Towards understanding the lithium transport mechanism in garnet-type solid electrolytes: Li+ ions exchanges and their mobility at octahedral/tetrahedral sites

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Abstract
The cubic garnet-type solid electrolyte Li7La3Zr2O12 with aliovalent doping exhibits a high ionic conductivity, reaching up to \( \sim 10^{-3} \) S/cm at room temperature. Fully understanding the Li+ transport mechanism including Li+ mobility at different sites is a key topic in this field, and Li\(_{7-2x-3y}AlyLa_3Zr_{2-x}W_xO_{12}\) \((0 \leq x \leq 1)\) are selected as target electrolytes. X-ray and neutron diffraction as well as ac impedance results show that a low amount of aliovalent substitution of Zr with W does not obviously affect the crystal structure and the activation energy of Li+ ion jumping, but it does noticeably vary the distribution of Li+ ions, electrostatic attraction/repulsion, and crystal defects, which increase the lithium jump rate and the creation energy of mobile Li+ ions. For the first time, high-resolution NMR results show evidence that the 24d, 96h, and 48g sites can be well-resolved. In addition, ionic exchange between the 24d and 96h sites is clearly observed, demonstrating a lithium transport route of 24d→96h→48g→96h→24d. The lithium mobility at the 24d sites is found to dominate the total ionic conductivity of the samples, with diffusion coefficients of 10–9 m² s⁻¹ and 10–12 m² s⁻¹ at the octahedral and tetrahedral sites, respectively.

Keywords
garnet, type, mechanism, transport, lithium, understanding, towards, ions, li, exchanges, sites, their, mobility, tetrahedral, solid, octahedral, electrolytes

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Towards Understanding the Lithium Transport Mechanism in Garnet-type Solid Electrolytes: Li⁺ Ions Exchanges and Their Mobility at Octahedral/Tetrahedral Sites

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KEYWORDS: solid electrolyte, garnet, aliovalent substitution, lithium transport mechanism, NMR.

ABSTRACT: The cubic garnet-type solid electrolyte Li₃La₅Zr₂O₁₂ with aliovalent doping exhibits a high ionic conductivity, reaching up to ~10⁻³ S/cm at room temperature. Fully understanding the Li⁺ transport mechanism including Li⁺ mobility at different sites is a key topic in this field, and Liₓ₋₃₋ₓAlₓLa₅Zr₂ₓ₋₁WₓO₁₂ (0 ≤ x ≤ 1) are selected as target electrolytes. X-ray & neutron diffraction as well as AC impedance results show that a low amount of aliovalent substitution of Zr with W does not obviously affect the crystal structure and the activation energy of Li⁺ ion jumping, but it does noticeably vary the distribution of Li⁺ ions, electrostatic attraction/repulsion, and crystal defects, which increase the lithium jump rate and the creation energy of mobile Li⁺ electrostatic attraction/repulsion, and crystal defects, which increase the lithium jump rate and the creation energy of mobile Li⁺ ions. For the first time, high resolution NMR results show evidence that the 24d, 96h, and 48g sites can be well resolved. In addition, ionic exchange between the 24d and 96h sites is clearly observed, demonstrating a lithium transport route of 24d-96h-48g-96h-24d. The lithium mobility at the 24d sites is found to dominate the total ionic conductivity of the samples, with a diffusion coefficient of 10⁻⁹ m² s⁻¹ and 10⁻¹² m² s⁻¹ at the octahedral and tetrahedral sites, respectively.

1. INTRODUCTION

Solid state batteries promise to lead the next generation of rechargeable, high energy density lithium batteries, due to their great advantages in safety and working voltage range compared to conventional liquid electrolyte lithium ion batteries, in which the intrinsic properties of liquid electrolytes plague their performance.¹,² Solid electrolyte is an important constituent of all solid state batteries and determines most of their performance.³ As a result, it has attracted great interest in recent years.⁴,⁵ Of various solid electrolytes, the garnet-type solid electrolyte Li₃La₅Zr₂O₁₂ shows great prospects with regard to the development of highly safe lithium ion batteries, because of its high ionic conductivity at room temperature, in parallel with its good chemical and electrical stability.⁶

Li₃La₅Zr₂O₁₂ with a cubic structure was first reported by Murugan et al. as a solid electrolyte with an ionic conductivity as high as 2.4 × 10⁻⁴ S cm⁻¹ at 22 °C, achieved only in aluminacruceles.⁷ It was found that aliovalent doping at 24d (Li) and 16a (Zr) sites could dramatically enhance the stability and ionic conductivity of the cubic phase, using elements such as Al³⁺, Ga³⁺, Nb⁵⁺, Ta⁵⁺, Te⁶⁺, W⁶⁺, etc.²,⁴,⁸,⁹,¹⁰,¹¹,¹²

Therefore, an important question regarding this material is how such doping affects the ionic conductivity. In order to address this issue, we need to understand the states of the lithium ions at respective sites and how lithium migrates through the crystal structure. Using density function theory,
Xu et al. concluded that the Li\(^+\) ions jumped from one tetrahedral site to a neighboring octahedral site and then leaped forward to another tetrahedral site in the Li\(_2\)La\(_2\)Zr\(_2\)O\(_7\) structure.\(^{21}\) Some preliminary study has also been carried out to investigate Li migration and jumping via neutron powder diffraction (NPD) in Li\(_2\)La\(_2\)Zr\(_2\)O\(_7\), yielding a similar conclusion.\(^{22,23}\) However, Thompson et al. drew an opposite conclusion with NPD results and claimed that the ionic conductivity of Li\(_2\)La\(_2\)Zr\(_2\)O\(_7\) trended with the occupancy of octahedral sites, and deduced that the lithium jumps from one octahedral site to a neighboring octahedral site, bypassing tetrahedral sites entirely.\(^{24}\)

