR resonance is higher than that of the compound with two $^{27}$Al MAS NMR resonances. The highest bulk Li ion conductivity was observed for Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$, which showed no $^{27}$Al NMR signal (Figure 2). Figure 6 shows Arrhenius plots for Li ion conductivity of “Al-free” Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ (present work), comparison with cubic LLZ prepared at 1230°C, Li$_{6.4}$La$_3$Zr$_{1.4}$Sb$_{0.6}$O$_{12}$, Al-doped Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ and Al-free tetragonal LLZ.

4. CONCLUSIONS

In summary, Ba, Ta, and Nb-substituted Li$_7$La$_3$Zr$_2$O$_{12}$ have been shown to be promising, highly conductive Li ion electrolytes for application in solid-state Li ion batteries. Multi-element doped Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ and Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ had significantly increased bulk Li-ion conductivity.
conductivities compared to LLZ, obtaining as high as 0.5 mS cm$^{-1}$ and 0.7 mS cm$^{-1}$ at room temperature with the activation energies of 0.26 eV and 0.24 eV, respectively. NMR measurements were used to better understand the effect of Al doping on the processing and properties of these materials and indicate Al may not play as much of a role as previously thought in enhancing conductivity as Al-free Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ exhibits higher conductivity at room temperature compared to Al incorporated Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (x = 0.1, 0.2 and 0.3).

AUTHOR INFORMATION

Corresponding Author
*E-mail: vthangad@ucalgary.ca

ACKNOWLEDGEMENTS

This work was supported by US DOE ARPA-E under the RANGE program, contract # DE-AR0000384. Authors also thank Dr. W. Michael Schoel, Microscopy Facility, University of Calgary for helping with SEM and EDX studies, and Mr. Jianjun Li, Department of Chemistry, University of Calgary for helping with $^7$Li and $^{27}$Al NMR analysis measurements.
Table 1. The AC Impedance Parameters of Garnets \( \text{Li}_{6.65}\text{La}_{2.75}\text{Ba}_{0.25}\text{Zr}_{1.4}\text{Ta}_{0.5}\text{Nb}_{0.1}\text{O}_{12} \) and \( \text{Li}_{6.4}\text{La}_{3}\text{Zr}_{1.4}\text{Ta}_{0.6-x}\text{Nb}_{x}\text{O}_{12} \) (\( x = 0.1, 0.2 \) and 0.3) at 21 °C.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \text{Li}<em>{6.65}\text{La}</em>{2.75}\text{Ba}<em>{0.25}\text{Zr}</em>{1.4}\text{Ta}<em>{0.5}\text{Nb}</em>{0.1}\text{O}_{12} )</th>
<th>( x = 0 )</th>
<th>( x = 0.1 )</th>
<th>( x = 0.2 )</th>
<th>( x = 0.3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb (ohm)</td>
<td>909</td>
<td>190</td>
<td>1042</td>
<td>910</td>
<td>931</td>
</tr>
<tr>
<td>R1(ohm)</td>
<td>( 1.7 \times 10^5 )</td>
<td>( 1.6 \times 10^5 )</td>
<td>( 5.8 \times 10^5 )</td>
<td>828</td>
<td>197</td>
</tr>
<tr>
<td>CPE1(F)</td>
<td>( 2.8 \times 10^{-6} )</td>
<td>( 1.1 \times 10^{-5} )</td>
<td>( 4.7 \times 10^{-6} )</td>
<td>( 2.5 \times 10^{-6} )</td>
<td>( 1.9 \times 10^{-4} )</td>
</tr>
<tr>
<td>n1</td>
<td>0.88</td>
<td>0.85</td>
<td>0.88</td>
<td>0.78</td>
<td>0.59</td>
</tr>
<tr>
<td>C1</td>
<td>( 2.5 \times 10^{-6} )</td>
<td>( 1.7 \times 10^{-5} )</td>
<td>( 5.4 \times 10^{-6} )</td>
<td>( 4.3 \times 10^{-7} )</td>
<td>( 1.9 \times 10^{-5} )</td>
</tr>
<tr>
<td>R2</td>
<td>393</td>
<td>344</td>
<td>103</td>
<td>106</td>
<td>50</td>
</tr>
<tr>
<td>CPE2(F)</td>
<td>( 2.3 \times 10^{-7} )</td>
<td>( 4.7 \times 10^{-8} )</td>
<td>( 8.4 \times 10^{-8} )</td>
<td>( 2.2 \times 10^{-8} )</td>
<td>( 2.2 \times 10^{-8} )</td>
</tr>
<tr>
<td>n2</td>
<td>0.67</td>
<td>0.57</td>
<td>0.84</td>
<td>0.92</td>
<td>0.98</td>
</tr>
<tr>
<td>C2</td>
<td>( 2.3 \times 10^{-9} )</td>
<td>( 1.4 \times 10^{-11} )</td>
<td>( 9.1 \times 10^{-9} )</td>
<td>( 6.8 \times 10^{-9} )</td>
<td>( 1.7 \times 10^{-8} )</td>
</tr>
<tr>
<td>CPE3</td>
<td>( 3.0 \times 10^{-6} )</td>
<td>( 5.8 \times 10^{-6} )</td>
<td>( 3.1 \times 10^{-6} )</td>
<td>( 2.9 \times 10^{-6} )</td>
<td>( 5.2 \times 10^{-6} )</td>
</tr>
</tbody>
</table>
Table 2. Bulk Li ion Conductivity at 25 °C and 53°C and Activation Energy of the Garnets.

