Enhancing the Lithium Ion Conductivity in Lithium Superionic Conductor (LISICON) Solid Electrolytes through a Mixed Polyanion Effect

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Supporting Information

ABSTRACT: Lithium superionic conductor (LISICON)-related compositions $\text{Li}_{4+x}\text{Si}_{1-x}\text{X}_4$ (X = P, Al, or Ge) are important materials that have been identified as potential solid electrolytes for all solid state batteries. Here, we show that the room temperature lithium ion conductivity can be improved by several orders of magnitude through substitution on Si sites. We apply a combined computer simulation and experimental approach to a wide range of compositions ($\text{Li}_4\text{SiO}_4$, $\text{Li}_{3.75}\text{Si}_0.75\text{P}_0.25\text{O}_4$, $\text{Li}_{4.25}\text{Si}_0.75\text{Al}_0.25\text{O}_4$, $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$, and $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$), which include new doped materials. Depending on the temperature, three different Li$^+$ ion diffusion mechanisms are observed. The polyanion mixing introduced by substitution lowers the temperature at which the transition to a superionic state with high Li$^+$ ion conductivity occurs. These insights help to rationalize the mechanism of the lithium ion conductivity enhancement and provide strategies for designing materials with promising transport properties.

KEYWORDS: energy storage, solid electrolyte, LISICON, diffusion mechanism, mixed polyanion effect

1. INTRODUCTION

Lithium ion batteries are widely used in electric vehicles and portable devices. However, owing to various intrinsic drawbacks of liquid electrolytes (for example, chemical and thermal instability and complex reactions at the solid/liquid interface), other technologies with better performance for specific applications are required. Among various electrochemical energy storage devices, all solid state batteries (ASSBs) have been proposed to provide improved chemical and electrochemical stability (wide potential window), greater safety, and easier device fabrication.

The search for new, stable, and highly conducting solid electrolytes has increased significantly in recent years. Considerable research efforts have been carried out in exploring crystal structural families with high ionic conductivity, including the sodium superionic conductor (NASICON; e.g., $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$), the lithium superionic conductor (LISICON; e.g., $\gamma\text{Li}_2\text{PO}_4$), and the thio-LISICON ($\text{Li}_2\text{S}_{12}$). Among these structural families, the compositions $\text{Li}_{2}\text{GeP}_2\text{S}_{12}$ (10 mS/cm at 25 °C) and $\text{Li}_{5}\text{Si}_{1.5}\text{P}_{1.4}\text{Si}_{1.7}\text{Cl}_{0.3}$ (25 mS/cm at 25 °C) reported by Kanno et al. present the highest ionic conductivities to date. However, sulfide chemistry can be challenging in terms of its high sensitivity to moisture. It is believed that the reproducible synthesis of phase pure materials will be a particular issue that will be difficult to overcome. In contrast, oxide-based LISICON materials can be obtained from traditional solid state reactions and present fewer air-sensitivity issues. Previous studies show that the formation of solid solutions (such as $\text{Li}_{4}\text{Si}_{1-x}\text{P}_x\text{O}_4$ or $\text{Li}_{4}\text{Si}_{1-x}\text{Al}_x\text{O}_4$) can significantly improve the ionic conductivity. However, there is limited work on additional doping of these LISICON systems.

The mechanism for such drastic enhancement of conductivity in the solid solution compositions is considered to be caused by the increased concentration of defects which act as charge carriers. Our previous work revealed an interstitialcy or knock-on type mechanism in the case of lithium ion diffusion in $\text{Li}_{1.5}\text{SiO}_3\text{P}_{0.5}\text{O}_4$ at 573 K. However, the influence of the polyanion groups (e.g., $\text{SiO}_4\text{PO}_4$) has not been discussed in...
The tracer nature of the superionic transition in LISICON materials. The crystal structure and ion diffusion mechanisms at the atomic scale is important to aid understanding of ion diffusion processes. In this study, we investigate the temperature dependence of the crystal structure and ion diffusion mechanism, and whether the coexistence of various \( \text{XO}_4 \) tetrahedra (\( \text{(SiO}_4 \))\(^{−}\), \( \text{(PO}_4 \))\(^{3−}\), and \( \text{(AlO}_4 \))\(^{5−}\)) within a given structure leads to lower lithium ion transport barriers similar to the “mixed anion effect” reported in polymer and glass-ceramic systems. We synthesized, characterized, and modeled a series of compositions (\( \text{Li}_4\text{Si}_0.75\text{P}_0.25\text{O}_4 \), \( \text{Li}_3.75\text{Si}_0.75\text{P}_0.25\text{O}_4 \), \( \text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4 \)) which are formed through cationic substitution on the Si\(^{4+}\) site of the \( \text{Li}_4\text{SiO}_4 \) (green) and their relation to the three parent LISICON-like \( \text{Li}_6\text{SiO}_4 \) structure (see Figure 1 for compositional relations).

