Study of diffusion and conduction in lithium garnet oxides Li$_x$La$_3$Zr$_{x-5}$Ta$_{7-x}$O$_{12}$ by machine learning interatomic potentials

Jin Dai, Yue Jiang and Wei Lai

Lithium garnet oxides are an attractive family of solid-state electrolytes due to their high Li-ion conductivity and good chemical stability against Li metal. Experimental study of these materials is often troubled by chemical contamination (e.g. Al) or lithium loss, while computational study, theoretically with controlled composition, is often limited either by accuracy (e.g. conventional interatomic potential) or efficiency (e.g. density-function theory or DFT). In this work, we report the study of diffusion and conduction of lithium garnets by a machine learning interatomic potential (MLIP) that is approaching DFT accuracy but orders of magnitude faster. We found that this MLIP is more accurate than other commonly applied models to study lithium garnets and is able to predict diffusion and conduction properties that are consistent with experiments. Computational studies enabled by this MLIP, combined with experimental data, suggest that ionic conduction is non-Arrhenius and maximum conductivity occurs around $x = 6.6$ to $6.8$ in Li$_x$La$_3$Zr$_{x-5}$Ta$_{7-x}$O$_{12}$.

1. Introduction

Li-ion batteries are widely used in portable electronics and electrical vehicles. Due to the flammability of organic liquid electrolytes in the current Li-ion batteries, many materials have been investigated as solid-state alternatives. Among them, lithium garnet oxides have attracted much attention due to their safety and stability. Since Thangadurai et al. first reported Li ion conduction in Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta) in 2003 and then high-conductivity cubic Li$_5$La$_3$Zr$_{O_{12}}$ in 2007, many experimental and computational efforts have been devoted to investigate the Li garnet series Li$_x$La$_3$Zr$_{x-5}$Ta$_{7-x}$O$_{12}$ ($x = 5-7$).

As ionic conductivity is one of the most important material properties for solid electrolytes, many experimental results have been reported for various compositions of Li$_x$La$_3$Zr$_{x-5}$Ta$_{7-x}$O$_{12}$ ($x = 5-7$), including both Al contaminated (through alumina crucibles), Al doped, and nominally Al-free phases. Fig. 1 summarizes some work of Al-free and Al-contaminated experiments. For example, Wang et al. and Li et al. used alumina crucibles and found that ionic conductivity reaches a maximum at $x = 6.7$ (0.96 \times 10^{-3} \text{ S cm}^{-1}) and $x = 6.4$ (1.0 \times 10^{-3} \text{ S cm}^{-1}), respectively. The difference between these two is that the former is for the bulk and the latter for the total. On the other hand, Buschmann et al., Inada et al., Matsuda et al. and Yi et al. synthesized Al-free compositions of Li$_x$La$_3$Zr$_{x-5}$Ta$_{7-x}$O$_{12}$ and found that ionic conductivity reaches a maximum at $x = 6.6$ (2.6 \times 10^{-4} \text{ S cm}^{-1}), x = 6.5 (6.1 \times 10^{-4} \text{ S cm}^{-1}), x = 6.6 (4.7 \times 10^{-4} \text{ S cm}^{-1})$, and $x = 6.7 (1.03 \times 10^{-3} \text{ S cm}^{-1})$, respectively. Furthermore, Kataoka et al. synthesized single crystals and found that $x = 6.6$ has the highest ionic conductivity of $1.1 \times 10^{-3}$ \text{ S cm}^{-1}. Thus, it appears that it is controversial as to what is the composition for the maximum conductivity in Li$_x$La$_3$Zr$_{x-5}$Ta$_{7-x}$O$_{12}$ even in Al-free samples.

