Grain Boundary Contributions to Li-Ion Transport in the Solid Electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO)

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Supporting Information

ABSTRACT: The oxide with nominal composition Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) is a promising solid electrolyte thanks to its high (bulk) Li-ion conductivity, negligible electronic transport, chemical stability against Li metal, and wide electrochemical window. Despite these promising characteristics, recent measurements suggest that microstructural features, specifically, grain boundaries (GBs), contribute to undesirable short-circuiting and resistance in polycrystalline LLZO membranes. Toward the goal of understanding GB-related phenomena, the present study characterizes the energetics, composition, and transport properties of three low-energy ($\Sigma 3$ and $\Sigma 5$) symmetric tilt GBs in LLZO at the atomic scale. Monte Carlo simulations reveal that the GB planes are enriched with Li, and to a lesser extent with oxygen. Molecular dynamics simulations on these off-stoichiometric boundaries were used to assess Li-ion transport within and across the boundary planes. We find that Li transport is generally reduced in the GB region; however, the magnitude of this effect is sensitive to temperature and GB structure. Li-ion diffusion is comparable in all three GBs at the high temperatures encountered during processing, and only 2–3 times slower than bulk diffusion. These similarities vanish at room temperature, where diffusion in the more compact $\Sigma 3$ boundary remains relatively fast (half the bulk rate), while transport in the $\Sigma 5$ boundaries is roughly 2 orders of magnitude slower. These trends mirror the activation energies for diffusion, which in the $\Sigma 3$ boundaries are up to 35% larger than in bulk LLZO, and are identical to the bulk in the $\Sigma 5$ boundary. Diffusion within the $\Sigma 5$ boundaries is observed to be isotropic. In contrast, intraplane diffusion in the $\Sigma 3$ boundary plane at room temperature is predicted to exceed that of the bulk, while transboundary diffusion is ~200 times slower than in the bulk. Our observation of mixed GB transport contributions (some boundaries support fast diffision, while others are slow) is consistent with the limited GB resistance observed in polycrystalline LLZO samples processed at high temperatures. These data also suggest that higher-energy GBs with less-compact structures should penalize Li-ion conductivity to a greater degree.

I. INTRODUCTION

Batteries with enhanced energy densities and safety are desirable for emerging applications such as all-electric vehicles. One pathway to improve performance beyond that of existing Li-ion battery chemistries is through the development of solid electrolytes. A viable solid electrolyte would facilitate the use of high-capacity anodes, such as metallic lithium, and accelerate the adoption of high-capacity cathodes, such as Li–S or Li–air. Solidelectrolytes could also improve safety, by replacing the flammable organic liquid electrolytes used in conventional Li-ion batteries.

Among the handful of Li-ion-conducting solids, the garnet with nominal composition Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) is one of the most promising solid electrolytes. LLZO exhibits high ionic conductivity ($10^{-4}$–$10^{-3}$ S cm$^{-1}$ in supervelodoped LLZO), limited electronic transport, chemical stability and extremely low interfacial resistance with Li metal anodes, against Li metal and has a large bandgap ($\sim 6$ eV). LLZO also has a high shear modulus, which is believed to aid in suppressing Li dendrite formation during battery charging. Typical protocols for the synthesis of LLZO generate samples that are polycrystalline. It is well-known that interfaces between individual crystallites, grain boundaries (GBs), can strongly influence the properties of essentially all types of materials. In the case of LLZO, GB-related phenomena have been implicated in two areas: the transport of Li-ions and short-circuiting.

Regarding transport, GBs can either suppress or enhance the rates of ion diffusion in polycrystalline oxides. For example, ionic diffusion is enhanced (relative to bulk diffusion) due to the presence of GBs in Al$_2$O$_3$, HfO$_2$, and UO$_2$. Conversely, GBs hinder ion transport in SrTiO$_3$, YSZ, and doped CeO$_2$.