This work represents the first successful doping of more than three elements on the silicon site and the first application of van Hove analysis of these systems, which sheds new light on the nature of the superionic transition in LISICON materials. The findings here are directly transferable to the high conductivity sulfide-based thio-LISICON systems and offer design strategies to further improve the conductivity.

### 2. METHODS


\( \text{Li}_6\text{SiO}_4 \), \( \text{Li}_3.75\text{Si}_0.75\text{P}_0.25\text{O}_4 \), \( \text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4 \), and \( \text{Li}_4\text{Al}_{0.16}\text{Si}_{0.16}\text{P}_{0.16}\text{O}_4 \) were synthesized by solid state reactions at 800 °C with 12 h under Ar flow, followed by slow cooling to 298 K and then grinding. The Si/Al/P relative atomic concentration was calculated from the relation:

\[
\frac{\sigma}{D_i} = \frac{nq^2}{kT}
\]

where \( \sigma \) is the density of charge carriers (number of \( \text{Li}^+ \) ions per volume unit), \( q \) is the charge, \( k \) is the Boltzmann constant, and \( T \) is the system temperature. Such atomistic modeling techniques have been applied successfully to a range of lithium (and sodium) battery materials.

#### 3. RESULTS AND DISCUSSION


The crystal structures of \( \text{Li}_6\text{SiO}_4 \), \( \text{Li}_3.75\text{Si}_0.75\text{P}_0.25\text{O}_4 \), \( \text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4 \), \( \text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4 \) were investigated using powder X-ray diffraction. The obtained diffraction patterns for the four samples are shown in Figure 2.

These four samples are well-crystallized and single phase. It is known that \( \text{Li}_6\text{SiO}_4 \) crystallizes in a monoclinic “supercell” (space group \( P2_1/m \), no. 11) with \( Z = 14 \) at 298 K and undergoes a phase transition to a “subcell” with \( Z = 2 \) at temperatures higher than 750 K. This transition is due to a disordering within the \( \text{Li}^+ \) crystallographic positions. In contrast, the crystal structures at 298 K of the substituted compositions \( \text{Li}_3.75\text{Si}_0.75\text{P}_0.25\text{O}_4 \), \( \text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4 \), and \( \text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4 \) can be described using the subcell model. The cell parameters obtained through full pattern profile matching are listed in Table 1.

The crystal structures can be described as isolated polyanionic tetrahedra (\( \text{SiO}_4 \text{PO}_4 \)) connected to \( \text{LiO}_4 \) (\( n = 4, 5, 6 \)) polyhedra through corner and/or edge sharing. For \( \text{Li}_6\text{SiO}_4 \) and \( \text{Li}_3.75\text{Si}_0.75\text{P}_0.25\text{O}_4 \) detailed structural descriptions were reported in previous studies. In \( \text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4 \), the Si and P atoms share the same crystallographic sites, and (\( \text{SiO}_4 \))\(^{−}\) and (\( \text{PO}_4 \))\(^{3−}\) coexist in a disordered manner.
To the best of our knowledge, no investigation for the crystal structure of Li$_{4.25}$Si$_{0.75}$Al$_{0.25}$O$_4$ has been reported in the past. Ortiz-Landeros et al. stated only that Li$_{4+x}$Si$_{1-x}$Al$_x$O$_4$ (0 $\leq$ x $\leq$ 0.5) compositions show an X-ray diffraction pattern very similar to that of Li$_4$SiO$_4$. In this work, we carried out powder neutron diffraction and single crystal X-ray diffraction for Li$_{4.25}$Si$_{0.75}$Al$_{0.25}$O$_4$. The refinement results of the crystal structure are listed in the Supporting Information. From neutron diffraction data, the refined lithium amount is 4.1(3) per formula. The crystal structure of Li$_{4.25}$Si$_{0.75}$Al$_{0.25}$O$_4$ is very similar to that of Li$_{3.75}$Si$_{0.75}$P$_{0.25}$O$_4$, with a unit cell containing two XO$_4$ tetrahedra and similar distribution of lithium crystallographic sites. Each X site is statistically shared by 0.75 Si and 0.25 Al atoms. In the mixed XO$_4$ group, the average X–O bond length is 1.690 Å, which is very close to the value of 1.684 Å obtained by linear interpolation between the average Si–O distance in Li$_4$SiO$_4$ (1.641 Å) and Al–O distance in β-Li$_5$AlO$_4$ (1.814 Å) as reported by Hoppe et al.62 This is a strong indication that the experimental Si/Al stoichiometry of the powder is very close to the nominal one and that the structural model we are using is valid.