A lot of work has also been done in modelling. Computational studies have advantages over experiments as simulation materials are literally Al free and without the complicated grain boundaries, while normally experimental samples are polycrystalline and are added with an arbitrary amount of extra Li to compensate for the Li loss in the preparation process, i.e. usually inaccurate Li composition. Both density-functional theory (DFT) and interatomic potential (IP, also called force field) based molecular dynamics (MD) simulations have been performed to study lithium garnet series, not just limited to Li$_x$La$_3$Zr$_{x-5}$Ta$_{7-x}$O$_{12}$. DFT-MD simulations are generally limited to high temperatures and a relatively short trajectory (e.g. tens of ps), while IP-MD simulations are limited by the IP models that usually have low accuracy. In recent years, the machine learning interatomic potentials (MLIP) based on the artificial neural network (NN) model have received considerable...
attention as they show a combination of DFT accuracy and IP efficiency.\textsuperscript{18–21} The present work, to be best of our knowledge, will be the first to apply MLIP based MD simulations to investigate lithium garnet series Li\textsubscript{1-x}La\textsubscript{3}Zr\textsubscript{x}/C\textsubscript{0}5Ta\textsubscript{7-x}/C\textsubscript{0}xO\textsubscript{12} (x = 5, 6, 6.5, 6.75 and 7), named Li\textsubscript{5}, Li\textsubscript{6}, Li\textsubscript{6.5}, Li\textsubscript{6.75}, and Li\textsubscript{7} afterwards.

Since experimental investigations, e.g. ionic conductivity and diffusivity, of Li\textsubscript{1-x}La\textsubscript{3}Zr\textsubscript{x}/C\textsubscript{0}5Ta\textsubscript{7-x}/C\textsubscript{0}xO\textsubscript{12} are often in the low-temperature range (<500 K), while computational studies are often in the high-temperature range (>700 K), another objective of the present work is to bridge this temperature gap by performing ionic conductivity measurements of two Al-free compositions, Li\textsubscript{6} and Li\textsubscript{6.5}, in a temperature range of 295–973 K. This is the first time that the ionic conductivities of these two Al-free compositions have been reported in such a wide temperature range. This wide-temperature measurement, together with our MLIP-MD simulations, also allows us to check if it is appropriate to apply the Arrhenius relation to the temperature dependence of lithium garnet oxides, as commonly done in the literature.

The present work is organized as follows. First, we compare the force/virial errors of MLIP, along with other commonly applied methods such as Core,\textsuperscript{22,23} induced dipole (ID),\textsuperscript{24} the self-consistent-charge density functional tight-binding (named DFTB afterwards),\textsuperscript{25} and check how well they can reproduce self-diffusivity and ionic conductivity of Li\textsubscript{6}. Second, we present the MLIP error against DFT for all compositions of Li\textsubscript{5}, Li\textsubscript{6}, Li\textsubscript{6.5}, Li\textsubscript{6.75}, and Li\textsubscript{7} and show how this MLIP is approaching DFT accuracy. Third, we examine the temperature dependence of diffusion and conduction of various compositions including the defect structure. Finally, we turn to composition dependence and focus on the question of which composition gives the highest ionic conductivity, by considering both experimental literature and present computational results.

2. Methods

2.1 Potential parameters

Potential parameters of the Core model, where an atom is treated as a fixed point charge, were taken from the work of Chen \textit{et al.}\textsuperscript{23} Potential parameters of ID and MLIP were obtained from DFT-MD results. DFT calculations for all compositions were performed using the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{26} within the projector augmented-wave (PAW)\textsuperscript{27} approach using the PBEsol\textsuperscript{28} exchange–correlation functional. The plane-wave energy cutoff was 500 eV and a single \Gamma point
was sampled. First, we performed MD simulations, using an NPT ensemble, at 1200 K for 3 ps with a 1 fs time step. We used the average structure of the MD trajectory to obtain the atomic charges in the DDEC6 scheme,\(^29\) which are listed in Table 1.

The MLIP model was trained with the SNU Interatomic Machine-learning Potential\(^{18}\) package,\(^{18}\) with atom-centered symmetry functions\(^{28}\) as the descriptor and neural network (310-30-30-1) as the regressor. DFT-MD trajectories of Li\(_5\), Li\(_6\), and Li\(_7\) were used with energy, force, and cell-virial included in the training. For each composition, configurations were sampled every 4 fs after skipping the first 100 fs. 90% of this DFT dataset was used for training and 10% was used for validation. The ID model (80% of formal charge) of Li\(_6\) was trained with CP2K\(^{30,31}\) on the ID-MD trajectory including only forces but all configurations, (80% of formal charge) of Li\(_6\) was trained with CP2K 30,31 on the ID model.