In LLZO, GB resistance has been reported to decrease Li-ion conductivity. These effects can be partially minimized by altering the synthesis conditions to increase the density of LLZO (by reducing porosity), increase the grain size (i.e.,

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minimize the volume fraction of GBs), and/or improve contact at the GBs.\textsuperscript{25,26} For example, increasing the hot-pressing temperature to 1100 °C resulted in higher-density LLZO samples (99% of theoretical density) and larger grain sizes; consequently, the GB contribution to the total resistance decreased to 8%, compared to a larger 26% contribution for hot-pressing at a lower temperature of 1000 °C.\textsuperscript{25}

Regarding short-circuiting, recent studies have shown that Li metal "dendrites" can penetrate stiff LLZO membranes along its GB network, resulting in cell failure.\textsuperscript{27–30} This surprising result indicates that microstructural features, and not elastic properties alone,\textsuperscript{17,20} should be considered in the design of practical solid electrolytes.

The preceding examples suggest that understanding the connection between structure and transport (of Li metal and Li-ions) at GBs will accelerate the development of solid electrolytes. Despite the importance of GBs, the atomic-scale processes occurring at GB in LLZO remain poorly understood. The present study aims to close this knowledge gap by combining classical Monte Carlo (MC) and molecular dynamics (MD) simulations to predict the energetics, composition, and transport properties of three low-energy (\(\Sigma 3\) and \(\Sigma 5\)) symmetric tilt GBs\textsuperscript{41} in LLZO.

Our calculations reveal that the equilibrium composition near GBs in LLZO (i.e., in the GB plane) is enriched with Li, and to a lesser extent with oxygen. MD simulations on these off-stoichiometric structures indicate that the mobility of Li-ions is generally reduced in all three GBs (compared to bulk LLZO), although the magnitude of this reduction can be small in compact boundaries, and at the high temperatures encountered during synthesis (~1000 K). The suppression of Li-ion mobility is largest in the \(\Sigma 5\) boundaries, where our calculations predict activation energies for diffusion are up to 35% greater than in the bulk. In contrast, diffusion in the compact \(\Sigma 3\) boundary is characterized by an activation energy that is identical to bulk LLZO. Consequently, the rate of Li migration in this GB is only slightly suppressed, with the suppression attributed to the diffusion prefactor. Similar to the bulk, diffusion in both of the \(\Sigma 5\) GBs is largely isotropic. In contrast, diffusion in the \(\Sigma 3\) boundary is anisotropic at lower temperatures. In this case, diffusion in the boundary plane is faster than bulk transport, while transboundary diffusion (i.e., across the boundary plane) is approximately 200 times slower than the bulk.

These data suggest that low-energy GBs provide a "mixed" contribution to Li-ion transport in LLZO: more compact boundaries allow for fast diffusion (i.e., comparable to bulk), while diffusion is significantly retarded in boundaries with larger excess volumes. GBs with larger excess volumes will disrupt the percolating ring structure of the Li-sublattice to a greater extent; this ring structure contributes to fast Li-ion diffusion in the bulk. The opposing impact of these boundaries indicates that the net effect of GBs on Li-ion transport could be modest in samples that are processed under conditions amenable to achieving a high fraction of low-energy, compact boundaries. This observation is consistent with experimental measurements showing that the GB resistance in LLZO is relatively small in samples that are processed at high temperatures.\textsuperscript{25}

Although the low energies of the GBs studied here suggest that they will be present in annealed samples,\textsuperscript{41,42} lower-temperature synthesis routes could generate higher-energy GBs with less-compact structures. Such GBs are expected to have a larger impact on Li-ion conductivity, and therefore should be considered in future studies.

\section*{II. METHODS}

Calculations were performed using the cubic polymorph of LLZO.\textsuperscript{43} The cubic phase has a much higher Li-ion conductivity than the tetragonal variant,\textsuperscript{44} and is thus the preferred polymorph for use in a battery. Consistent with experimental measurements of partial occupancy on the Li sublattice, Li was quasirandomly distributed on the 24d and 96h sites, resulting in occupancies of 0.542 and 0.448, respectively, as described in an earlier study.\textsuperscript{17} Symmetric tilt GBs with coincident-site lattice (CSL) designations of \(\Sigma 3\) and \(\Sigma 5\) were examined.\textsuperscript{41,42,45} Three boundary geometries were considered: \(\Sigma 5(310)/[001]\), \(\Sigma 5(210)/[001]\), and \(\Sigma 3(112)/[110]\).\textsuperscript{42,46} The tilt angles for these GBs are 36.9°, 53.1°, and 70.5°, respectively.
present, a thorough experimental characterization of GBs in LLZO has not yet been reported; however, the geometries examined here are likely to be relevant boundaries, as they have been identified as low-energy orientations in BCC metals. The low energies of these GBs suggest that they are likely to be present in samples processed at high temperatures, such as in hot-pressing.