3.2. Ionic Conductivity Enhancement by Mixing Tetrahedral Groups. The ionic conductivity of each material has been measured by EIS technique as a function of temperature. Figure 3 shows a typical Nyquist plot obtained for Li$_4$SiO$_4$ at 473 K.

A semicircle can be observed at high frequencies, which can be attributed to the solid electrolyte lithium ion conduction.

The spectra were fitted by an equivalent circuit (insert in Figure 3) composed by an initial resistor R1 (for the device and current collectors resistance) in series with one resistor R2 (for solid electrolyte resistance) in parallel with a constant phase element CPE2 (for the nonideal capacitance between particles) and in series with another CPE3 (for the impedance of both the top and bottom electrode—electrolyte junctions). The ionic conductivity $\sigma$ was then calculated using the equation:

$$\sigma = \frac{h}{RS}$$

in which $h$ is the thickness of the solid electrolyte pellet, S the pellet surface, and R the resistance obtained from the fitted R2 value. A fast reduction of the semicircle diameter is noticed upon heating, in line with the enhancement of the ionic conductivity with temperature.

The ionic conductivities have also been calculated using the MD method described in detail in the Methods section. In Figure 4, the experimental and MD simulated ionic conductivity values of Li$_4$SiO$_4$, Li$_{3.75}$Si$_{0.75}$P$_{0.25}$O$_4$, Li$_{4.25}$Si$_{0.75}$Al$_{0.25}$O$_4$, Li$_4$Al$_{0.33}$Si$_{0.33}$P$_{0.33}$O$_4$, and Li$_4$Al$_{0.33}$Si$_{0.33}$Ge$_{0.33}$P$_{0.33}$O$_4$ are plotted in the form of log ($\sigma$T) as a function of 1000/T.

For each composition, the EIS measured and the MD simulated ionic conductivity values are in good agreement and follow the expected Arrhenius relationship:
positions previously observed using di...

...appears to be applicable for sul...

...valid not only for the oxide LISICON type materials but also...

...are increased by 2 orders of magnitude with...

...both mixed...

...cm for Li3.75Si0.75P0.25O4 and 2.10...

...A further enhancement of the ionic conductivity is seen in the...

...temperature range (RT to 473 K, with...

...low ionic conductivity in the typical solid state battery working...

...Li4Al1/3Si1/6Ge1/6P1/3O4 is as high as 0.9 mS/cm at 300 K,

...is significant that the MD simulated ionic conductivity of...

...composition Li4Al0.33Si0.33P0.33O4 with...

...that helps to enhance conductivity values in the...

...concentration of charge carriers is not the key factor

...compositions, it seems that the variation of the...

...compositions. In Figure 4, we can see that there is no significant difference in ionic
cconductivities between these two compositions. In comparison to the ionic conductivity values of other
compositions, it seems that the variation of the concentration of charge carriers is not the key factor
that helps to enhance conductivity values in the substituted compositions.

...substituted compositions.