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The Haven ratio is 1 for ideal solutions where the motion of ions is independent and uncorrelated.

### 2.2 Molecular dynamics simulations

As mentioned in the introduction, there was Li loss during the high-temperature synthesis and an arbitrary amount of lithium precursor was often added to compensate for this. It is thus worthwhile comparing the normal (nominal composition) to defect structures with Li loss. In this work, in addition to Li\(_5\), Li\(_6\), Li\(_6.5\), Li\(_6.75\), and Li\(_7\), we also added the Li\(_{28}\)La\(_2\)Zr\(_{1.5}\)Ta\(_{0.5}\)O\(_{11.69}\) (10 mol% Li\(_2\)O off of Li\(_6.5\), named the Li\(_6.5\) defect afterwards).

### 2.3 Methods to study self-diffusion and ionic conduction from MD trajectories

Li diffusion was investigated by the incoherent density correlation function, from which the residence time, jump length, and self-diffusivity \(D_{Li}\) could be extracted.\(^{34}\) Ionic conductivity was calculated using the Einstein–Helfand equation\(^{35}\) by examining the coherent conductivity

\[
\sigma = \frac{1}{k_B T V} \lim_{t \to \infty} \frac{1}{t^2} \left( \sum_{i=1}^{N} \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right)
\]

where \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(V\) is the volume of the simulation cell, \(N\) is the number of atoms, \(z_e\) and \(r_i\) are the charge and coordinate of the \(i\)th atom, \(e\) is the elementary electron charge and \(t\) is the time. This (coherent) ionic conductivity is directly related to experimental measurement. We can also calculate the Nernst–Einstein conductivity from the self-diffusivity:

\[
\sigma_{NE} = \frac{(z_{Li} e)^2 D_{Li}}{k_B T \epsilon_{Li}}
\]

Where \(\epsilon_{Li}\) is the lithium concentration. The ratio of \(\sigma_{NE}\) to \(\sigma\) is known as the Haven ratio:

\[
H_R = \frac{\sigma_{NE}}{\sigma}
\]

The Haven ratio is 1 for ideal solutions where the motion of ions is independent and uncorrelated.

### Table 2. MD simulation details

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Parameters</th>
<th>Core</th>
<th>ID</th>
<th>DFTB</th>
<th>MLIP</th>
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<tr>
<td>NPT</td>
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<td>30–75</td>
<td>30–50</td>
</tr>
<tr>
<td>NVT</td>
<td>Thermostat (ps)</td>
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<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Time step (fs)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Trajectory length (ns)</td>
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<td>—</td>
<td>0.5–3</td>
<td>—</td>
</tr>
<tr>
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<td>Thermostat (ps)</td>
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<tr>
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<td>Trajectory length (ps)</td>
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<td>50</td>
</tr>
<tr>
<td>NVE</td>
<td>Time step (fs)</td>
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<td>1</td>
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<td>1</td>
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<tr>
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<td>—</td>
<td>0.5–40</td>
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<td>Approximate simulation time per ns trajectory (h)</td>
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<td>170</td>
<td>20</td>
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</table>

MD simulations of the Core and MLIP models were performed using Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)\(^{34}\) with \(2 \times 2 \times 2\) supercells. MD simulations of the ID and DFTB models were performed using CP2K with \(2 \times 2 \times 2\) and \(1 \times 1 \times 1\) supercells, respectively. Details of MD simulations including the ensemble, thermostat, barostat, etc. are listed in Table 2, along with approximate simulation cost. DFT-MD simulation of \(2 \times 2 \times 2\) supercells is expected to be 5 or 6 orders of magnitude slower than MLIP.
2.4 Experiments