Figure 1 shows the structure of the initial (unrelaxed) GB computational cells. The cells contain 160 (\(\Sigma 5(310)\)), 80 (\(\Sigma 5(210)\)), and 96 (\(\Sigma 3(112)\)) formula units of LLZO, respectively. All cells contained stoichiometric quantities of LLZO. Structural parameters for the GB cells are listed in Table S1. Geometry optimization calculations were performed using the conjugate gradient algorithm implemented in LAMMPS. The excess volume of the GBs was evaluated by relaxing the atom positions and simultaneously allowing lattice expansion along the x-direction of the computational cell (i.e., normal to the GB plane).

The energies of the GBs were evaluated (following geometry optimization) according to

\[
\chi_{\text{GB}} = \frac{E_{\text{GB}} - nE_{\text{bulk}}}{2A}
\]

where \(E_{\text{GB}}\) is the total energy of the GB-containing cell, \(n\) is the number of LLZO formula units in that GB cell, \(E_{\text{bulk}}\) is the total energy per formula unit of bulk LLZO, and \(A\) is the area of the GB plane. The factor of 2 accounts for the fact that each simulation cell contains 2 GBs. A supercell based on a 3 \(\times\) 3 \(\times\) 3 replication of the conventional unit cell was used for bulk LLZO.

Molecular dynamics and Monte Carlo simulations were conducted using LAMMPS. All calculations were performed using a force-field based on Morse-type interactions derived from softBV bond valence parameters. Prior calculations with this force-field yielded good agreement with measured static and dynamic properties of LLZO.

Figure S1 summarizes our computational procedure. After an initial geometry optimization, the GB-containing and bulk LLZO cells were heated to selected target temperatures using the NPT MD ensemble. This procedure accommodates thermal expansion and volume changes associated with the presence of the GBs. The time step for MD was 2 fs. Upon reaching the target temperature (ranging from 700 to 1100 K), the cells were then equilibrated with MD using the NVT and (subsequently) NVT ensembles for 3 ns for each ensemble.

Next, NVT Monte Carlo simulations were performed using the Metropolis algorithm, with a maximum displacement value, \(v_{\text{max}} = 0.5\) Å, selected to achieve a displacement-acceptance ratio of approximately 0.1. More than 10\(^5\) MC move attempts were performed for each GB cell; the goal of the MC calculations is to establish the stoichiometry of the GB region, which can potentially differ from the bulk stoichiometry due to segregation. The composition as a function of position normal to the GB plane was obtained by averaging within 60 contiguous rectangular regions in the MC-equilibrated cells.

Finally, the diffusivity of Li was calculated using NVT MD at five temperatures: 700, 800, 900, 1000, and 1100 K. Supercells built from 1 \(\times\) 1 \(\times\) 4, 1 \(\times\) 2 \(\times\) 4, and 1 \(\times\) 2 \(\times\) 3 replicas of the MC-equilibrated cells (resulting in 640, 640, and 576 formula units of LLZO) were used for the \(\Sigma 5(310)\), \(\Sigma 5(210)\), and \(\Sigma 3(112)\) systems, respectively.

The diffusion coefficient was obtained by evaluating the mean squared displacement (MSD) of Li ions over a time \(t\)

\[
D = \frac{1}{2dt} \langle (r(t) - r(t_0))^2 \rangle
\]

Here, \(d\) is the dimensionality of the system, \(t_0\) is the initial time, and the angled brackets indicate an average over all Li ions. Following a 1 ns startup period, MSD data were collected over a 5 ns MD window. Three NVT calculations of the MSD were performed for each simulation using different initial velocities; the standard deviations of these runs were used to establish error bars about the mean diffusivities. The diffusivity at room temperature was evaluated by extrapolating higher-temperature data collected between 700 and 1100 K. This extrapolation is necessary because the cubic phase of undoped LLZO is unstable with respect to the lower-conductivity tetragonal polymorph at room temperature. Characterization of GB phenomena in doped LLZO is suggested as a valuable follow-on study.