...polyanion groups and the lithium population in three main ways:

...Lithium carrier concentration: The tetrahedral anion charge m influences not only the interaction between the
tetrahedral group and Li+ ions but also the number of charge carriers per formula. For example, with the same
amount of substitution (25%) on the Si site, Li4SiO4 shows 3.75 Li per formula, but
Li4.25Si0.75Al0.25O4 has 4.25 Li per formula. In Figure 4, we can see that there is no significant difference in ionic
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...Polanyion size: The X−O bond length gives a direct description of the size of the tetrahedra. For consistency, the
bond length values listed in Table 2 are taken from the average bond length in the corresponding ortho-
oxide: Al−O from β-Li3AlO4 (ICSD-16229). Si−O from Li4SiO4 (ICSD-8222). Ge−O from Li4GeO4 (ICSD-65177), and
P−O from γ-Li3PO4 (ICSD-77095). From PO4 to AlO4, the X−O bond length extends by 20%, which gives a 73% expansion of the
tetrahedron. In previous studies, the contribution of the tetrahedral motion to the cation ionic
conductivity has been discussed, known as the “paddle wheel effect”. The tetrahedral motion is affected by its
degree of distortion as well as its rotation. The distortion is represented by the X−O dissociation energy which
describes the strength of the bond. The rotation is strongly related to the molar mass of the tetrahedral
group. In the MD simulation study of LGPS, the Li+ mobility is reported to correlate with a 30° rotation of the
Ge4 and PS4 groups.

Substitution of silicon can alter the properties of the polyanion groups and the lithium population in three main ways:

1. Lithium carrier concentration: The tetrahedral anion charge m influences not only the interaction between the
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Ge4 and PS4 groups.

Table 2. Tetrahedral Anion Charge (m), X−O Distance in Li₄XO₄, X−O Dissociation Energy Values, Li⁺−(XO₄)⁻⁻ Interaction Minimum Positions for Different Types of Tetrahedra

<table>
<thead>
<tr>
<th>X−O distance (Å)</th>
<th>molar mass</th>
<th>X−O dissociation energy (eV)</th>
<th>Li⁺−(XO₄)⁻⁻ binding energy (eV)</th>
<th>Li⁺−(XO₄)⁻⁻ equilibrium distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XO₄)⁻⁻</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(AlO₄)⁻⁻</td>
<td>1.814</td>
<td>91</td>
<td>5.03</td>
<td>−6.08</td>
</tr>
<tr>
<td>(SiO₄)⁻⁻</td>
<td>1.641</td>
<td>92</td>
<td>5.15</td>
<td>5.3</td>
</tr>
<tr>
<td>(GeO₄)⁻⁻</td>
<td>1.760</td>
<td>137</td>
<td>6.99</td>
<td>−5.06</td>
</tr>
<tr>
<td>(PO₄)⁻⁻</td>
<td>1.520</td>
<td>95</td>
<td>6.17</td>
<td>−4.07</td>
</tr>
</tbody>
</table>

Figure 4. Li⁺ ionic conductivity (σ), Arrhenius plots for Li3SiO4 (blue), Li3.75Si0.75P0.25O4 (red), Li4AlSi0.75Al0.25O4 (dark yellow), Li4Al0.33Si0.33P0.33O4 (green), and Li4Al1/3Si1/6Ge1/6P1/3O4 (orange). MD simulated values are shown in solid squares. Conductivity values deduced from EIS measurements are shown in circles. Linear fits for experimental values are plotted in solid lines. The activation energies are derived in the temperature range of 50−300 °C.

\[
\sigma T = A \exp \left( -\frac{E_a}{kT} \right) \tag{3}
\]