Powders of \( \text{Li}_6 \) and \( \text{Li}_{6.5} \) were prepared with a solid-state reaction where stoichiometric quantities of \( \text{LiOH·H}_2\text{O} \) (Alfa Aesar, 98%), \( \text{La}_2\text{O}_3 \) (Alfa Aesar, 99%), \( \text{ZrO}_2 \) (Alfa Aesar, 99.7%) and \( \text{Ta}_2\text{O}_5 \) (Alfa Aesar, 99.85%) were used as raw materials. \( \text{La}_2\text{O}_3 \) powders were heated at 900 °C for 12 h in a MgO crucible (all crucibles and lids used in this work were MgO to avoid Al contamination). An extra 10 wt% \( \text{LiOH·H}_2\text{O} \) was added to compensate Li loss during calcination. The powders were wet-milled in a roller mixer for 12 h in polyethylene jars filled with 2-propanol and then the slurry was dried by infrared heating. The mixed powders were heated at 900 °C for 12 h with a heating and cooling rate of 2 °C min\(^{-1}\) in MgO crucibles covered by MgO lids. Afterwards, extra 10 wt% or 5 wt% \( \text{LiOH·H}_2\text{O} \) was added into the calcined powders of \( \text{Li}_6 \) and \( \text{Li}_{6.5} \), respectively, and ball-milled again, and finally pressed into 13 mm diameter pellets and sintered at 1150 °C for 12 h. The silver paste was applied to both sides of the pellets as blocking electrodes and heated at 700 °C. Impedance tests at a temperature range of 22–700 °C were performed using the same setup as in our previous work\(^{36}\) with air flow. A sinusoidal voltage with an amplitude of 10 mV was applied for the frequency range of 3 MHz to 1 Hz.

3. Results and discussion

3.1 Comparing different models for \( \text{Li}_6 \)

Before studying the whole series of \( \text{Li}_5, \text{Li}_6, \text{Li}_{6.5}, \text{Li}_{6.75}, \text{Li}_7, \) and \( \text{Li}_{6.5} \) defects, we want to compare the results of MLIP vs other commonly utilized models, using a representative composition of \( \text{Li}_6 \). We will compare the model force/virial against DFT values, and lattice parameters, self-diffusivity, and ionic conductivity against experimental values.

3.1.1 Force and virial. Atomic force (3 for each atom) and cell-virial (6 for each structure) values from the trained MLIP, ID, and DFTB models against DFT values out of 145 structures are shown in Fig. 2. Deviation from the DFT results is assessed by the root mean squared error (RMSE). The RMSE of force and virial for the MLIP model are 0.14 eV Å\(^{-1}\) and 0.20 GPa, respectively, which are lower than that of the Core, DFTB, and ID models.

3.1.2 Lattice parameters of \( \text{Li}_6 \) using different models. We first checked the temperature dependence of the lattice parameters, shown in Fig. 3 to see if these four models could reasonably predict the thermal expansion of \( \text{Li}_6 \). We include diffraction results from various literatures\(^{6,8,15,37}\) in the figure for comparison. Most experimental measurements of the lattice parameters were performed at room temperature. At room temperature, the lattice parameters of the MLIP, Core, and ID models have an error between 0.1–0.3%, while the DFTB model’s error is ~0.6%. If we use the 10 K and 300 K measurement results from \(\text{Wang et al.}^{15}\) as a reference, we see that all four models predict a nearly constant thermal expansion and similar expansion coefficients. Specifically, the thermal expansion coefficients for the MLIP, Core, ID, and DFTB models are 1.74 × 10\(^{-5}\) K\(^{-1}\), 1.51 × 10\(^{-5}\) K\(^{-1}\), 1.57 × 10\(^{-5}\) K\(^{-1}\), and 1.91 × 10\(^{-5}\) K\(^{-1}\), respectively.

