Structural and Mechanistic Insights into Fast Lithium-Ion Conduction in Li₄SiO₄—Li₃PO₄ Solid Electrolytes

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Supporting Information

ABSTRACT: Solid electrolytes that are chemically stable and have a high ionic conductivity would dramatically enhance the safety and operating lifespan of rechargeable lithium batteries. Here, we apply a multi-technique approach to the Li-ion conducting system (1−z)Li₄SiO₄−zLi₃PO₄ with the aim of developing a solid electrolyte with enhanced ionic conductivity. Previously unidentified superstructure and immiscibility features in high-purity samples are characterized by X-ray and neutron diffraction across a range of compositions (z = 0.0−1.0). Ionic conductivities from AC impedance measurements and large-scale molecular dynamics (MD) simulations are in good agreement, showing very low values in the parent phases (Li₄SiO₄ and Li₃PO₄) but orders of magnitude higher conductivities (10⁻² S/cm at 573 K) in the mixed compositions. The MD simulations reveal new mechanistic insights into the mixed Si/P compositions in which Li-ion conduction occurs through 3D pathways and a cooperative interstitial mechanism; such correlated motion is a key factor in promoting high ionic conductivity. Solid-state ⁶Li, ⁷Li, and ³¹P NMR experiments reveal enhanced local Li-ion dynamics and atomic disorder in the solid solutions, which are correlated to the ionic diffusivity. These unique insights will be valuable in developing strategies to optimize the ionic conductivity in this system and to identify next-generation solid electrolytes.

1. INTRODUCTION

The revolution in portable electronic devices has been powered by rechargeable lithium-ion batteries. Such batteries with liquid electrolytes, however, have cycle life and safety issues, whereas all-solid-state batteries with inorganic electrolytes may be regarded as a safer long-term solution.¹−⁶ Many structural families⁷−¹² have been investigated to identify potential ion-conducting solid electrolytes, including framework-type materials based on NASICON, LISICON, thio-LISICON, and garnet structures. Recently, a sulfur-based Li₂S–P₂S₅ glass–ceramic solid electrolyte has been reported to show an ionic conductivity (1.7 × 10⁻² S/cm at room temperature) higher than those of many commonly used liquid electrolytes.¹³ However, sulfide-based electrolytes are very hygroscopic¹⁴ and must be prepared in a water-free environment. They also operate in limited voltage windows. Although oxides do not currently have as high ionic conductivity as sulfides, they exhibit higher stability and are easier to synthesize and handle.

The Li₄SiO₄−Li₃PO₄ solid solution system and the end-member parent phases have been identified as potential solid electrolytes,¹⁵−²⁷ but not all compositions have been fully characterized. It has been reported that the ionic conductivity can be increased by 3 orders of magnitude for Li₄−xSi₁−yPₓO₄ or γ-Li₃ySiP₁−yO₄ compositions, compared with the two end members, Li₄SiO₄ and γ-Li₃PO₄.¹⁸

This drastic enhancement of conductivity is believed to be caused by the increased concentration of Li-ion vacancies in Li₄−xSi₁−yPₓO₄ and Li-ion interstitials in Li₃ySiP₁−yO₄, with the ionic defects acting as charge carriers. However, an atomic-scale understanding of the conduction mechanisms and local structures in this system is still lacking; such detail is important for developing strategies for optimizing the conductivity, as well as identifying next-generation materials.

Both Li₄SiO₄ and γ-Li₃PO₄ are related to the LISICON-type structure with X₀₆-based (X = Si or P) tetrahedral units (Figure 1), and Li–O polyhedra. The crystal structure of Li₄SiO₄ was initially reported²⁸ to be monoclinic (space group P2₁/m, with β very close to 90°) and to contain six partially occupied crystallographically independent lithium sites. However, in the correct description lithium sites are fully occupied, giving rise to a complex 7-fold superstructure.²⁹ γ-Li₃PO₄

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Li₃PO₄ system, using a powerful combination of experimental γ-defect arrangements are considered, as well as large-scale (MD) techniques, in which the relative energies of possible ordering and Li-ion dynamics. The crystal structures and ion spectroscopy is used to provide insights into local structural possess the same crystal structure, despite being closely related various di-solubility limits and computational techniques. Very high purity Li₄SiO₄, purchased from Sigma-Aldrich, including LiOH, then slowly heated to 80 °C to evaporate water. The resulting solid was pulverized and cold-pressed into pellets under 40 MPa. The pellets were then heated in alumina combustion crucibles at 900 °C for 10 h under Ar flow, followed by slow cooling to room temperature, and then pulverized. Energy-dispersive X-ray (EDX) analysis indicated no contamination of Al from the crucible. Scanning electron microscopy showed that the synthesized samples consist of aggregates of about 100 μm in size and smaller individual particles of about 10–50 μm. Since these samples are quite reactive with CO₂, they were stored in a glovebox. Single crystals of Li₃SiO₄ were prepared by a similar method, except that the final heating temperature was set to 1200 °C, and the cooling rate was set to 10 °C/h. To produce pure γ-Li₄PO₄, commercially available β-Li₄PO₄ was heated at 850 °C for 10 h, cooled to room temperature, and pulverized.