where A is a pre-exponential factor related to charge carrier concentration and \(E_a\) is the activation energy. Li3SiO4 shows low ionic conductivity in the typical solid state battery working temperature range (RT to 473 K, with \(\sigma_{373K} = 4.10^{-6} \text{ S/cm}\)). In both mixed “binary” compositions, the ionic conductivity values are increased by 2 orders of magnitude with \(\sigma_{373K} = 1.10^{-4} \text{ S/cm}\) for Li3Si0.75P0.25O4 and 2.10^{-4} S/cm for Li4Al0.75Al0.25O4. A further enhancement of the ionic conductivity is seen in the “ternary” composition Li4Al0.33Si0.33P0.33O4 with \(\sigma_{373K} = 1.10^{-3} \text{ S/cm}\). These results indicate that substitution on the Si sites (thus creating either Li vacancies or Li⁺ interstitial sites) can effectively promote lithium ion diffusivity. This conclusion is valid not only for the oxide LISICON type materials but also appears to be applicable for sulfide-based solid electrolytes. It is significant that the MD simulated ionic conductivity of Li4Al1/3Si1/6Ge1/6P1/3O4 is as high as 0.9 mS/cm at 300 K, which is one of the highest values among oxide-based solid electrolytes. We notice that the slopes of the data are not strictly linear in the temperature range of 300−1173 K, suggesting that the Li diffusion mechanism is temperature-dependent. Nevertheless, the non-Arrhenius behavior is consistent with the order−disorder transition in the Li⁺ positions previously observed using diffraction techniques.

We now address the cause of this conductivity enhancement in substituted compositions. All of these compositions crystallize in the LISICON-like structure with isolated tetrahedra and a wide distribution of Li ions on their crystallographic sites. The crystal structure and Li distribution are the same in our MD simulations for these compositions; hence, the influence of structural differences and cation ordering is minimized, which allows us to focus on the effect arising from the mixing of the polyanion groups. In general, the presence of various polyanion groups in the structure improves cation mobility by lowering the energy barrier for Li⁺ migration. A similar phenomenon has been observed in the Li2S−GeS2−LiBr−Li system: the mixing of S2⁻, I⁻, and Br⁻ anions lowers the activation energy and improves cation mobility. The mechanism is termed as the mixed anion effect. As an analogue, the ionic conductivity enhancement in the Li3SiO4-related compositions can be termed as the mixed polyanion effect because the mixing anions are XO₄ groups.

To evaluate the influence of each type of polyanion group, several intrinsic structural and energy characteristics of XO₄ tetrahedra (X = Al³⁺, Si⁴⁺, Ge⁴⁺, and P⁵⁺) are listed in Table 2.
(3) Lithium potential energy surface: We calculated the interaction between a Li⁺ ion and a \((\text{XO}_4)^{m−}\) group. In the calculation one Li⁺ ion and one \((\text{XO}_4)^{m−}\) group were set in a 40 × 40 × 40 Å lattice. The lattice energy was calculated as a function of separation \(r\) and is plotted in Figure 5 for each \((\text{XO}_4)^{m−}\) group. The results illustrate that the interaction between Li⁺ and XO₄ can vary considerably in both the depth of the potential well and the equilibrium separation. The minimum energy value \(E_{\text{min}}\) shows a difference as large as 1 eV between Li⁺-(PO₄)³⁻ and Li⁺-(SiO₄)⁴⁻ and 2 eV between Li⁺-(PO₄)³⁻ and Li⁺-(AlO₄)⁴⁻. The equilibrium separation can vary by 0.25 Å.

The nonuniform potential wells for different Li⁺-(XO₄)\(^{m−}\) interactions may modify the overall potential energy surface. In Li₄SiO₄, lithium occupies a much more uniform set of potential wells, and the activation energy is relatively high (0.76 eV). In the substituted compositions Li₃.75Si₀.75P₀.25O₄, Li₄.25Si₀.75Al₀.25O₄, Li₄Al₀.33Si₀.33P₀.33O₄, and Li₄Al₁/₃Si₁/₃Ge₁/₃P₁/₃O₄ the mixing of these XO₄ groups with different sizes and binding energies to Li⁺ affects the conduction mechanisms, we performed statistical analysis of the lithium diffusion. In our previous study,²⁰ we showed that at 573 K, Li⁺ diffusion in Li₄SiO₄ progresses via isolated Li⁺ hops with a low conductivity of around 10⁻⁶ S/cm. By contrast, the substituted composition Li₃.75Si₀.75P₀.25O₄ displayed conductivity 3 orders of magnitude higher (10⁻³ S/cm) at the same temperature with Li⁺ diffusion occurring via highly correlated motion. To further quantify these changes in diffusive behavior, we calculated and plotted the van Hove correlation functions for Li₄SiO₄, Li₄Si₀.75P₀.25O₄, and Li₄Al₁/₃Si₁/₃Ge₁/₃P₁/₃O₄ using trajectories obtained from our MD simulations, which can be split into the self-part \(G_r\) and the distinct-part \(G_d\) as follows:

\[
G_r(r, t) = \frac{1}{4n^3\pi^2N} \sum_{i=1}^{N} \delta(r - |r_i(t_0) - r(t + t_0)|) t_0
\]

\[
G_d(r, t) = \frac{1}{4n^3\pi^2N} \sum_{i \neq j}^{N} \delta(r - |r_i(t_0) - r_j(t + t_0)|) t_0
\]