3.1.3 Diffusion and conduction properties comparison among different models. Self-diffusivity and ionic conductivity from the four models are plotted in Fig. 4, along with the experimental results from single crystal measurements. All four models predict similar self-diffusivity and conductivity at high temperatures. However, if we examine the whole temperature, the MLIP model agrees with the experiments the best, while the ID and Core models significantly over- and under-estimate, respectively, the low-temperature diffusion and conduction. While it is understandable that the Core model did not perform well due to the very large force error (Fig. 2), it is surprising to see the predication from the ID model, as its force error is comparable to that of MLIP. We believe that this indicates that the ID model lacks transferability. The DFTB model predicts diffusion and conduction similar to those of MLIP, but its force error is much higher. Thus it is possible some self-cancellation leads to its reasonable performance. In addition, the DFTB model is much more computationally expensive compared with the other three models. As shown in Table 2, the simulation time for the 1 ns trajectory is approximately 170 hours for a 1 × 1 × 1 supercell, while the other models take less than 40 hours for supercells that are 8 times bigger.

Self-diffusivity from MLIP is slightly higher than the experimental values at low temperatures. It is worth noting that the work of Stanje et al.\(^{37}\) only measured the relaxation time from

![Image](image.png)
nuclear magnetic resonance experiments and assumed a jump length of 2 Å. As will be shown later in Fig. 6b, we found the jump length is 2.3 Å at 400 K. If 2.3 instead of 2 Å was used, the agreement of MLIP to the experiment will be even better.

3.2 Force/virial error and lattice parameter of Li₅, Li₆, Li₆.₅, Li₆.₇₅, and Li₇

Force and virial error against DFT (i.e. PBEsol) for the whole series studied in the present work are shown in Table 3. To understand the meaning of these numbers, we also compared the error between two different exchange–correlation functionals, i.e. PBE vs PBEsol, and found the force error was about 0.1 eV Å⁻¹. In other words, we can argue the DFT error might be around 0.1 eV Å⁻¹ and our MLIP model is approaching DFT accuracy but much faster (DFT will be 5 to 6 orders of magnitude slower based on our estimate). Furthermore, it is transferable as it shows similar errors for different compositions, i.e. Li₅ to Li₇.

Before applying this MLIP model to study the diffusion and conduction properties, we want to check if it can reproduce the structure of different compositions in terms of lattice parameters. The temperature dependence of lattice parameters is shown in Fig. 5a. For cubic phases such as Li₅, Li₆, Li₆.₅, and Li₆.₇₅ defects, lattice parameters increase linearly with increasing temperatures with similar thermal expansion coefficients. The lattice parameters of Li₆.₅ and Li₆.₅ defects are almost the same. For Li₇, the tetragonal to cubic phase transition takes place within a temperature range between 1000 and 1100 K, which is slightly higher than the experimental value of 913 K. For Li₆.₇₅, the tetragonal to the cubic phase transition is around 700–800 K.

Fig. 5b shows calculated lattice parameters at room temperature as a function of x (Li content) in LiₓLa₃ZrTaO₁₂. The experimental data of single crystals from Kataoka et al.,¹⁰ Al-free powder samples from Buschmann et al.,³⁹ Matsuda et al.,⁶ Awaka et al.,⁸ and Thompson et al.⁴⁰ are shown in the plot for comparison. For cubic phases, the lattice parameter increases linearly with increasing Li content. Our simulation data agree very well with the experimental values reported in the literatures. Both simulation and experimental results suggest that the cubic to tetragonal transition takes place at around x = 6.6 at room temperature, with the exception of Kataoka et al.¹⁰ where it was cubic even at x = 6.8.

3.3 Temperature dependence of self-diffusion

Fig. 6a–c summarizes the residence time, jump length, and self-diffusivity of Li₅, Li₆, Li₆.₅, Li₆.₇₅, and Li₇ at the temperature range of 400–1200 K. In terms of self-diffusivity (Fig. 6c), temperature dependence is roughly Arrhenius with activation

