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Study of diffusion and conduction in lithium garnet oxides $Li_xLa_3Zr_{x-5}Ta_{7-x}O_{12}$ by machine learning interatomic potentials

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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_xLa₃Zr_{x-5}Ta_{7-x}O₁₂.

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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.¹ Since Thangadurai *et al.* first reported Li ion conduction in Li₅La₃M₂O₁₂ (M = Nb, Ta) in 2003² and then high-conductivity cubic Li₇La₃Zr₂O₁₂ in 2007,³ many experimental and computational efforts have been devoted to investigate the Li garnet series Li_xLa₃Zr_{x-5}Ta_{7-x}O₁₂ (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-} La₃Zr_{x-5}Ta_{7-x}O₁₂ (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.*⁴ and Li *et al.*⁵ 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.*,⁶ Inada *et al.*,⁷ Matsuda *et al.*⁸ and Yi *et al.*⁹ synthesized Al-free compositions of $\text{Li}_x\text{La}_3\text{Zr}_{x-5}\text{Ta}_{7-x}\text{O}_{12}$ and found that ionic conductivity reaches a maximum at x = 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.*¹⁰ 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 $\text{Li}_x\text{La}_3\text{Zr}_{x-5}\text{Ta}_{7-x}\text{O}_{12}$ 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 complication of 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)^{11,12} and interatomic potential (IP, also called force field)¹³⁻¹⁷ based molecular dynamics (MD) simulations have been performed to study lithium garnet series, not just limited to $Li_xLa_3Zr_{x-5}Ta_{7-x}O_{12}$. 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

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Fig. 1 Summary of the composition dependence of ionic conductivity of Li_xLa₃Zr_{x-5}Ta_{7-x}O₁₂ from the literature.⁴⁻¹⁰ SC: single crystal.

attention as they show a combination of DFT accuracy and IP efficiency.^{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 $\text{Li}_x\text{La}_3\text{Zr}_{x-5}\text{Ta}_{7-x}\text{O}_{12}$ (x = 5, 6, 6.5, 6.75 and 7), named Li_5 , Li_6 , $\text{Li}_{6.5}$, $\text{Li}_{6.75}$, and Li_7 afterwards.

Since experimental investigations, *e.g.* ionic conductivity and diffusivity, of $\text{Li}_x\text{La}_3\text{Zr}_{x-5}\text{Ta}_{7-x}O_{12}$ are often in the lowtemperature 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_6 and $\text{Li}_{6.5}$, 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,^{22,23} induced dipole (ID),²⁴ the self-consistent-charge density functional tight-binding (named DFTB afterwards),²⁵ and check how well they can reproduce self-diffusivity and ionic conductivity of Li_6 . Second, we present the MLIP error against DFT for all compositions of Li_5 , Li_6 , $\text{Li}_{6.5}$, $\text{Li}_{6.75}$, and Li_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 *et al.*²³ Potential parameters of ID and MLIP were obtained from DFT-MD results. DFT calculations for all compositions were performed using the Vienna *ab initio* simulation package (VASP)²⁶ within the projector augmented-wave (PAW)²⁷ approach using the PBEsol²⁸ exchange–correlation functional. The plane-wave energy cutoff was 500 eV and a single Γ point

Table 1 DDEC6 charge of each composition

	Li_5	Li ₆	Li _{6.5}	Li _{6.75}	Li_7
La	1.87	1.88	1.88	1.84	1.89
Та	2.32	2.33	2.33	2.23	_
Zr	_	2.23	2.23	2.18	2.25
0	-1.20	-1.26	-1.29	-1.28	-1.32
Li	0.83	0.82	0.82	0.81	0.81

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 packagE-version Neural Network (SIMPLE-NN) package,¹⁸ with atom-centered symmetry functions²⁰ as the descriptor and neural network (310-30-30-1) as the regressor. DFT-MD trajectories of Li₅, Li₆, and Li₇ 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 DFT-MD trajectory including only forces but all configurations, as we did previously for Li7.32 DFTB parameterization for the Li-La-Zr-Ta-O chemical space was obtained with the Tight-Approximation-enhanced binding Global Optimization (TANGO) method³³ with CP2K as the DFT package including both energy and force. It is worth noting that MLIP does not include atomic charge parameters. The numbers in Table 1 were only used for the calculation of conductivity. With DFTB, the Mulliken charge was utilized.

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 Li₅, Li₆, Li_{6.5}, Li_{6.75}, and Li₇, we also added the Li_{5.88}La₃Zr_{1.5}Ta_{0.5}O_{11.69} (10 mol% Li₂O off of Li_{6.5}, named the Li_{6.5} defect afterwards).

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.