In these two equations, the self-part \(G_r\) and the distinct-part \(G_d\) are functions of the Li⁺-Li⁺ pair distance \(r\) of the simulation time \(t\). The angular brackets denote the ensemble average from the initial time \(t_0\). \(N\) denotes the number of Li⁺ ions in the system. \(\delta()\) is the one-dimensional Dirac delta function. \(r_i(t)\) denotes the position of the \(i\)th Li⁺ ion at time \(t\). For a given \(r\) and \(t\), the self-part \(G_r(r, t)\) or its transformed version \(r^2G_r(r, t)\) is related to the probability of finding one atom after it travels a distance \(r\) after a time interval of \(t\); the distinct-part \(G_d(r, t)\) or its transformed version \(r^2G_d(r, t)\) compares the positions of a particle to the position of another particle at different time and is related to the probability of finding atom \(j (j \neq i)\) with a distance \(r\) (compare to the position of atom \(i\)) at \(t_0\) after a time interval of \(t\). In the particular case with \(t = 0\), \(G_d(r, t)\) is reduced to the static Li⁺-Li⁺ pair distribution function.

The transformed correlation function thus offers a measure of how correlated the motions of Li⁺ ions are. If \(r^2G_r(r, t)\) retains its shape over different time intervals, then noncorrelated ion hopping is indicated, whereas peak broadening indicates correlated motion, disorder on the Li⁺ sublattice and, in extreme cases, liquid-like diffusive behavior. This method has been successfully used to investigate the diffusion mechanism in other ion conducting materials such as Na₃PS₄ and garnet-type Li₄-xLax(Zr₂-xM₀x)O₁₂ but has never been applied to LISICON systems.

In Figure 6, the transformed version of the self-part, \(r^2G_s(r, t)\), is plotted as a function of \(r\) for Li₄SiO₄ and Li₄AlₓSi₁−ₓGe₁/₆P₁/₆O₄ at various simulation temperatures (373, 573, 773, and 973 K). (The \(r^2G_r(r, t)\) for Li₄Si₀.75P₀.25O₄ and the \(r^2G_d(r, t)\) for the three compositions can be found in the Supporting Information). For each temperature, six time interval values, \(t = 1, 10, 50, 100, 250,\) and 500 ps, were chosen to investigate the structural dynamics evolution. From these simulated data, we can classify three distinct types of diffusive behavior according to the shape of \(r^2G_s(r, t) = f(r)\) and \(r^2G_d(r, t) = g(r)\).

**Type I: Local Oscillation.** Li₄SiO₄ at 373 K (Figure 6a) and 573 K (Figure 6b) and Li₄Al₁/₃Si₁/₃Ge₁/₆P₁/₆O₄ at 373 K (Figure 6c); the calculated data show only one peak appearing between 0 and 0.5 Å. This peak suggests a high probability of finding lithium ions with this displacement value; this probability shows weak time dependence. Such a correlation function is typical of atomic vibrations around equilibrium positions. This finding is in good agreement with the result found in the density plot of MD simulations in our previous work.²⁰ This peak also appears in the other plots of Figure 6 (and is listed in Table 3). As the temperature increases, a right shift of the peak position is observed, which is in agreement with the fact that the Li⁺ ions have higher thermal energy at higher temperatures.

Figure 5. Simulated interaction between a Li⁺ ion and different \((\text{XO}_4)^{m−}\) tetrahedral groups. The interaction includes a long-range Coulomb term, a short-range Morse function, and a repulsive contribution.
At each temperature, the peak position for Li$_4$Al$_{1/3}$Si$_{1/6}$Ge$_{1/6}$P$_{1/3}$O$_4$ appears at an r value slightly larger than that for Li$_4$SiO$_4$, indicating that the motion of Li$^+$ ions is less constricted. The mechanism of Li$^+$ ion dynamics in these cases can be considered as a local oscillation.