<table>
<thead>
<tr>
<th>Solid electrolytes</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>53°C</td>
</tr>
<tr>
<td>Li$<em>{6.65}$La$</em>{2.75}$Ba$<em>{0.25}$Zr$</em>{1.4}$Ta$<em>{0.5}$Nb$</em>{0.1}$O$_{12}$</td>
<td>5.27×10$^{-4}$</td>
<td>1.62×10$^{-3}$</td>
</tr>
<tr>
<td>Li$<em>{6.4}$La$</em>{3}$Zr$<em>{1.4}$Ta$</em>{0.6}$O$_{12}$</td>
<td>7.24×10$^{-4}$</td>
<td>1.96×10$^{-3}$</td>
</tr>
<tr>
<td>Li$<em>{6.4}$La$</em>{3}$Zr$<em>{1.4}$Ta$</em>{0.5}$Nb$<em>{0.1}$O$</em>{12}$</td>
<td>4.44×10$^{-4}$</td>
<td>1.50×10$^{-3}$</td>
</tr>
<tr>
<td>Li$<em>{6.4}$La$</em>{3}$Zr$<em>{1.4}$Ta$</em>{0.4}$Nb$<em>{0.2}$O$</em>{12}$</td>
<td>4.55×10$^{-4}$</td>
<td>1.37×10$^{-3}$</td>
</tr>
<tr>
<td>Li$<em>{6.4}$La$</em>{3}$Zr$<em>{1.4}$Ta$</em>{0.3}$Nb$<em>{0.3}$O$</em>{12}$</td>
<td>6.06×10$^{-4}$</td>
<td>1.69×10$^{-3}$</td>
</tr>
<tr>
<td>Li$<em>{7}$Li$</em>{2}$Zr$<em>{2}$O$</em>{12}$ (LLZ)</td>
<td>1.74×10$^{-4}$</td>
<td>0.41×10$^{-3}$</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. Powder X-ray diffraction of as-prepared Li_{6.65}La_{2.75}Ba_{0.25}Zr_{1.4}Ta_{0.5}Nb_{0.1}O_{12} and Li_{6.4}La_{3}Zr_{1.4}Ta_{0.6-x}Nb_{x}O_{12} (x = 0, 0.1, 0.2 and 0.3) showing the formation of cubic garnet-type phase (space group $Ia\bar{3}d$; No. 230), similar to that of cubic Li$_7$La$_3$Zr$_2$O$_{12}$. Peak corresponding to La$_2$Zr$_2$O$_7$ impurity is marked by (♦) in the Ba-substituted Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$. For comparison, stimulated PXRD of the parent cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) is shown$^{29}$.  