2.3 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 ($D_{\rm Li}$) could be extracted.¹⁴ Ionic conductivity was calculated using the Einstein–Helfand equation³⁵ by examining the coherent conductivity

$$\sigma = \frac{1}{k_{\rm B}TV} \lim_{t \to \infty} \frac{1}{6t} \left\langle \left(\sum_{i=1}^{N} z_i er_i(t) - \sum_{i=1}^{N} z_i er_i(0) \right)^2 \right\rangle$$

where $k_{\rm B}$ is the Boltzmann constant, *T* is the temperature, *V* is the volume of the simulation cell, *N* is the number of atoms, z_i and \mathbf{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:

$$\sigma_{\rm NE} = (z_{\rm Li}e)^2 \frac{D_{\rm Li}}{k_{\rm B}T} (c_{\rm Li})$$

Where c_{Li} is the lithium concentration. The ratio of σ_{NE} to σ is known as the Haven ratio:

$$H_{\rm R} = \frac{\sigma_{\rm NE}}{\sigma}$$

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

Table 2 MD simulation details. Approximate simulation time of four models for 1 ns of trajectory is shown (core, ID, and MLIP models were using 64 CPUs while the DFTB model was using 28 CPUs). It is worth noting that the DFTB model is using $1 \times 1 \times 1$ while other models are using $2 \times 2 \times 2$ supercells. DFT-MD is expected to be 5 or 6 orders of magnitude slower than MLIP

Ensemble	Parameters	Core	ID	DFTB	MLIP
NPT	Thermostat (ps)	0.05	0.1	0.1	0.1
	Barostat (ps)	0.25	0.5	0.5	0.5
	Timestep (fs)	1	1	1	1
	Lattice parameter average range (ps)	30-50	30-50	30-75	30-50
NVT	Thermostat (ps)	_	_	1	_
	Timestep (fs)	_	_	1	_
	Trajectory length (ns)	_	_	0.5 - 3	_
NVE equilibration	Thermostat (ps)	0.1	0.1	_	0.1
1	Trajectory length (ps)	50	50	_	50
NVE	Timestep (fs)	1	1	_	1
	Trajectory length (ns)	0.5-300	0.5-8	_	0.5 - 40
<i>NVT</i> /NVE	Approximate simulation time per ns trajectory (h)	0.3	40	170	20

2.4 Experiments

Powders of Li₆ and Li_{6.5} were prepared with a solid-state reaction where stoichiometric quantities of LiOH·H₂O (Alfa Aesar, 98%), La₂O₃ (Alfa Aesar, 99.9%), ZrO₂ (Alfa Aesar, 99.7%) and Ta_2O_5 (Alfa Aesar, 99.85%) were used as raw materials. La_2O_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% LiOH·H2O 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 calcined at 1000 °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% LiOH·H2O was added into the calcined powders of Li6 and Li65, 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 work³⁶ 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 Li₆

Before studying the whole series of Li_5 , Li_6 , Li_6 , $Li_{6.5}$, $Li_{6.75}$, Li_7 , and $Li_{6.5}$ defects, we want to compare the results of MLIP vs other commonly utilized models, using a representative composition of 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 \AA^{-1} and 0.20 GPa, respectively, which are lower than that of the Core, DFTB, and ID models.

3.1.2 Lattice parameters of Li₆ 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 Li₆. 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 $\sim 0.6\%$. If we use the 10 K and 300 K measurement results from 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} , 1.51×10^{-5} , 1.57×10^{-5} , 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 $1 \times 1 \times 1$ 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



Fig. 2 A comparison of (a) atomic forces and (b) cell virials of Core, DFTB, ID, and MLIP (scatter points) against DFT (black lines) for Li6.



Fig. 3 Lattice parameter as a function of temperature of $Li_6La_3ZrTaO_{12}$ from different models. Literature values of Al-free samples at room temperature^{6,8,15,37} are shown for comparison. XRD: X-ray diffraction; ND: neutron diffraction. Solid lines are the linear fit.

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 $\rm Li_5, \, Li_6, \, Li_{6.5}, \, Li_{6.75}, \, and \, Li_7$

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

Table 3The root mean squared error (RMSE) values of atomic forces, andcell virials between MLIP and DFT for all the compositions studied. RMSEbetween PBE and PBEsol are shown for comparison

	Force (eV $Å^{-1}$)	Virial (GPa)
Li ₅ PBE vs. Li ₅ PBEsol	0.10	2.57
MLIP vs. Li ₅ PBEsol	0.15	0.23
MLIP vs. Li ₆ PBEsol	0.14	0.20
MLIP vs. Li _{6 5} PBEsol	0.12	0.21
MLIP vs. Li _{6 75} PBEsol	0.12	0.22
MLIP vs. Li ₇ PBEsol	0.11	0.22

parameters. The temperature dependence of lattice parameters is shown in Fig. 5a. For cubic phases such as Li_5 , Li_6 , $\text{Li}_{6.5}$, and $\text{Li}_{6.5}$ defects, lattice parameters increase linearly with increasing temperatures with similar thermal expansion coefficients. The lattice parameters of $\text{Li}_{6.5}$ and $\text{Li}_{6.5}$ defects are almost the same. For Li_7 , 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.³⁸ For $\text{Li}_{6.75}$, 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 Li_xLa₃Zr_{x-5}Ta_{7-x}O₁₂. 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