**Type II: Ion Hopping.** For Li$_4$SiO$_4$ at 773 K (Figure 6c) and Li$_4$Al$_{1/3}$Si$_{1/6}$Ge$_{1/6}$P$_{1/3}$O$_4$ at 573 K (Figure 6f), the intensity of the probability peak around 0.40 Å decreases with the evolution of the simulation time. Therefore, the probability of finding a Li$^+$ ion around its equilibrium position is reduced, indicating that Li$^+$ ions have left their original position and migrated to other sites. Another feature in these Type II plots is the presence of a second peak at around $r = 2.4$ Å, which is the distance between a Li$^+$ ion and its closest Li$^+$ site in the lattice (varying from 1.8 to 2.9 Å). The appearance of this peak is the signal for Li$^+$ ion jumping to its neighboring site and staying on that site for a certain residual time. Similar to the peak at 0.40 Å, this peak is also time dependent, but its intensity increases with the measurement interval. For time-scales greater than ~100 ps, sufficient Li$^+$ hops occur to give an appreciable probability of finding a Li$^+$ ion on its neighboring site. The hopping can also be seen in the distinct-part of the van Hove correlation function (see the Supporting Information). In the distinct-part curve, there is a peak locating at around 0.4 Å, suggesting that the lithium sites are occupied by a new Li$^+$ ion other than the one at $t = 0$. These features suggest that Li$^+$ ion diffusion undergoes a hopping mechanism in the type II conditions.

**Type III: Correlated Superionic Flow.** Li$_4$SiO$_4$ at 973 K (Figure 6d) and Li$_4$Al$_{1/3}$Si$_{1/6}$Ge$_{1/6}$P$_{1/3}$O$_4$ at 773 K (Figure 6g) and 973 K (Figure 6h). In these type III plots, those curves at $t = 1$ ps have shapes similar to those in the type I plots. However, the intensity of the peak is much weaker (it should be noted that the scales of the vertical axis are not same), indicating a lower probability of finding a Li$^+$ ion around its original position. The peak has a large tail, showing that some of the Li$^+$ ions are displaced for distances larger than 1.5 Å in 1 ps. The curves at $t = 10$ ps are similar to those in the type II plots with a relatively low intensity peak at 0.4 Å and a broad peak at 2.8 Å, suggesting that in these conditions, 10 ps is long enough for a Li$^+$ ion to diffuse to its neighboring site. As the simulation time goes above 100 ps, no other significant peaks can be observed in these plots.

These data show that at high temperatures, a significant disordering of the Li$^+$ sublattice in the structure occurs, which leads to a more liquid-like distribution of Li$^+$ ions. The diffusivity of the Li$^+$ ions at these temperatures is significantly enhanced, leading to the nonlinear Arrhenius behavior in the conductivity values in Figure 4. The Li$^+$ dynamics can thus be considered to undergo a phase transition into “superionic flow.”

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**Table 3. First Peak Position (Å) in the Self-Part of the van Hove Correlation Function**

<table>
<thead>
<tr>
<th></th>
<th>373 K</th>
<th>573 K</th>
<th>773 K</th>
<th>973 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$SiO$_4$</td>
<td>0.20</td>
<td>0.30</td>
<td>0.35</td>
<td>0.45</td>
</tr>
<tr>
<td>Li$<em>4$Al$</em>{1/3}$Si$<em>{1/6}$Ge$</em>{1/6}$P$_{1/3}$O$_4$</td>
<td>0.25</td>
<td>0.30</td>
<td>0.40</td>
<td>0.50</td>
</tr>
</tbody>
</table>