Explanations of the enhanced ionic conductivity of the garnet-type electrolytes are usually correlated with the lithium stoichiometry in the compounds, although detailed transport mechanisms are seldom investigated, in particular the sitting sites of Li\(^+\) ions as well as their mobility and rate-determining steps.\(^{25,26,27}\) Previously, we reported on the synergistic effects of Al and Te using Al\(_2\)O\(_3\) and ZrO\(_2\) crucibles, demonstrating that the concentration of Li sites and ion dynamics can be modulated by aliovalent ions and accurately monitored by using NPD and solid state NMR techniques.\(^{28}\)

In this work, we elaborate further the effects of binary aliovalent substitution on enhancing the ionic conductivity and bolster the lithium transport mechanism in Li\(_{2-x}\)Al\(_x\)La\(_2\)Zr\(_2\)O\(_7\)\(_{(0 ≤ x ≤ 1)}\) with a cubic garnet structure. Furthermore, we illustrate the relationship between composition, crystal structure, lithium dynamics, and ionic conductivity in the garnet-type electrolytes.

2. Experimental Section

A conventional solid state reaction was used to synthesize the garnet-type electrolyte. The starting materials, LiOH·H\(_2\)O, La\(_2\)O\(_3\), ZrO\(_2\), and WO\(_3\) (purities of 95.0%, 99.99%, 99.0% and 99.99% respectively, all from the Sinopharm Chemical Reagent Co., Ltd.), were mixed and ground by a planetary grinder, with isopropanol used as grinding reagent. The precursors were ground for 12 h and dried in a 120 °C box, then calcined at 800 °C for 12 h. After the second grinding and drying, the material was pressed into pellets at 2 MPa by uniaxial cold pressing. Finally, the pellets with W, covered with green constituent powder, were sintered at 1150, 1175, and 1200 °C for 12 h in Al\(_2\)O\(_3\) crucibles. In order to get a pure phase with cubic symmetry, the pellet with the composition of Li\(_2\)La\(_2\)Zr\(_2\)O\(_7\) (i.e. without W doping) was sintered at different temperatures for 36 h in an alumina crucible.

The crystal structure of the as-prepared garnet electrolyte powder was characterized using X-ray powder diffraction. A Panalytical X’Pert (Philips, Netherlands) instrument with Cu Ka radiation was used for this purpose.

High-resolution NPD was also used to study the material, due to its high sensitivity for “light” atoms. The powders were stored and loaded into 6-mm vanadium cans in an Ar-filled glove box, which were sealed properly in an air-tight condition. The NPD data was collected using ECHIDNA, the high-resolution neutron powder diffractometer at the Australian Nuclear Science and Technology Organisation (ANSTO).\(^{29}\) The neutron beam wavelength was 1.625±8(8) Å, determined using the La\(_{60}\)B\(_{40}\) NIST standard reference material 660b. The NPD data was obtained in the 2θ angular range of 4 to 164° with a step size of 0.125°. GSAS-II was employed to perform Rietveld analysis of the obtained NPD data.\(^{30}\) The refining parameters that were optimized included background coefficients, zero-shift, peak shape parameters, lattice parameters, the positional parameters of Li (48g), Li (96h), O (96h), the fractional factors of all Li, Zr, W, and O, and isotropic atomic displacement parameters (U\(_{iso}\)). During the refinement, the total occupancy of Zr and W, sharing 162 sites, was constrained to be unity, and the U\(_{iso}\) of all elements was set to be equivalent.

The density of sintered pellets was measured using the Archimedes method. Theoretical density was calculated from the lattice parameters determined by XRD. A Hitachi S-4800 scanning electron microscope was used to check the cross-section morphology of samples.