<table>
<thead>
<tr>
<th>Composition</th>
<th>Force (eV Å⁻¹)</th>
<th>Virial (GPa)</th>
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<tbody>
<tr>
<td>Li₅ PBE vs. Li₅ PBEsol</td>
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<td>2.57</td>
</tr>
<tr>
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<td>0.23</td>
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<td>MLIP vs. Li₆ PBEsol</td>
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<td>MLIP vs. Li₆.₅ PBEsol</td>
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<tr>
<td>MLIP vs. Li₇ PBEsol</td>
<td>0.11</td>
<td>0.22</td>
</tr>
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</table>
energies (0.26–0.33 eV), except for Li7, where the cubic (0.27 eV) and tetragonal (1.33 eV) phase have very different activation energies. Li5 has the highest diffusivity at high temperatures while Li6.5 has the highest diffusivity at low temperatures. Self-diffusivity is related to residence time ($t$) and jump length ($l$) as $l^2/(6t)$. Fig. 6b indicates that jump lengths have a narrow range of 1–3 Å, with shorter jumps at higher temperatures. The nearest neighbor tetrahedral and octahedral sites in lithium garnets are 1.5–2.5 Å. The plot of residence time, the average time a Li spends on a site before jumping to the next site, largely follows Fig. 6c, as the jump length is relatively temperature insensitive.

To show a comparison of self-diffusivities between the results calculated from our MD simulations and those from the experiments, we plotted the results of Li5 and Li6.5 separately in Fig. 6(d and e). A comparison for Li6 was shown previously in Fig. 4a. Computed self-diffusivity values are slightly lower than those from quasi-elastic neutron scattering (QENS) measurements for Li5, while they are slightly higher than those from pulse-field NMR measurements for single crystals of Li6.5.
compared the normal and defect structure of Li_{6.5}. Self-diffusivities of these two structures are almost the same at high temperatures, e.g. 900–1200 K, while the defect structure has noticeably lower diffusivity at low temperatures.

3.4 Temperature dependence of ionic conductivity

Similar to the self-diffusivity plot, we present in Fig. 7a the ionic conductivity of Li_{5}, Li_{6}, Li_{6.5}, Li_{6.75}, and Li_{7} and in Fig. 7d–f the comparison to experiments. As discussed in the introduction, MD simulations are usually performed at high temperatures while the experiments are carried out at low temperatures. If we only have ionic conductivity data of a limited temperature range, we usually assume an Arrhenius relation. However, examination of our wide-temperature experimental measurement of ionic conductivities of Li_{6} and Li_{6.5} from the present work, along with that from Stanje et al.\textsuperscript{37} and Jin et al.\textsuperscript{44} in Fig. 7d and e, clearly suggests a non-Arrhenius behavior. Given this, we chose a common non-Arrhenius model, Vogel–Tammann–Fulcher (VTF) equation\textsuperscript{45–47} with 

\[ \sigma = A \cdot \exp \left[ \frac{-B}{T - T_0} \right], \]

where \(A\) is a pre-exponential factor, \(B\) the artificial activation energy, and \(T_0\) the Vogel temperature below which ions are not mobile. We applied the VTF fit to our MD data, except for Li_{7} where we applied the Arrhenius fit for the cubic (0.13 eV) and tetragonal (1.15 eV) phases separately. The transition temperature \(T_0\) is plotted in Fig. 7b. Its values are below 200 K and decrease with increasing Li content, which suggests that higher Li content might lead to higher conductivity at low temperatures.

If we extrapolate MD data through the VTF fit to lower temperatures, we can see they agree well with the single crystal data from experiments, except for Li_{6.75}. In Fig. 7d, we also compared the Nernst–Einstein conductivity from the self-diffusivity and (coherent) ionic conductivity of Li_{6}. Ionic conductivity is higher than the Nernst–Einstein conductivity, which indicates the ionic motion is positively cooperated, i.e. ions moving together are faster than moving alone. This positive cooperation was called concerted in the studies of Li_{7}.\textsuperscript{11,48} Haven ratio, i.e., Nernst–Einstein over ionic conductivity, is plotted in Fig. 7c for all compositions, with values between 0.1 and 0.4. A Haven ratio of ~0.3 was reported by He et al.\textsuperscript{48} (900 K) and Mottet et al.\textsuperscript{49} The temperature dependence of the Haven ratio indicates a higher value (less cooperation) at higher temperatures. This is intuitive as it is expected that the thermal agitation tends to break the atomic cooperation, which makes the atomic motion more independent. In Fig. 7e, we compared the ionic conductivity of Li_{6.5} and Li_{6.5} defects. Similar to the self-diffusivity comparison in Fig. 6e, the ionic conductivity of the normal structure is higher.