3.3 Temperature dependence of self-diffusion

Fig. 6a–c summarizes the residence time, jump length, and selfdiffusivity of Li₅, Li₆, Li_{6.5}, Li_{6.75}, and Li₇ at the temperature range of 400–1200 K. In terms of self-diffusivity (Fig. 6c), temperature dependence is roughly Arrhenius with activation



Fig. 4 (a) Self-diffusivity and (b) ionic conductivity of Li₆ as a function of inverse temperature from different models. Single crystal (SC) data from Stanje et al.³⁷ are shown for comparison.



Fig. 5 (a) Lattice parameters as a function of temperature of Li₅, Li₆, Li_{6,5}, Li_{6,7}, Li₇, and Li_{6,5} defects. The solid lines are a guide to the eye. (b) Lattice parameters from MLIP-MD at room temperature *versus x* (Li content). Literature values of single crystals (SC)¹⁰ and Al-free powders^{6,8,39,40} are shown for comparison.



Fig. 6 Inverse temperature dependence of (a) residence time, (b) jump length, and (c) self-diffusivity of Li of Li₅, Li_{6,5}, Li_{6,5}, Li_{6,75}, and Li₇. The solid lines are a guide to the eye and shades in (b) are the range of error. (d and e) Self-diffusivity as a function of inverse temperature for Li₅ and Li_{6,5}. Experimental data from pulse-field gradient NMR measurements of single crystal (SC)⁴¹⁻⁴³ and QENS measurement¹⁴ are shown for comparison.

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 Li_{6.5} has the highest diffusivity at low temperatures. Self-diffusivity is related to residence time (*t*) and jump length (*l*) as l2/(6t). Fig. 6b indicates that jump lengths have a narrow range of 1–3.5 Å, with shorter jumps at higher temperatures. The nearest neighbor tetrahedral and octahedral sites in lithium garnets are 1.5–2.5 Å.¹⁴ 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 Li_5 and $Li_{6.5}$ separately in Fig. 6(d and e). A comparison for Li_6 was shown previously in Fig. 4a. Computed self-diffusivity values are slightly lower than those from quasi-elastic neutron scattering (QENS) measurements¹⁴ for Li_5 , while they are slightly higher than those from pulse-field NMR measurements^{41–43} for single crystals of $Li_{6.5}$. In Fig. 6e, we also

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 , $\text{Li}_{6.5}$, $\text{Li}_{6.75}$, 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 $\text{Li}_{6.5}$ from the present work, along with that from Stanje *et al.*³⁷ and Jin *et al.*⁴⁴ in Fig. 7d and e, clearly suggests a non-Arrhenius model, Vogel-Tam-

mann–Fulcher (VTF) equation^{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 Li₇ 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 Li6. 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 Li₇.^{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 \sim 0.3 was reported by He et al.48 (900 K) and Mottet et al.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 Li6.5 and Li6.5 defects. Similar to the selfdiffusivity 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



Fig. 7 (a) lonic conductivity of Li₅, Li₆, Li_{6,5}, Li_{6,5}, Li_{6,5}, and Li₇ as a function of inverse temperature. Solid lines are fits to the VTF equation (except for Li₇ where two Arrhenius fits are applied to the high and low temperatures). Error bars of Li_{6,75} and Li₇ represent the ionic conductivity in the *ab* and *c* directions. (b) Vogel temperature (T_0) of different Li content. (c) H_R for the composition series. Solid lines are a guide to the eye. (d–f) Comparison of results from (a) and experimental values for Li₆, Li_{6,5}/Li_{6,5} defect, and Li_{6,75}. Experimental values include single crystal (SC),^{10,37,41,43} Al-free,⁹ and Al contaminated powders (through alumina crucibles).⁴⁴

Fig. 8



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 Li_{6.75}. 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. Yi et al.9 showed Li_{6.7} has the highest ionic conductivity. Inada et al.⁷ found Li_{6.75} to be cubic and its ionic conductivity is lower than that of $Li_{6.5}$. Matsuda *et al.*⁸ reported the peak at $Li_{6.6}$ 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 Li_{6.2} to Li_{6.8} to be cubic with a peak conductivity at Li_{6.6}. 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. Li_{6.5} 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 $Li_x La_3 Zr_{x-5} Ta_{7-x} O_{12}$ (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 Li₆La₃Zr-TaO₁₂ as a model material. This MLIP also produces selfdiffusivity 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.

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