AC impedance measurements were undertaken to measure conductivity, using a Solartron 1260 impedance analyzer with the frequency range of 1 to 10\(^6\) Hz and an amplitude of 100 mV. The measurement cell was constructed as follows: first, silver slurry was spread onto the surfaces of pellets and cured at 600 °C for 30 minutes in order to vaporize any organic solvent. Next, the silver-coated pellets were placed between two pieces of steel for testing. Test temperatures were varied from -50 to 150 °C at 20 °C intervals to study the temperature-dependent relationship. The electronic conductivity was measured by the DC polarization method, using a Solartron 1287 electrochemical analyzer with a polarization potential of 0.1 V. The holding time was 10,000 seconds. The magic angle spinning nuclear magnetic resonance (MAS NMR) technique was used to probe the local chemical environment of the atoms and to analyze the lithium dynamics of the materials. The \(^{6}Li\) and \(^{27}Al\) MAS NMR spectra were gathered at Larmor frequencies of 58.9 MHz and 104.3 MHz respectively, on a Bruker Avance 400 NMR spectrometer with a sample spinning speed of 12 kHz. The chemical shifts of the \(^{6}Li\) and \(^{27}Al\) were calibrated by using LiCl powder (0 ppm) and Al(OH)\(_3\) (0 ppm) respectively. \(^{27}Al\) MAS NMR spectra were collected using a pulse length of 1 μs and a recycle delay of 0.1 s. \(^{6}Li\) MAS NMR spectra were collected using a 1/4 π pulse and a recycle delay of 40 s. The saturation recovery method was used here to characterize the spin lattice relaxation times for different lithium sites. In order to reduce the Li\(_2\) signal in \(^{6}Li\) MAS NMR spectra, a π pulse was first applied to invert the magnetization from the +Z to −Z axis, and then after a recovery time of 2 s at which the strong peak (Li\(_2\)) was zero-crossing while the other signals still remained in the −Z axis, due to their difference in T\(_1\), a 1/2 π pulse was applied to flip those signals along the −Z axis into the xy plane for observation, with a recycle delay of 110 s. The saturation recovery method was used here to characterize the spin lattice relaxation times for different lithium sites. In order to reduce the Li\(_2\) signal in \(^{6}Li\) MAS NMR spectra, a π pulse was first applied to invert the magnetization from the +Z to −Z axis, and then after a recovery time of 2 s at which the strong peak (Li\(_2\)) was zero-crossing while the other signals still remained in the −Z axis, due to their difference in T\(_1\), a 1/2 π pulse was applied to flip those signals along the −Z axis into the xy plane for observation, with a recycle delay of 110 s. The diffusion coefficient was detected by a static 8 mm \(^{7}Li\) probe. \(^{7}Li\) PFG NMR spectra were collected at the Larmor frequency of 158 MHz using a 1/2 π pulse and a recycle delay of 2 s. A series of pulse field gradients between 50 ~ 400 G/cm was applied, with a duration time of 1.42 s and a diffusion time of 10 μs.

3. Results and discussion

3.1. Crystal Structure and Morphologies. Figure 1 shows the XRD patterns of Li\(_{2-x}\)Al\(_x\)La\(_2\)Zr\(_2\)O\(_7\)\(_{(0 ≤ x ≤ 1)}\) sintered at different temperatures. The sample with the
composition of Li$_{2-2x}$Al$_x$La$_{1-x}$Zr$_2$W$_x$O$_{12}$, sintered at 1150 °C for 36 h, shows a pure cubic structure. The samples with the composition of $x = 0.25$ and 0.5 also show a pure cubic structure. It was very difficult to synthesize a pure cubic phase when the W doping reached $x = 0.75$. In most circumstances, a small amount of W salts can be detected in the samples (with peaks visible at 18°). Higher sintering temperatures reduced the amount of the impurity phase, suggesting that high sintering temperatures favored the formation of solid solutions. Finally, at the composition of $x = 1$, more impurities were detected in the samples. As the substitution content increases, the lattice parameters decrease monotonically, as seen in Figure S1. In octahedral coordination, the ionic radius of Zr$^{4+}$ is 0.72 Å and the ionic radius of W$^{6+}$ is 0.60 Å. Assuming no phase transition, the monotonic decrease in lattice parameters with increasing W content indicates the successful substitution of Zr$^{4+}$ by W$^{6+}$ and the formation of the Li$_{2-2x}$Al$_x$La$_{1-x}$Zr$_2$W$_x$O$_{12}$ ($0 \leq x \leq 1$) solid solutions. The samples with the same composition showed a decrease in lattice parameters when the sintering temperature increases, indicating that more Li$^+$ vacancies and O defects were formed in the garnet structure at higher sintering temperatures.

As alumina crucibles were used during the sintering process, it was necessary to know the content of Al and its local environment in the samples. Our NMR and EDS results show that a fraction of Al occupies the 24d sites, and the other randomly exists along grain boundaries in the form of LaAlO$_3$, in some batches, with an Al content of 0.2 mol for both $x = 0.25$ and $x = 0.5$. When the W content reaches $x = 0.75$, there is no Al detectable in the samples. A similar “synergistic effect” of Al and Te could be found in our previous paper. Detailed information is listed in Supporting Information, Figure S2 and Table S1.

The model proposed by Goodenough et al. was used for the Rietveld refinement of the NPD data for the Li$_{2-2x}$Al$_x$La$_{1-x}$Zr$_2$W$_x$O$_{12}$ ($0.25 \leq x \leq 0.75$) samples. The W atoms were considered to occupy the Zr ($16d$) sites, due to the close values of their ionic radii. However, the presence of relatively heavy La and Zr atoms in the structure complicated the refinement of the “light” aluminum and lithium atoms. Furthermore, the neutron scattering length for Al is rather low and thus it was difficult to quantify a small concentration in the compound. With the NMR and EDS results, the Al occupancy is 0.0667 and located at the 24d sites for both $x = 0.25$ and 0.5, while the Al occupancy is 0 for $x = 0.75$. The best fits of the NPD data were obtained with the parameters listed in Table 1 and the results of Rietveld refinement are shown in Figure 2 and Figure S3.

The lithium number is slightly higher than expected from the stoichiometry of the formula unit, but still smaller than the tolerance of 7.5. The occupancy of lithium in the 24d sites ranges from 32 to 41%, and the smallest value, with $x = 0.25$, might have been due to the occupancy of Al at these sites. The Li occupancy in the 48g sites ranges from 40% to 35%, which decreases along with the total lithium content. Finally, the Li occupancy in the 96f sites remains constant. The partial occupancy of lithium at different sites might have been the reason for the observed high ionic conductivity of the Li$_{2-2x}$Al$_x$La$_{1-x}$Zr$_2$W$_x$O$_{12}$ ($0.25 \leq x \leq 0.75$) system. In addition, oxygen defects were also detected from the Rietveld analysis.