The diffusivity of Li-ions near the GB and in the bulk region was distinguished by dividing the space within the cells into 10 adjacent, nonoverlapping rectangular regions. The regions corresponding to the GBs comprise 20% of the cell volume, and fall within fractional coordinates 0.45 < \(x\) < 0.55, and 0.95 < \(x\) < 0.05. Atoms were assigned to a region based on their position at the end of the 1 ns startup MD phase.

Although all Li-ions in bulk LLZO are typically considered to be mobile, this assumption may not be valid near GBs due to the distinct atomic structure of the GB plane. The possibility for immobile Li was assessed by calculating the mobility of each Li ion. More specifically, a given Li-ion was defined as immobile if its MSD was always less than 4 Å\(^2\) when assessed at 0.5 ns intervals within the 5 ns MD window. As shown below, this analysis confirms that essentially all Li species in bulk LLZO are mobile, whereas a significant fraction of Li at GBs is immobile.

III. RESULTS

Energies and Excess Volumes. GB energies and excess volumes for the three systems described above were evaluated following geometry optimization at 0 K. The calculated excess volumes for the \(\Sigma 5(310)\), \(\Sigma 5(210)\), and \(\Sigma 3(112)\) GBs are, respectively, 313, 243, and 10 Å\(^3\). These volumes are a small fraction, 1% or less, of the total volume of the GB-free cell. The corresponding GB energies are 1.36, 1.39, and 1.01 J/m\(^2\). The observed correlation between the GB energy and excess volume
is consistent with previous calculations on Cu and Ni GBs\textsuperscript{52} where the \(\Sigma5\) systems exhibited larger energies and excess volumes compared to the \(\Sigma3\) system. Similarly, the trend in LLZO GB energies is in good agreement with calculations on the same GBs in BCC Fe, where the energies for \(\Sigma5(310)\) and \(\Sigma5(210)\) were reported to be higher than that of \(\Sigma3(112)\).\textsuperscript{42,46}

Monte Carlo equilibration at 1000 K resulted in more uniformity and a reduction in magnitude of the GB energies and volumes. Relaxation of the MC-equilibrated GBs yielded excess volumes of 30, 80, and 13 Å\(^3\) for the \(\Sigma5(310)\), \(\Sigma5(210)\), and \(\Sigma3(112)\) GBs, with corresponding GB energies of 0.73, 0.52, and 0.54 J/m\(^2\). The reductions in GB volume and energy are a consequence of (local) changes to the composition in the GB plane that occur during the MC equilibration.

**Grain Boundary Composition.** Composition plots for the \(\Sigma5(310)\) GB at 1000 K are shown in Figure S2 following each step in the calculation procedure: for the as-built GB, after initial relaxation, following MD heating, and (finally) after MC equilibration. All atoms are uniformly distributed in the as-built cell. However, changes in the composition profiles begin to emerge following the initial structure relaxations. These effects are further magnified following heating via NPT MD and following MC calculations. Figure S3 compares the initial (unrelaxed) GB structures to those obtained following the MC equilibration step (Figure S1) at 1000 K for each GB.

Figure 2 shows the average equilibrium composition predicted by MC as a function of position normal to the GB plane at 1000 K for each GB. (Figure S4 shows that the composition profiles at \(T = 700\) K are similar.) For all GBs examined, the concentration of lithium and oxygen in/near the GB is predicted to exceed that in the bulk region. Changes to the Zr and La concentrations in the GB region are also evident in Figure 2, but appear to be relatively small. To approximately quantify GB segregation, we computed the ratio of the number of Li in the immediate GB region, \(N_{Li}(GB)\), to the average value in the bulk, \(N_{Li}(av\ bulk)\): \(\Gamma_{Li} = N_{Li}(GB)/N_{Li}(bulk)\). For the \(\Sigma5(310)\), \(\Sigma5(210)\), and \(\Sigma3(112)\) GBs we obtain \(\Gamma_{Li}\) values of 1.47, 1.79, and 2.43, respectively. Evaluating the same ratio for oxygen, \(\Gamma_{O}\) yields 1.18, 1.11, and 0.93. (The slight decrease in oxygen content in the \(\Sigma3(112)\) boundary is due to the sampling region being narrowly centered (1.06 Å width) on the GB plane; in this GB the enrichment of oxygen occurs in the first sublayer outside of the boundary plane.) Li and oxygen accumulation in the GB tends to increase at lower temperatures, as shown in Table S2. The cosegregation of Li cations and O anions would maintain local electroneutrality in the boundary region, and suggests the formation of new GB phases with an approximate composition of Li\(_2\)O. Additional details regarding composition variations in the GBs are presented in Figure S5.