3.5 Composition dependence

To examine the composition dependence of diffusion, we plotted in Fig. 8a the self-diffusivity at 1200 K and 400 K to...
represent high and low temperature, respectively. At 1200 K, the self-diffusivity decreases with increasing Li content, suggesting a vacancy mechanism. At high temperatures, each Li ion has enough thermal energy to move around. However, as Li ions must move through a network of interconnected tetrahedral and octahedral sites, they will be competing for the vacant sites. At low temperatures, e.g. 400 K, Li ions do not have sufficient thermal energy so only some of them are moving around. Adding more Li will increase the overall Li–Li repulsion and initiate more Li to move, leading to overall increasing diffusivity with increasing composition.

The composition dependence of ionic conductivity is shown in Fig. 8b. It is worth noting that we could not detect Li conduction at 400 K for Li7 so MD simulation suggests the maximum conductivity at 400 K occurs at Li6.75. If we compare Fig. 8b with Fig. 1 presented in the introduction for room temperature experimental values from various literatures, we can see the overall composition dependence looks similar. The difference is the peak composition. For example, results from Buschmann et al.6 indicate the peak composition is Li6.5. Yi et al.9 showed Li6.7 has the highest ionic conductivity. Inada et al.7 found Li6.75 to be cubic and its ionic conductivity is lower than that of Li6.5. Matsuda et al.8 reported the peak at Li6.6 and Li content 6.625 to 7 to be tetragonal. While these reports are all on polycrystalline samples, Kataoka et al.10 synthesized single crystals and found Li6.2 to Li6.8 to be cubic with a peak conductivity at Li6.6. From the perspective of experiments, single crystals are probably preferred over polycrystals as they are less susceptible to the influence of density and grain boundary segregation (e.g. space charge layer). However, an arbitrary amount of Li excess had to be added to all these samples, which makes the composition used for conductivity measurement a little ambiguous after an arbitrary amount of Li loss during the high temperature processing. Our MD results suggest that Li loss, e.g. Li6.5 defect, will decrease the ionic conductivity. Finally, experimental samples are also subjected to H2O and CO2 contamination to form LiOH and Li2CO3 and it is reasonable to expect such contamination will be more severe when Li is more mobile, i.e. high Li content. Nonetheless, it is probably reasonable to argue the maximum conductivity occurs somewhere between 6.6 and 6.8 based on combined experimental and computational results.

4. Conclusions

In this work, we studied the diffusion and conduction of lithium garnet oxides LiLa3Zr7−xTa5−xO12 (x = 5, 6, 6.5, 6.75, and 7) with MD simulations based on a machine learning interatomic potential (MLIP). We found that this MLIP is approaching DFT accuracy in force error. It is more accurate than other commonly applied models such as Core, induced dipole (ID), and DFTB and predicts diffusion and conduction properties that agree with single crystal experimental data much better than the other three models, when using LiLa3Zr7Ta5O12 as a model material. This MLIP also produces self-diffusivity and ionic conductivity values agreeing with experimental data across the x composition range. Examination of computational and experimental ionic conductivities suggests that the temperature dependence is non-Arrhenius which can be fit to a Vogel–Tammann–Fulcher equation with a Vogel temperature below room temperature. Examination of the computational and experimental values together also suggests that the maximum room-temperature conductivity occurs between x = 6.6 to 6.8 with the precise composition depending on Al/H2O/CO2 contamination, Li loss, grain boundary, density, etc.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We wish to acknowledge the Michigan State University High Performance Computing Center and the Institute for Cyber-Enabled Research for access to their computing resources. We acknowledge the financial support by a gift from Mercedes-Benz Research & Development North America (MBRDNA). Yue...
Jiang would like to acknowledge the financial support from the China Scholarship Council (No. 201806240110).

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