![Figure 1. XRD patterns of Li$_{2-2x}$Al$_x$La$_{1-x}$Zr$_2$W$_x$O$_{12}$ ($0 \leq x \leq 1$) sintered at different temperatures: (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.5$, (d) $x = 0.75$, (e) $x = 1$.](image1)

![Figure 2. Rietveld refinement of the structural models, based on NPD data collected at room temperature from Li$_{2-2x}$Al$_x$La$_{1-x}$Zr$_2$W$_x$O$_{12}$ samples with $x = 0.25$ and sintered at 1150 °C.](image2)
For rerelease, the sintering properties of the material increased the sintering properties of the material. Exceptionally, a small amount of W substitution was observed in the samples, a small amount of W substitution was observed in the samples. As the sintering temperature increased, the W regions of the W salts reacted with the samples such that the impurity content started to decrease. However, for x = 1, the impurities became overwhelming in quantity and thus severely interfered with the crystallization of the garnet phase. At this composition, in Figure 3, no obvious grains can be seen in the cross sections. Overall, from the morphologies of the samples, a small amount of W substitution significantly increased the sintering properties of the material. Excess-

### Table 1. Refined structural parameters of Li$_{y}$Al$_{x}$La$_{z}$Zr$_{w}$O$_{12}$ (space group Ia-3d, No.230).

<table>
<thead>
<tr>
<th>Stoichiometry formula</th>
<th>Refinement results</th>
<th>Lattice parameter a</th>
<th>Li</th>
<th>Zr</th>
<th>W(R/S)</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{5/9}$Al$</em>{x}$La$<em>{z}$Zr$</em>{w}$O$_{12}$</td>
<td>Li$<em>{6.76(10)}$Al$</em>{0.25}$La$<em>{1.12(6)}$Zr$</em>{5.76(10)}$O$_{12}$</td>
<td>6.59%</td>
<td>12.954(1)</td>
<td>0.32(3)</td>
<td>0.81(2) / 0.875</td>
<td>0.942(7)</td>
</tr>
<tr>
<td>Li$<em>{6.57(10)}$Al$</em>{0.75}$La$<em>{1.25}$Zr$</em>{5.90(10)}$O$_{12}$</td>
<td>Li$<em>{6.76(10)}$Al$</em>{0.75}$La$<em>{1.25}$Zr$</em>{5.90(10)}$O$_{12}$</td>
<td>6.70%</td>
<td>12.924(1)</td>
<td>0.41(3)</td>
<td>0.38(2) / 0.42(3)</td>
<td>0.933(8)</td>
</tr>
<tr>
<td>Li$<em>{6.57(10)}$Al$</em>{0.25}$La$<em>{1.12(6)}$Zr$</em>{5.76(10)}$O$_{12}$</td>
<td>Li$<em>{6.76(10)}$Al$</em>{0.25}$La$<em>{1.12(6)}$Zr$</em>{5.76(10)}$O$_{12}$</td>
<td>6.60%</td>
<td>12.900(1)</td>
<td>0.39(3)</td>
<td>0.35(2) / 0.35(2)</td>
<td>0.625(8)</td>
</tr>
<tr>
<td>Li$<em>{6.57(10)}$Al$</em>{0.25}$La$<em>{1.12(6)}$Zr$</em>{5.76(10)}$O$_{12}$</td>
<td>Li$<em>{6.76(10)}$Al$</em>{0.25}$La$<em>{1.12(6)}$Zr$</em>{5.76(10)}$O$_{12}$</td>
<td>6.71%</td>
<td>12.900(1)</td>
<td>0.39(3)</td>
<td>0.35(2) / 0.35(2)</td>
<td>0.625(8)</td>
</tr>
</tbody>
</table>

# Fixed to the same value as from the EDS results. R: refinement results; S: stoichiometry formula.

The compositions Li$_{5/9}$Al$_{x}$La$_{z}$Zr$_{w}$O$_{12}$ and Li$_{5/9}$Al$_{x}$La$_{z}$Zr$_{w}$O$_{12}$ were obtained at the sintering temperature of 1150 °C, while Li$_{5/9}$La$_{z}$Zr$_{w}$O$_{12}$ was obtained by sintering at 1200 °C.

Figure 3 shows the morphologies of the Li$_{y}$Al$_{x}$La$_{z}$Zr$_{w}$O$_{12}$, W$_{0.75}$O$_{12}$ samples sintered at different temperatures. For x = 0, the grains can be clearly seen in the cross sections and become larger as the sintering temperature increases. For x = 0.25, the grains contact well with each other, that it is difficult to distinguish the grain boundaries in the cross sections. For x = 0.5, the grain boundaries can be clearly distinguished. With an increase in sintering temperature, the grains become larger, but the size of the grain is distributed inhomogeneously. For x = 0.75, at the sintering temperature of 1150 °C, the large grains are surrounded by many small particles. An increase in sintering temperature causes these large grains to increase in size and the small particles to vanish. Combined the XRD patterns with the SEM results, a likely explanation for this behavior is that the small particles were regions of the W-salt impurities. As the sintering temperature increased, the W-salts reacted with the samples such that the impurity content started to decrease. However, for x = 1, the impurities became overwhelming in quantity and thus severely interfered with the crystallization of the garnet phase. At this composition, in Figure 3, no obvious grains can be seen in the cross sections. Overall, from the morphologies of the samples, a small amount of W substitution significantly increased the sintering properties of the material. Exces-

![Figure 3](image-url)
sive W substitution, on the other hand, gave rise to poor contact between grains. Based on the Li content in the samples and their morphologies, the composition of $x = 0.25$ appears to have exhibited the best ionic conductivity.\textsuperscript{21}

Figure 3 also describes the elemental distribution at $x = 0.25$. The elements O, Al, La, Zr and W are distributed homogeneously in the cross section, indicating the formation of solid solutions. The relative density is a key factor when evaluating the sintering properties of ceramics. Here, the relative densities of the Li$_{2-x}$Al$_x$La$_2$Zr$_{2-x}$W$_x$O$_{12}$ ($0 \leq x \leq 1$) samples are between 93\% - 95\%, which are slightly higher than that of the sample without W substitution (Table S3). The substitution of W is an effective way to decrease the sintering requirements and increase the sintering properties.