Our observation of deviations from the bulk stoichiometry at GBs in LLZO is consistent with prior reports involving other oxides. For example, yttrium enrichment at GBs has been observed in Y-doped BaZrO\(_3\)\textsuperscript{53} and Y-stabilized zirconia (YSZ).\textsuperscript{54} Similarly, oxygen deficiencies have been reported at GBs in BaTiO\(_3\)\textsuperscript{55} and SrTiO\(_3\).\textsuperscript{56} Differences in GB chemical composition (relative to bulk) correlate with decreased oxygen transport behavior near GBs in YSZ and SrTiO\(_3\).\textsuperscript{38,39} Reduced ionic conductivity at GBs in other oxides has been rationalized, at least in part, by the presence of a space charge layer in the vicinity of the GB.\textsuperscript{37–39} These layers manifest as a reduction in the carrier concentration, with the magnitude of...
the depletion decreasing with distance normal to the boundary plane. Can the variations in Li⁺ concentration near the GB region predicted here be considered a space charge layer? We think not, for two reasons. First, the Li⁺ concentrations predicted by our calculations exhibit oscillatory behavior as a function of position; Li⁺ is generally enriched in the GB plane, but then depleted in adjacent layers. Such behavior differs from the monotonic decay in carrier concentration expected for a space charge layer. Second, the formation of a space charge layer signals a violation in electroneutrality. However, our calculations do not allow for such violations, as they maintain a fixed stoichiometry equal to that of bulk LLZO. (Li⁺ depleted in one location must accumulate elsewhere.) A “grand canonical” simulation open to Li exchange with an electrode is needed to capture these electroneutrality violations.

Nevertheless, the presence of nonstoichiometric compositions at GBs in LLZO could impact Li-ion diffusion. To explore this possibility, the transport properties of Li ions in the GB region were evaluated using MD simulations, and compared to the behavior observed in bulk LLZO.

**Li-Ion Transport.** The GB compositions predicted by MC equilibration were used as input configurations to MD calculations. Figure S6 shows the calculated Li-ion MSD for bulk LLZO and for the three GB-containing simulation cells. In the latter cases, the MSD for atoms in the GB region and in the bulk regions are separately identified. In all of the GB-containing cells the MSD is smaller in the GB region than in the bulk. This indicates that Li transport is impeded by the presence of these GBs.

The trajectories of Li ions were examined to clarify the impact of GBs on transport. Figure 3 illustrates trajectories recorded during 5 ns MD simulations at 700 K for the three GB systems. (A trajectory is a record of the instantaneous locations of the Li ions during the MD time window. Species with a high diffusivity will exhibit a connected, percolating trajectory; in contrast, slowly diffusing components will exhibit gaps in its trajectory.) The trajectory images indicate fragmentation of the Li-ion diffusion path across, and within, the GB plane. Figure S7 shows that the Li-ion trajectories at $T = 1000$ K are qualitatively similar, but slightly more connected. For comparison, trajectories of all atoms in the simulation cell are presented in Figure S8. Only Li exhibits a percolating trajectory; the trajectories of all other atoms are much more localized.

Figure 3a–c illustrates the Li-ion trajectories as viewed along the GB tilt axis (i.e., along the z-direction). A magnification of these trajectories within the GB region is shown in Figure S9. Compared to the bulk region, it is clear that the trajectories are more fragmented in the immediate vicinity of the GB. Figure 3d–f depicts the trajectories in the GB plane as viewed along a direction parallel to the GB normal (i.e., along the x-direction). (The region plotted corresponds to the red rectangular area shown in Figure 3a–c.) For comparison, the trajectories in similarly oriented bulk regions, corresponding to the regions in the black rectangles in Figure 3a–c, are shown in Figure 3g–i. These images convey a disruption to the connectivity of the Li-ion trajectory within the GB, suggesting a local reduction in Li-ion mobility.