Figure 2. Typical cross sectional SEM of solid state prepared (a-d) Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (a) x = 0; (b) x = 0.1; (c) x = 0.2; (d) x = 0.3 and (e) Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ pellets.  

Figure 3. (A) Typical solid state $^7$Li MAS NMR and (B) $^{27}$Al MAS NMR spectra for Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ and Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (x = 0, 0.1, 0.2 and 0.3). For comparison, corresponding data for the parent cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) prepared under the same condition is shown. The chemical shift values of Al and Li were expressed against solid Al(NO$_3$)$_3$ and LiCl, respectively. 

Figure 4. AC impedance spectra of (a-d) Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (a and f) x = 0; (b and g) x = 0.1; (c and h) x = 0.2; (d and i) x = 0.3 and (e and j) Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ at 21°C and 53°C. 

Figure 5. Arrhenius plots for Li ion conductivity of Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ (x = 0), Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ (x = 0.1), Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.4}$Nb$_{0.2}$O$_{12}$, Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.3}$Nb$_{0.3}$O$_{12}$, Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$, and undoped Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) prepared at 1150 °C. 

Figure 6. Arrhenius plots for Li ion conductivity of Al-free Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ (present work), comparison with cubic LLZ prepared at 1230°C$^7$, Li$_{6.4}$La$_3$Zr$_{1.4}$Sb$_{0.6}$O$_{12}$$^{12}$, doping Al-Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$$^{21}$ and Al-free tetragonal LLZ$^{33}$. 

15
Figure 1.

\[
\text{Li}_{6.65}\text{La}_{2.75}\text{Ba}_{0.25}\text{Zr}_{1.4}\text{Ta}_{0.5}\text{Nb}_{0.1}\text{O}_{12} \\
\text{La}_2\text{Zr}_2\text{O}_7
\]

\[
\begin{align*}
\text{x=0.3} & & \\
\text{x=0.2} & & \\
\text{x=0.1} & & \\
\text{x=0} & & 
\end{align*}
\]

\[
\begin{align*}
(112) & & (123) & & (004) & & (224) & & (125) & & (116) & & (046) & & (127) & & (245) & & (048) & & (248) & & (048) \\
(022) & & (023) & & (024) & & (025) & & (026) & & (027) & & (028) & & (029) & & (030) & & (031) & & (032) & & (033)
\end{align*}
\]

\[
\text{Intensity (a.u.)}
\]

\[
2\theta \text{ (degree)}
\]
Figure 2.
Figure 3.
(a) $Z''(k\Omega)$ vs $Z'(k\Omega)$ for $x=0$.

(b) $Z''(k\Omega)$ vs $Z'(k\Omega)$ for $x=0.1$.

(c) $Z''(k\Omega)$ vs $Z'(k\Omega)$ for $x=0.2$.

(f) $Z''(k\Omega)$ vs $Z'(\Omega)$ for $x=0$.

(g) $Z''(k\Omega)$ vs $Z'(\Omega)$ for $x=0.1$.

(h) $Z''(k\Omega)$ vs $Z'(\Omega)$ for $x=0.2$.

In all cases, the plots show fitting lines and data points for $Z''$ and $Z'$ as a function of frequency $Z$.

- **(a)**: 1998 Hz for $R_b + R_1$.
- **(b)**: 251 Hz for $R_b + R_1$.
- **(c)**: 501 Hz for $R_b + R_1$.
- **(f)**: 1995 Hz for $Rs + R_1$.
- **(g)**: 2512 Hz for $Rs + R_1$.
- **(h)**: 1259 Hz for $Rs + R_1$.
Figure 4.
Figure 5.
Figure 6.
REFERENCES


The garnet materials Li$_{6.65}$La$_{2.75}$Ba$_{0.25}$Zr$_{1.4}$Ta$_{0.5}$Nb$_{0.1}$O$_{12}$ and Li$_{6.4}$La$_{3}$Zr$_{1.4}$Ta$_{0.6-x}$Nb$_x$O$_{12}$ (x = 0, 0.1, 0.2 and 0.3) exhibit high ionic conductivity up to 0.7 mS cm$^{-1}$ at room temperature.