3.2. Electrical properties of Li$_{2-x}$Al$_x$La$_2$Zr$_{2-x}$W$_x$O$_{12}$ ($0 \leq x \leq 1$) solid solutions. AC impedance measurements were used to calculate the impedance and conductivity of the lithium ion conductors. Figure 4 shows the Nyquist plots of Li$_{2-x}$Al$_x$La$_2$Zr$_{2-x}$W$_x$O$_{12}$ ($x = 0.25$). In the case of testing temperature below 25 °C, there exists a semicircle and a curve at the high and low frequency sides. With an increase of testing temperature, the semicircle at the high frequency side gradually decreases and eventually vanishes after 50 °C. This phenomenon was previously explained in the Te system\textsuperscript{16}. Two long conductive lines were used during the impedance testing, and the inductance was considered in the fitting process. When the testing temperature was below 25 °C,

![Figure 4](image)

**Figure 4.** Nyquist plots of Li$_{2-x}$Al$_x$La$_2$Zr$_{2-x}$W$_x$O$_{12}$ ($x = 0.25$) sintered at 1150 °C for 12h. (a) collected at low temperature, (b) collected at high temperature.

![Figure 5](image)

**Figure 5.** Arrhenius plots of Li$_{2-x}$Al$_x$La$_2$Zr$_{2-x}$W$_x$O$_{12}$ ($0 \leq x \leq 1$) sintered at 1150 °C for 12h.
trapping effect” at low temperatures. Table S3 details the conductivities and activation energies of the Li\(_{y}\)Al\(_{x}\)La\(_{3}\)Zr\(_2\)W\(_{12}\)O\(_{42}\) \((0 \leq y \leq 1)\) solid solutions. Activation energies listed in Table S3 are from the high temperature side, with the electrical properties at low temperatures being discussed in the next section. In addition, the electrical conductivities and activation energies of the garnet phases with the same composition appear not be affected by the sintering temperature.

As a solid electrolyte used in lithium ion batteries, Li\(_{y}\)Al\(_{x}\)La\(_{3}\)Zr\(_2\)W\(_{12}\)O\(_{42}\) \((0 \leq y \leq 1)\) is required to be a purely lithium ionic conductor with a negligible electronic conductivity. The DC polarization method was applied to measure the electronic conductivities of the samples, as documented in Supporting Information, Figure S5. The electronic conductivities of samples are on the order of \(10^{-8} - 10^{-9} \text{ S cm}^{-1}\) and the transference number of lithium is nearly unity. This demonstrates that Li\(_{y}\)Al\(_{x}\)La\(_{3}\)Zr\(_2\)W\(_{12}\)O\(_{42}\) \((0 \leq y \leq 1)\) were pure lithium ionic conductors and therefore suitable for lithium ion batteries.

The saturation recovery method was used to characterize the spin-lattice relaxation time (T\(_1\)). Figure S6 shows the saturation recovery of the \(\footnote{\text{Li}}\) signals. A bi-exponential function fitted the data very well, as shown in the red curves, yielding two different T\(_1\) values, as listed in Table 2. Apparently, the larger component with the shorter T\(_1\) value (between 1.0 \(\sim\) 5.0 s) belong to for the lithium in the octahedral sites, while the smaller component with the longer T\(_1\) value (in the range of 14 \(\sim\) 28 s) represents the lithium in the tetrahedral sites. It was also indicated that the Li at the octahedral (48g) sites with the shorter T\(_1\) value should exhibit a higher mobility than the Li at the tetrahedral (24d) sites with the longer T\(_1\) in our case.

Here we utilized the difference in T\(_1\) to suppress the strong signals from the octahedral sites. This was done by incorporating the inversion recovery with a given recovery time, in such a way that the shorter T\(_1\) component (i.e. the \(\footnote{Li}\) signals from the octahedral sites) was relaxed to the null point while the longer T\(_1\) component (i.e. the \(\footnote{Li}\) signals from the tetrahedral sites) still remained in the z axis.\(^{24}\) Figure 7 shows the \(\footnote{\text{Li}}\) spectrum after suppressing the strong signals at 1.9 ppm. Interestingly, there exists an additional peak at 1.6 ppm, which is completely buried in Figure 6. This peak should have a similar T\(_1\) value to 0.8 ppm. Because of its very weak signal intensity, this newly discovered peak at 1.6 ppm most likely belongs to those lithium ions occupying the distorted octahedral sites (96h), and the peak at 1.9 ppm should belong to the lithium at the 48g sites.