Another strategy for assessing the impact of GBs on Li-ion transport is to identify the location of Li-ions exhibiting low mobility. Low-mobility atoms were previously defined as those having an MSD that is always less than 4 Å² when assessed at 0.5 ns intervals in a 5 ns MD window. To place this threshold MSD in context, we note that 97.2% of the Li species in bulk LLZO have MSDs larger than 4 Å² at 700 K.

**Figure 4.** Mobile (blue) and immobile (red) Li ions in the Σ5(310) GB simulation cell during 5 ns of MD at 800–1000 K. For clarity, the size of the mobile Li atoms is reduced.

**Figure 5.** Calculated Li-ion diffusivity for the three GB cells. (a) Total diffusivity and (b) diffusivity decomposed along each Cartesian direction at 1000 K as a function of position normal to the GB plane. (c) Arrhenius plots for Li-ion diffusivity in the GB regions over the temperature range 700–1100 K compared to that in bulk LLZO.
Table 1. Calculated Transport Properties (Activation Energy for Diffusion, $E_a$, and Diffusivity, $D$) in Bulk LLZO and in Three GBs

<table>
<thead>
<tr>
<th>System</th>
<th>$E_a$ (eV)</th>
<th>$D$ (10^{-7} cm^2/s) at 1000 K</th>
<th>$D$ (10^{-13} cm^2/s) at 1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>0.52</td>
<td>13.5</td>
<td>1.01</td>
</tr>
<tr>
<td>Σ5(310)</td>
<td>0.64</td>
<td>4.30</td>
<td>0.22</td>
</tr>
<tr>
<td>Σ3(210)</td>
<td>0.71</td>
<td>5.50</td>
<td>0.17</td>
</tr>
<tr>
<td>Σ3(112)</td>
<td>0.52</td>
<td>5.10</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Li-ion diffusivities in the GB region are reported for calculations at 700 and 1000 K, and extrapolated to 300 K. The total diffusivity ($D$) and the diffusivity projected along the three Cartesian coordinates are reported: $D_x$, $D_y$, and $D_z$ correspond to diffusion within the GB plane; $D_y$ corresponds to diffusion across the GB plane.

The MSD distribution for Li atoms in bulk LLZO is shown in Figure S10. Figure 4 illustrates the location of mobile (blue) and immobile (red) Li-ions in the Σ5(310) GB cell at temperatures ranging from 800 to 1000 K. The data clearly indicate that immobile Li exists in the simulation cells, and is confined to the GB region. Moreover, the amount of immobile Li increases with decreasing temperature, as expected. Figures S11 and S12 show the location of immobile Li from other viewing directions, and for the other GBs.

Figure S13 illustrates the percentage of immobile Li as a function of position and temperature in the Σ5(310) simulation cell. The plot shows sharp increases in immobile Li in the GB region, consistent with the behavior shown in Figure 4. At the lowest temperature examined, 700 K, approximately 70% of the Li in the GB region is immobile. Similar behavior is observed for the other two GBs, shown in Table S5: immobile Li accounts for about 70% of the Li in the Σ5(210) boundary, while a smaller fraction of Li, only about 45%, is immobile in the Σ3(112) boundary. The higher mobility in the Σ3(112) boundary correlates with its smaller excess volume, and will be shown to follow trends in the activation energy and diffusivity across the three boundaries (see below).

Figure S shows the calculated Li-ion diffusivity data for the GB-containing simulation cells. Panel a displays the total diffusivity for each GB system as a function of position in the GB region, consistent with the behavior shown in Figure 4. At the lowest temperature examined, 700 K, approximately 70% of the Li in the GB region is immobile. Similar behavior is observed for the other two GBs, shown in Table S3. The data clearly indicate that immobile Li exists in the simulation cells, and is confined to the GB region. This behavior is consistent with the behavior shown in Figure 4. At the lowest temperature examined, 700 K, approximately 70% of the Li in the GB region is immobile. Similar behavior is observed for the other two GBs, shown in Table S3. The data clearly indicate that immobile Li exists in the simulation cells, and is confined to the GB region. Nevertheless, the extent of this reduction varies significantly across the different GBs, and (as expected) is also temperature dependent. For example, as shown in Table 1, GB diffusion at 1000 K is largely independent of GB type, and only 2–3 times smaller than in the bulk. At 700 K GB diffusion is 5 and 2 times smaller for the Σ5 and Σ3 boundaries, respectively. We therefore conclude that at these higher temperatures GBs slow Li-ion diffusion only slightly.