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**Figure 6.** Transformed version of the self-part of the van Hove correlation function $\hat{r}^2G_s(r,t)$ for Li$_4$SiO$_4$ (a–d) and Li$_4$Al$_{1/3}$Si$_{1/6}$Ge$_{1/6}$P$_{1/3}$O$_4$ (e–h) at (from left to right) 373, 573, 773, and 973 K. For each temperature, six curves for $t = 1$, 10, 50, 100, 250, and 500 ps are plotted. At each temperature, the six curves indicate one of the three mechanism types as shown in (i). Li$^+$ ions are shown in yellow, XO$_4$ groups are shown in red.
The discussion above indicates that the mechanism of Li\(^+\) ion diffusion in each composition is temperature-dependent. From low to high temperature, the mechanism evolves from type I local oscillation to type II isolated hopping and to type III superionic flow. The diffusion mechanism changes from local oscillation to isolated hopping at intermediate temperature and to superionic flow, a faster Li\(^+\) ion mobility is achieved, thus promoting higher ionic conductivity. The mixed polyanion effect causes different compositions to show a transition to the next diffusion mechanism type at a temperature much lower than that in Li\(_4\)SiO\(_4\). For instance, Li\(_4\)Al\(_{1/3}\)Si\(_{1/3}\)Ge\(_{1/3}\)P\(_{1/3}\)O\(_4\) shows a transition to superionic motion at a temperature much lower than that for Li\(_4\)SiO\(_4\); hence, the room temperature conductivity is several orders of magnitude greater. In general, these results indicate the atomic scale origin of the orders of magnitude increase in ionic conductivity observed in substituted LISICON materials.

4. CONCLUSIONS
The lithium ion transport properties of a range of compositions (Li\(_2\)SiO\(_4\), Li\(_4\)Al\(_{1/3}\)Si\(_{1/3}\)Ge\(_{1/3}\)P\(_{1/3}\)O\(_4\), Li\(_4\)Al\(_{0.33}\)Si\(_{0.33}\)P\(_{0.33}\)O\(_4\), and Li\(_4\)Al\(_{1/3}\)Si\(_{1/6}\)Ge\(_{1/6}\)P\(_{1/3}\)O\(_4\)) in the LISICON-type structural family were investigated using a combination of synthesis, diffraction, impedance, and modeling techniques. This includes the first detailed report of the crystal structure, including atomic positions and site occupancies of Li\(_4\)Al\(_{0.33}\)Si\(_{0.33}\)P\(_{0.33}\)O\(_4\), and the transport properties of a new composition Li\(_4\)Al\(_{0.33}\)Si\(_{0.33}\)P\(_{0.33}\)O\(_4\). The following main findings emerge from our investigation.

First, the ionic conductivity of Li\(_4\)SiO\(_4\) is not high but can be enhanced through successful substitution on the Si\(^{4+}\) site. Such doping leads to a mixed polyanion effect which will modify the potential energy surface and decrease the Li\(^+\) ion conduction barrier. Second, the MD modeling results reveal three temperature-dependent mechanisms for Li\(^+\) ion diffusion: (i) local oscillation at low temperature, (ii) isolated hopping at intermediate temperature, and (iii) superionic motion at high temperature. Moreover, we showed that the type of mechanism in operation depends on both the temperature and composition. Li\(_4\)Al\(_{1/3}\)Si\(_{1/3}\)Ge\(_{1/3}\)P\(_{1/3}\)O\(_4\) shows a transition to superionic motion at a temperature much lower than that of Li\(_4\)SiO\(_4\); hence, the room temperature ionic conductivity of 0.9 mS/cm is several orders of magnitude higher. The results are generally applicable to all materials in the LISICON family, which share the same structural motif of Li-rich compounds with isolated polyanion tetrahedra.

These insights are important to rationalize how ionic transport is related to local structure and composition, and to develop new strategies for designing solid electrolyte materials with high ionic conductivity. A future avenue to exploit this effect would be mixed oxysulfide compositions where the size difference in tetrahedra would be even greater than that in the oxides considered here, although a major challenge presented by such oxysulfides (and by substituted LISICONs in general) is the suppression of phase separation.

**ASSOCIATED CONTENT**

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b14402.

Equation and values of parameters used in the interatomic potentials, self-part of the van Hove correlation function for Li\(_{4.25}\)Si\(_{0.75}\)Al\(_{0.25}\)O\(_4\) distinct-part of the van Hove correlation function, single crystal measurement conditions and refinement results, Havens ratio values, crystallographic data, and powder neutron diffraction pattern for Li\(_{4.25}\)Si\(_{0.75}\)Al\(_{0.25}\)O\(_4\).

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**Notes**

The authors declare no competing financial interest.

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