With the appearance of the new peak at 1.6 ppm (96h), we deconvoluted the experimentally observed peaks with three mixed Lorentz-Gaussian peaks (Figure 6). The deconvolutions fitted well with the experimental data, yielding relative Li populations in the 24d, 48g, and 96h sites, as listed in Table 2. The integrated area corresponds the number of lithium

\[
\text{\footnote{Li} MAS NMR spectra of } \text{Li}\(_{y}\)\footnote{Al}\(_{x}\)\footnote{La}\(_{3}\)\footnote{Zr}\(_2\)\footnote{W}\(_{12}\)\footnote{O}\(_{42}\) \((0 \leq y \leq 1)\) sintered at 1150 °C for 12h.
\]

Figure 7. \(\footnote{\text{Li}}\) MAS NMR spectra of \(\text{Li}\(_{y}\)\footnote{Al}\(_{x}\)\footnote{La}\(_{3}\)\footnote{Zr}\(_2\)\footnote{W}\(_{12}\)\footnote{O}\(_{42}\) \((0 \leq y \leq 1)\) gathered by incorporating the inversion recovery with a given recovery time.

\[
\text{\footnote{Li} MAS NMR spectra of } \text{Li}\(_{y}\)\footnote{Al}\(_{x}\)\footnote{La}\(_{3}\)\footnote{Zr}\(_2\)\footnote{W}\(_{12}\)\footnote{O}\(_{42}\) \((0 \leq y \leq 1)\)
\]
Table 2. Fitting results of $^6$Li MAS NMR spectra of Li$_{2-x}$Al$_x$La$_{1-y}$Zr$_{2-x}$W$_x$O$_{12}$ (0 ≤ x ≤ 1) solid solutions.

<table>
<thead>
<tr>
<th>x</th>
<th>c.s. (ppm)</th>
<th>L.W. (Hz)</th>
<th>area (%)</th>
<th>occ. T1</th>
<th>c.s. (ppm)</th>
<th>L.W. (Hz)</th>
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The occupancy at the 24d sites is between 30 ~ 40% and the total amount of Li at the octahedral sites (48g and 96h) are similar. However, the difference in $^6$Li intensities as a function of the applied pulse field gradient. Figure 8 clearly shows a sharp peak and a broad peak in the spectra, where the sharp peak is attributed to the $^6$Li ions occupying the octahedral sites, and the broad peak is assigned to the $^6$Li ions occupying the tetrahedral sites based on the NMR fitting results. The abovementioned results confirm that the $^6$Li ions jumped from one tetrahedral site to neighboring octahedral sites and vice versa. In the crystal structure of the garnet phase, the 96h sites are between 24g and 24d sites, this is in agreement with our deduction of lithium attribution. The above results confirm that the $^6$Li ions in the tetrahedral 24d sites involve in the lithium migration pathway and support the $^6$Li ions jump along 24d-96h-24g-24d. Furthermore, the 24d sites exhibiting a lower mobility were expected to determine the overall conductivity.

![Figure 8. $^6$Li-$^6$Li exchange spectra of Li$_{2-x}$Al$_x$La$_{1-y}$Zr$_{2-x}$W$_x$O$_{12}$ (x = 0.5) sintered at 1150 °C for 12h.](https://example.com/figure8.png)

An important question regarding the lithium migration pathway is whether the Li$^+$ ions jump from the octahedral site to its neighboring octahedral sites, bypassing the tetrahedral sites? Or the 24d sites are in fact involved in the lithium migration pathway? In NMR, two-dimensional chemical exchange experiments can be used to measure the slow exchange between the lithium ions at the tetrahedral and octahedral sites. Unfortunately, it is extremely difficult to observe any exchange signals between the less populated lithium at the tetrahedral sites and the much more populated lithium at the octahedral sites, especially when the latter has a much shorter T1, than the former. Again, we incorporated the inversion recovery with a given recovery time to suppress the strong signals from the octahedral sites at 1.9 ppm before doing the chemical exchange experiment. Figure 8 shows the two-dimensional $^6$Li-$^6$Li exchange spectrum after suppressing the strong signals at 1.9 ppm. Clearly, there exists a cross peak at (101=0.8, 022=1.6) ppm, indicating the correlation between the octahedral (96h) and tetrahedral (24d) sites; that is, the Li$^+$ ions jumped from one tetrahedral site to neighboring octahedral (96h) sites and vice versa. In the crystal structure of the garnet phase, the 96h sites are between 24g and 24d sites, this is in agreement with our deduction of lithium attribution. The above results confirm that the Li$^+$ ions in the tetrahedral 24d sites involve in the lithium migration pathway and support the Li$^+$ ions jump along 24d-96h-48g-96h-24d. Furthermore, the 24d sites exhibiting a lower mobility were expected to determine the overall conductivity.