While diffusion in bulk LLZO is isotropic, the distinct atomic structure near the GB could give rise to local anisotropic behavior. For example, fast diffusion along the tilt axis has been observed in some GBs. To assess the possibility for anisotropic GB diffusion, the total diffusivity at 1000 K is decomposed in Figure Sb into components along each of the Cartesian directions and as a function of position in the simulation cells. A summary of the directionally decomposed diffusivities in the GB region for all three boundaries is given in Table 1 at 300, 700, and 1000 K. Diffusion within the GB plane corresponds to the $yz$-plane, with the tilt axis parallel to the $z$-axis; diffusion in the $x$-direction would cross the GB plane (see inset in Figure S3).

Figure Sb shows that at 1000 K there is little evidence of anisotropic diffusion in any of the GBs examined. A similar conclusion applies to the two Σ5 boundaries at 700 K, as shown in Figure S14. For the Σ3 boundary, however, evidence of anisotropy begins to appear at 700 K. More specifically, slower diffusion is observed across the GB plane (i.e., in the $x$-direction), while diffusion in the GB plane approaches rates seen in the bulk. Anisotropy in the Σ3 system is magnified at 300 K (Table 1), where transboundary diffusion is predicted to be 200 times slower than bulk, while intraplanar transport is equal to or faster than the bulk.

Figure Sc shows Arrhenius plots for Li-ion diffusivity within the three GBs and bulk LLZO for $T = 700–1100$ K. The activation energies for diffusion, $E_a$, were extracted from the slope of these data, and are reported in Table 1. For bulk LLZO the calculated $E_a$ of 0.52 eV is in good agreement with prior studies of LLZO in this temperature range.

Diffusion within the GBs is predicted to exhibit activation energies that are equal to or larger than those for bulk diffusion. In the case of the Σ3 boundary, Figure Sc shows a similar slope in the diffusivity versus inverse temperature for bulk LLZO and for this GB. This behavior is consistent with the identical activation energies predicted, 0.52 eV, for these systems. The slightly slower diffusion in the GB illustrated in Figure Sc versus bulk must therefore result from a smaller prefactor, $D_0$, in the expression $D(T) = D_0 \exp(-E_a/k_BT)$. Extrapolating the Arrhenius plot for the Σ3 GB to 300 K shows that its total diffusivity is only a factor of 2 smaller than the bulk (Table 1). The limited impact of this GB on diffusivity is likely a reflection of its similar structure to that of bulk LLZO. For example, of the boundaries examined, the density of coincident sites (1/3) is the largest in the Σ3 GB, while its excess free volume is the smallest.

As for the two Σ5 boundaries, diffusion in these systems exhibits higher activation energies of 0.64 and 0.71 eV, reflecting their steeper slopes relative to bulk LLZO in the Arrhenius plot. While the diffusivity associated with these boundaries is similar to the Σ3 system at higher temperatures (>900 K), the Σ5 boundaries retard Li-ion diffusion to a greater extent at low temperatures. For example, extrapolation of the Arrhenius data to 300 K reveals that the Σ5 boundaries have diffusivities that are up to 2 orders of magnitude slower than the bulk. The larger slow-down in diffusion in the Σ5 boundaries can be traced to their lower density of coincident sites (1/S), and larger excess volumes. Both of these properties imply a larger disruption to the bulk LLZO crystal structure in the GB region (compared to the Σ3). Since bulk LLZO is a relatively fast Li-ion conductor, disruptions to its structure are
expected to slow Li transport by an amount proportional to the degree of disruption.

