Supporting Information

Atomistic Insight into Ion Transport and Conductivity in Ga/Al-Substituted Li$_7$La$_3$Zr$_2$O$_{12}$ Solid Electrolytes

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S1. Sampling the Potential Energy Distributions of \( \text{Ga}_x\text{Al}_{0.2-x} \)

In this work, a \( 3 \times 3 \times 3 \) LLZO supercell (containing 1944 available Li sites, 648 La atoms, 432 Zr atoms, and 2592 O atoms) is considered, with substituent Ga and Al cations confined to the tetrahedral (\( T_d \)) sites of the structure. There exists an enormous number of conceivable arrangements for the Li, Li vacancies, Al and Ga within the Li sublattice. A simple sampling approach consists of randomly adjusting the Li/Ga/Al/vacancy arrangements according to the desired stoichiometry\(^{1-4}\). Accordingly, for each \( x \) in \( \{0.0, 0.1, 0.2\} \), a total of 10000 random structures of \( \text{Ga}_x\text{Al}_{0.2-x} \) were generated, and those with the lowest total potential energy, \( \text{PE} \) (electrostatic + short range) for each value of \( x \) were selected for fine-tuning of interatomic parameters and subsequent atomistic simulations. Calculations of the \( \text{PE} \) on the static structures were performed using LAMMPS\(^5\). The potential parameters were taken from Jalem et al.\(^1\) for Ga-substituted LLZO, and from Pedone et al.\(^6\) for the Al-O potential. These parameters are reported in Table S1. Figure S1 depicts the resulting PE histograms.

![Figure S1: PE histograms for \( \text{Ga}_x\text{Al}_{0.2-x} \), with \( x \) in \( \{0.0, 0.1, 0.2\} \)](image)

S2. Fine Tuning of the Interatomic Potential

We model the short range interaction between atoms \( i \) and \( j \), \( U_{ij}^{\text{VdW}} \), using the Buckingham potential:

\[
U_{ij}^{\text{VdW}} = A_{ij} \exp \left( -B_{ij} |r_{ij}| \right) - \frac{C_{ij}}{|r_{ij}|^6},
\]

(S1)
where $|\mathbf{r}_{ij}|$ is the distance between particles and $A_{ij} \geq 0$, $B_{ij} > 0$ and $C_{ij} \geq 0$ are the Buckingham parameters. Initially, the potential parameters corresponded to those reported by Jalem et al.\textsuperscript{1} for Ga-substituted LLZO, and from Pedone et al.\textsuperscript{6} for the Al-O potential (Table S1).

Table S1: Buckingham parameters for Ga- and Al-substituted LLZO prior to fine tuning. The values were taken from Jalem et al.\textsuperscript{1} for Ga-substituted LLZO, and from Pedone et al.\textsuperscript{6} for the Al-O potential.

<table>
<thead>
<tr>
<th>Interactions</th>
<th>$A$ (eV)</th>
<th>$B$ (Å$^{-1}$)</th>
<th>$C$ (eV Å$^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$^{2.1-}$ - O$^{1.4-}$</td>
<td>13298.83</td>
<td>4.963</td>
<td>0.0</td>
</tr>
<tr>
<td>Al$^{2.1-}$ - O$^{1.4-}$</td>
<td>7042.593</td>
<td>4.316</td>
<td>101.495</td>
</tr>
<tr>
<td>Li$^{0.7+}$ - O$^{1.4-}$</td>
<td>876.86</td>
<td>4.110</td>
<td>0.0</td>
</tr>
<tr>
<td>La$^{2.1+}$ - O$^{1.4-}$</td>
<td>14509.63</td>
<td>4.102</td>
<td>30.83</td>
</tr>
<tr>
<td>Zr$^{2.8+}$ - O$^{1.4-}$</td>
<td>2153.80</td>
<td>3.439</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^{1.4-}$ - O$^{1.4-}$</td>
<td>4869.99</td>
<td>4.163</td>
<td>27.22</td>
</tr>
</tbody>
</table>

After fine tuning to match the structural cell parameters reported by Rettenwander et al.\textsuperscript{7}, we found that the optimal value of $B_{\text{Li-O}}$ varies with $x$. The variation of the optimal $B_{\text{Li-O}}$ with $x$ is shown in Fig. S2.

Figure S2: Buckingham parameter $B_{\text{Li-O}}$ for Ga$_x$Al$_{0.2-x}$ with $x$ in \{0.0, 0.05, 0.10, 0.15, 0.20\}. 
S3. Integrated Autocorrelation Function for LLZO

Sampling efficiency of MD and GSHMC methods can be compared by calculating the integrated autocorrelation function (IACF),

\[ \text{IACF}(f(t)) = \int_{0}^{\infty} \text{ACF}(f(t)) \, dt, \]  

(S2)

where \( f \) is a time dependent property, and, ACF is the autocorrelation function which is defined as

\[ \text{ACF}(f(t)) = \langle f(t_0)f(t_0 + t) \rangle_{t_0}. \]  

(S3)

The IACF in Eq. S2 estimates the time needed, on average, to generate a non-correlated sample. Low IACF values indicate a low correlation between samples, therefore, a more efficient sampling is achieved. For both MD and GSHMC simulations, and considering potential energy as the property of interest, IACFs for \( \text{Ga}_{0.0}\text{Al}_{0.2} \), \( \text{Ga}_{0.1}\text{Al}_{0.1} \) and \( \text{Ga}_{0.2}\text{Al}_{0.0} \) systems have been calculated at 233 K, 273 K and 313 K during the equilibration stage in the NVT ensemble (see Table S2).

Table S2: GSHMC and MD IACF values for \( \text{Ga}_{x}\text{Al}_{0.2-x} \) at different temperatures.

<table>
<thead>
<tr>
<th>( x )</th>
<th>233 K MD</th>
<th>233 K GSHMC</th>
<th>273 K MD</th>
<th>273 K GSHMC</th>
<th>313 K MD</th>
<th>313 K GSHMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>39.7</td>
<td>4.4</td>
<td>25.9</td>
<td>7.1</td>
<td>11.3</td>
<td>8.8</td>
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<tr>
<td>0.1</td>
<td>29.6</td>
<td>2.1</td>
<td>19.0</td>
<td>2.6</td>
<td>7.6</td>
<td>2.9</td>
</tr>
<tr>
<td>0.2</td>
<td>19.4</td>
<td>1.5</td>
<td>10.7</td>
<td>1.8</td>
<td>6.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

S4. Thermal Expansion in Al/Ga-Containing LLZO Garnet

Thermal expansion/contraction of Al/Ga-substituted LLZO has been calculated for temperatures between 193 K and 313 K for \( \text{Ga}_{0.0}\text{Al}_{0.2} \), \( \text{Ga}_{0.1}\text{Al}_{0.1} \) and \( \text{Ga}_{0.2}\text{Al}_{0.0} \). Our calculations reveal that increasing the Ga content in \( \text{Ga}_{x}\text{Al}_{0.2-x} \) garnets produce a subtle increase in the lattice parameter at all temperatures (see Fig. S3).
Figure S3: Thermal expansion in Ga$_x$Al$_{0.2-x}$, for $x$ in \{0.0, 0.1, 0.2\}

References