The diffusion coefficients of Li$_{2-x}$Al$_x$La$_{1-y}$Zr$_{2-x}$W$_x$O$_{12}$ (x = 0.5) were obtained at different temperatures using $^7$Li diffusion measurements. Figure 9 and Figure S7 show the decays of $^7$Li intensities as a function of the applied pulse field gradient. Figure S7 clearly shows a sharp peak and a broad peak in the spectra, where the sharp peak is attributed to the Li$^+$ ions occupying the octahedral sites, and the broad peak is assigned to the Li$^+$ ions occupying the tetrahedral sites based...
on their integrated areas. Clearly, the broad peak shows almost no decay within the range of the applied pulse field gradient, indicating that the Li\(^+\) ions occupying the tetrahedral sites diffuse rather slowly. While the sharp peak decays, indicating that the Li\(^+\) ions occupying the octahedral sites diffuse fast. Fitting the data using a Stejskal-Tanner function yielded the diffusion coefficients of \(1.30 \times 10^{-9} \text{ m}^2 \text{s}^{-1}\), \(1.47 \times 10^{-9} \text{ m}^2 \text{s}^{-1}\), and \(1.89 \times 10^{-9} \text{ m}^2 \text{s}^{-1}\) at the temperatures of 9.4, 25.6, and 50.6 °C, respectively.\(^25\) The diffusion coefficients obtained here characterize the diffusion rate for those Li at the octahedral sites, more precisely, the 48g sites. The inset in Figure 9 shows the Arrhenius plot of the diffusion coefficient at the 48g sites, giving rise to the activation energy of 6.12 kJ/mol, which is much smaller than that from the ionic conductivity, and is also much less than the activation energy of 31 kJ/mol from the average lithium jump rate that will be calculated in the next section. The average diffusion coefficient from the Nernst - Einstein relationship is on the order of \(10^{-12} \text{ m}^2 \text{s}^{-1}\), much lower than that obtained through the diffusion measurements, \(10^{-9} \text{ m}^2 \text{s}^{-1}\). Thus, we believe that the Li\(^+\) ions should have jumped only along the 24d pathway, because any Li\(^+\) ions jumping from one octahedral site to a neighboring octahedral site would have yielded a much higher ionic conductivity. Taking into account the lithium transport route of 24d-96h-48g-96h-24d and the fact that the mobility at the 24d sites determined the whole ionic conductivity of the sample, it is reasonable to conclude that the diffusion coefficient of Li at the 24d sites was on the order of \(10^{-12} \text{ m}^2 \text{s}^{-1}\).

### 3.4. Low temperature properties of Li\(_{2-2x\gamma}\text{Al}_x\text{La}_9\text{Zr}_{3-x}\text{W}_2\text{O}_{12} (0 \leq x \leq 1)\) solid solutions.

Figure 5 shows an inflexion point of the Arrhenius plot at 25 °C, where the activation energy of the ionic conductivity at low temperature is much higher than that at the high temperature side, a phenomena stemming from the “ion trapping effect”. For fast ion conductors, Nyquist plotting at low temperature can show a more complete semicircle, which is necessary for the collection of micro-information.

Usually, the AC conductivity and the frequency follow Jonscher’s universal power law (Equation (1)):\(^26\)

\[
\sigma(\omega) = \sigma_{dc} + A\omega^n = K\omega_p \left[ 1 + \left( \frac{\omega}{\omega_p} \right)^n \right], \tag{1}
\]

where \(\sigma_{dc}\) is the DC ionic conductivity, \(\omega\) is the angular frequency, \(\omega_p\) represents the jump rate of the charge carriers, \(A\) and \(K\) are the pre-factors, and \(n\) is a dimensionless frequency exponent which lies in the range 0 < \(n\) < 1. Figure 10 shows the frequency dependent \(\sigma(\omega)\). There are two platforms in the data, with the platform at the high frequency side representing the DC conductivity \(\sigma_{dc}\) and the decrease in ionic conductivity at the low frequency side being attributed to the electrode process. Here, the bulk properties are the only focus of the fitting, and so the Jonscher relationship was used to fit the data at the high frequency side. The intercept of the fitting curve on the Y axis represents the DC conductivity, while the jump rate \(\omega_p\) could be directly taken from the fitting results. The mobile ion concentration was calculated from the Nernst - Einstein - Smoluchowski relationship (Equation (2)):

\[
\sigma_{dc} = \frac{c\omega_p q^2 \alpha^2}{2\pi kT}, \tag{2}
\]

where \(c\) is the mobile ion concentration, \(q\) is the charge, \(\alpha\) is the jump distance, and set to be 2 Å, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature in degrees Kelvin. The results are listed in Table S4.

\(\sigma_{dc}\), \(\omega_p\), and \(c\) are important factors when studying solid electrolytes, and their relationships with test temperatures are given in Figure 11, S8, and S9. The data fits the Arrhenius plots well, indicating a thermal activation process. The activation energies were calculated and listed in Table 3. The sample with the composition of \(x = 1\), however, shows a large amount of impurities, which greatly affects the shape of the Nyquist plot and the fitting results. For that reason, only the data gathered from compositions with \(x = 0.25\), 0.5, and 0.75 are discussed.

The activation energy of the ionic conductivity at the high temperature side in this data shows a clear pattern, but because of the “ion trapping effect”, the difference in activation energy of various compositions is not as obvious at the low temperature side.
compared to that of c, indicating that the decrease in ionic conductivity is mainly affected by the decrease in \( \omega_p \). However, by examining different compositions, the activation energy of the jump rate at between 30 ~ 32 kJ/mol shows negligible differences, indicating that the barrier for lithium jumping is not obviously changed. The decrease in the crystal lattice size is thus apparently too small to affect the activation energy of the lithium jump rate. The decrease in lithium jump rate with x is mainly due to the decrease in attempt frequency, although the structural reasons for this phenomenon are not yet very clear. At 10 °C, only about 1% ~ 10% of

Table 3. Low temperature properties of \( \text{Li}_{7-2x} \text{Al}_x \text{Zr}_2 x \text{W}_4 \text{O}_{12} \) (0 ≤ x ≤ 1).