Taken together, our calculations suggest that low-energy GBs provide a “mixed” contribution to Li-ion transport in LLZO. That is, diffusion is generally faster (i.e., comparable to bulk) in compact boundaries, while diffusion is significantly retarded in boundaries with larger excess volumes. The opposing impact of these boundaries indicates that the net effect of GBs on Li-ion transport could be modest in samples that are processed under conditions amenable to achieving a high fraction of low-energy, compact boundaries. This observation is consistent with experimental measurements showing that the GB resistance in LLZO is relatively small in samples that are processed at high temperatures.25

Although the low energies of the GBs studied here suggest that they will be present in annealed samples,31,42 lower-temperature synthesis routes could generate higher-energy GBs with less-compact structures. Such GBs are expected to have a larger impact on Li-ion conductivity, and therefore should be considered in future studies.

Catarelli et al.53 used scanning electrochemical microscopy to map the local Li-ion conductivity across the surface of a polycrystalline LLZO sample composed of relatively large grains (~150 μm average diameter). Their study revealed that the resistance of the GBs to Li-ion migration was generally greater than in the bulk, consistent with the present study. Moreover, Catarelli and co-workers observed that the GB resistance varied considerably across the GB regions, suggesting a dependence on GB structure and composition. A structural dependence of GB diffusion is also predicted by the present computational results. Regarding the influence of composition on GB transport, the present atomistic models have emphasized transport in pristine (cubic) LLZO. Thus, the impact of adventitious impurities and intentional additives (e.g., dopants such as Al and Ta, or sintering aids) on GB phenomena are not considered here. While an examination of pristine LLZO is important for establishing the intrinsic properties of its GBs, more complex behavior with respect to GB composition can be expected in experiments. For example, several studies have reported Al enrichment at grain boundaries in Al-doped LLZO.22,54–70 Similarly, the presence of impurity phases (Li2CO3 and LiOH) at GBs, which result from reaction(s) with air, can also limit ionic conductivity.15,71 Computational studies that quantify the impact of segregation and second phase formation at GBs in LLZO would be a helpful next step.

IV. CONCLUSIONS

Recent measurements on the promising solid electrolyte LLZO suggest that grain boundaries contribute to undesirable short-circuiting and resistance in polycrystalline LLZO membranes. Toward the goal of understanding, and ultimately controlling, GB-related phenomena, the present study has examined the energetics, composition, and transport properties of three Σ3 and Σ5 model GBs in LLZO at the atomic scale. Due to their low energies, these boundaries are expected to comprise a significant fraction of the GB network in samples prepared at elevated temperatures. Our Monte Carlo simulations reveal that the GB planes of all boundaries examined are enriched with lithium and oxygen. Molecular dynamics simulations on these off-stoichiometric boundaries were used to assess Li-ion transport within and across the boundary planes.

Our calculations reveal that Li transport is generally slower in the GB region compared to the bulk. Nevertheless, the magnitude of this effect is sensitive to the GB structure and temperature. For example, Li-ion diffusion is comparable in all three GBs at high temperatures (>900 K), and only slightly slower than bulk diffusion. In contrast, room temperature diffusion differs significantly between the Σ3 and Σ5 systems: diffusion in the more compact Σ3 boundary remains relatively fast (~50% of the bulk rate), while transport in the Σ5 boundaries is roughly 2 orders of magnitude slower than the bulk. These trends are reflected in the activation energies for diffusion, which in the Σ5 boundaries are up to 35% larger than in bulk LLZO, and are equal to the bulk for the Σ3 boundary.

Diffusion within the Σ5 boundaries is isotropic, while anisotropic transport is observed in the Σ3 system at lower temperatures (<700 K). In the latter system, intraplane diffusion at 300 K is up to 4 times faster than the bulk, while transboundary diffusion is ~200 times slower.

Our observation of mixed GB transport contributions (some boundaries support fast diffusion, while others are slow) is consistent with the moderate GB resistance observed in polycrystalline LLZO samples processed at high temperatures. These data also suggest that higher-energy GBs with less-compact structures should penalize Li-ion conductivity to a greater degree. Additional experimental study is needed to quantify the presence, and characterize the structure, of high-energy boundaries as a function of processing temperature. Such studies would enable computational characterization of those systems, similar to the analyses performed here on low-energy GBs. The role of supervalent dopants on GB diffusion should also be examined.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b02805.

Additional grain boundary composition and structure data, Li-ion mean squared displacements, and Li-ion trajectories at various temperatures (PDF)

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Notes
The authors declare no competing financial interest.

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