<table>
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<th>( \omega_p/10^3 , \text{rad s}^{-1} )</th>
<th>( c/10^3 , \text{cm}^{-3} )</th>
<th>( \omega_r ) (rad s(^{-1}))</th>
<th>( E_a/HT ) (kJ/mol)</th>
<th>( E_a/LT ) (kJ/mol)</th>
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<td>( \sigma_{ac} )</td>
<td>( E_{ac} )</td>
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\( E_{dc} \) is the activation energy of ionic conductivity; \( \sigma_{ac} \) is the creation energy of mobile Li\(^+\) ions; \( E_{ac} \) is the activation energy of jump rate; \( E_{ip} \) is the ion trapping effect.
the total lithium is mobile in the garnet structure: most of the Li+ ions are fixed in the lattice and do not participate in lithium transport.27 With an increase in x, the creation energy of mobile Li+ ions increases from 2.9 kJ/mol to 11.6 kJ/mol at the high temperature side. The dissolution energy of W-O is 653.2 kJ/mol, which is smaller than the 760 kJ/mol of the Zr-O band.19 With an increase in W content, the average dissolution energies of the M-O band decrease, the O shows a stronger attraction to Li+, and the dissolution energy of the Li-O band increases. This causes the creation energy of mobile Li+ ions to increase. The activation energy of the jump rate ω0 is nearly constant. Therefore, the difference in activation energies of ionic conductivity is mainly affected by the creation energy of mobile Li+ ions. But at low temperatures, the ‘‘ion trapping effect’’ decreases from 8.1 kJ/mol to 1.1 kJ/mol, behavior that is mainly due to a decrease in Li+ ion content and crystal defects in the garnet structure. These two opposite behaviors cause the creation energy of mobile Li+ ions to exhibit a minor increase with x at the low temperature side, from 11 to 13 kJ/mol. Since the lithium mobility at 24d sites determines the total conductivity, the parameters obtained above are mainly attributed to the Li+ ions at 24d sites.

4. Conclusion

A series of Li2-xAlxLa2-xZrxW0.5O12 (0 ≤ x ≤ 1) solid solutions were synthesized and their properties were studied. The sample with the composition of x = 0.25 showed the highest ionic conductivity, with σa = 4.9 × 10^-4 S cm⁻¹, and the lowest activation energy, 34.1 kJ/mol. The ionic conductivities of the solid solutions decreased with the further substitution of W, while the activation energies increased. The decrease in ionic conductivity was due to a decrease in jump rate at the 24d sites, which determined the total ionic conductivity of the samples. The increase of activation energy was due to the heightened creation energy of mobile Li+ ions, and these mobile ions made up only a small amount of the total lithium. In addition, the ‘‘ion trapping effect’’ decreased with an increase in substitution content. The aliovalent substitution of W did not seriously affect the crystal structure or the activation energy of Li+ ion jumping, but it noticeably varied the distribution of Li+ ions, electrostatic attraction/repulsion, and crystal defects, which increased the lithium jump rate and the creation energy of mobile Li+ ions. This is the mechanism of the previously observed effect that aliovalent substitution has on ionic conductivity.

Three lithium sites, the tetrahedral 24d as well as the octahedral 48g and 96h, were successfully resolved by high resolution solid state NMR, with the diffusion coefficients of lithium found to be 10^-7 m² s⁻¹ at the octahedral sites and 10^-12 m² s⁻¹ at the tetrahedral sites. The lithium ions exchange between the 24d sites and 96h sites was observed, which directly demonstrated a lithium transport route of 24d-96h-48g-96h-24d. The tetrahedral sites were the key points and determined the ionic conductivity of the Li7-3yAlxLa2yZrx2yW0.5O12 structure. It is anticipated that a combination of AC impedance testing (at high and low temperature ranges) and the use of the ss-NMR technique would be a powerful way to study the lithium transfer performance and could be helpful in understanding the lithium dynamics in all solid electrolytes.

ASSOCIATED CONTENT

Supporting Information.

Lattice parameters of Li7-3yAlxLa2yZrx2yW0.5O12 (0 ≤ x ≤ 1); 27Al MAS NMR spectra of Li7-3yAlxLa2yZrx2yW0.5O12 (0 ≤ x ≤ 0.75); EDS results of Li7-3yAlxLa2yZrx2yW0.5O12 (0 ≤ x ≤ 0.75); Rietveld refinement of the structural models, based on NPD data from Li7-3yAlxLa2yZrx2yW0.5O12 samples; Nyquist plots of Li7-3yAlxLa2yZrx2yW0.5O12 (x = 0.25); Arrhenius plots of Li7-3yAlxLa2yZrx2yW0.5O12 (0 ≤ x ≤ 1); DC polarization curves of Li7-3yAlxLa2yZrx2yW0.5O12 (0 ≤ x ≤ 1); Li PFG NMR spectra of Li7-3yAlxLa2yZrx2yW0.5O12 (x = 0.5); Frequency dependent ω(ω) of Li7-3yAlxLa2yZrx2yW0.5O12 (ω = 0.25) and associated fitting results; Low temperature properties of Li7-3yAlxLa2yZrx2yW0.5O12 (0 ≤ x ≤ 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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ABBREVIATIONS

XRD, X-ray diffraction; EDS, energy dispersive spectrometry; NPD, neutron powder diffraction; SEM, scanning electron microscopy; NMR, nuclear magnetic resonance; c.s., chemical shift; L.W., line width; occu., occupancy.
REFERENCE

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Towards Understanding the Lithium Transport Mechanism in Garnet-type Solid Electrolytes: Li\(^+\) Ions Exchanges and Their Mobility at Octahedral/Tetrahedral Sites

![Diagram](image-url)