2. METHODS

2.1. Synthesis. The raw materials used in this work were all purchased from Sigma-Aldrich, including LiOH·H₂O (98%), SiO₂ (fumed, dried at 500 °C for 3 h) and β-Li₄PO₄ powders. Stoichiometric mixtures of raw materials were dispersed in distilled water, the quantity of which was adjusted to give an overall concentration of 0.6 mol of Li per liter of H₂O. The solution was then slowly heated to 80 °C to evaporate water. The resulting solid crystallizes in a structure similar to Li₄SiO₄ but with orthorhombic symmetry (space group Pnam), as illustrated in Figure 1. The positions of the Si and P atoms are quite similar, but the respective orientations of the SiO₄ and PO₄ tetrahedra are different: up—down—up—down for Li₄SiO₄ and down—down—up—up for γ-Li₄PO₄ (along a ≈ 2cₕ).

However, there have been limited structural studies of the complete solid solution. Early work by Hui and West determined that the Li₄SiO₄–Li₃PO₄ system did not yield one single continuous solid solution, as both end members do not possess the same crystal structure, despite being closely related to each other. More recent work by Arachi et al. proposed solubility limits x₄ ≈ 0.40 for Li₄-xSi₁₋ₓPₓO₄ and y₄ ≈ 0.40 for Li₁₋₄Siₓ₁₋₄Pₓ₊₁₋₄O₄, while the existence of single-phase Li₁₋₄Siₓ₁₋₄Pₓ₊₁₋₄O₄ remains uncertain.

Here, we investigate the crystal chemistry and ion transport properties of solid solution compositions within the Li₄SiO₄—Li₃PO₄ system, using a powerful combination of experimental and computational techniques. Very high purity Li₄SiO₄, LiₓSi₁₋ₓPₓO₄, Li₃SiₓPₓ₋₁₋₄O₄, and γ-Li₃PO₄ samples were obtained and further investigated by various diffraction (single-crystal, powder X-ray, powder neutron) techniques. Solid-state ⁷Li, ³¹Li, and ³¹P NMR spectroscopy is used to provide insights into local structural ordering and Li-ion dynamics. The crystal structures and ion transport are then investigated by atomistic molecular dynamics (MD) techniques, in which the relative energies of possible defect arrangements are considered, as well as large-scale simulations of ion transport mechanisms.

2.4. Solid-State NMR Spectroscopy. Powder samples of Li₃SiO₄, LiₓSi₁₋ₓPₓO₄, Li₃SiₓPₓ₋₁₋₄O₄, and Li₃SiₓPₓ₊₁₋₄O₄ and Li₃PO₄ were packed in 1,3,4,0, or 7.0 mm ZrO₂ rotors (Bruker) and closed with Kel-F or BN caps, depending on the temperature of the experiment. All sample handling was done under an Ar atmosphere in a glovebox with p(H₂O,O₂) < 0.1 ppm. Ambient and high-temperature (320–875 K) ³¹Li magic angle spinning (MAS) NMR experiments were performed at 9.4 T (Avance III console) using a Bruker double-resonance 7.0 mm MAS probe with laser heating of the sample. Temperature calibration using KBr was done before measuring the samples. ³¹Li NMR signal line shapes were determined by one-pulse experiments with high-power pulses of 2.1 μs (7.0 mm MAS) and 0.9 μs (4.0 mm MAS) and a repetition time of 5.0 s. A saturation recovery pulse sequence was applied to determine ³¹Li spin–lattice relaxation time constants (T₁) at variable temperatures. Ambient temperature ³¹Li MAS NMR experiments were performed at 11.7 T (Avance III HD console) using a Bruker triple-resonance 4.0 mm MAS probe, including a temperature calibration on the ³¹Pb shift in lead nitrate before the actual experiment. ³¹Li pulse optimization was done on Li₂CO₃ and followed by NMR signal line shape measurements on LiₓSi₁₋ₓPₓO₄, LiₓSiₓPₓ₋₁₋₄O₄, and LiₓSiₓPₓ₊₁₋₄O₄ using a one-pulse sequence with high-power pulses of 4.45 μs and a repetition time of 25 s. The ³¹Li and ³¹P Li NMR shifts were referenced to a 1 M LiCl solution in D₂O. Activation energies were derived by both

Figure 1. Schematic representations of the crystal structures of the end member phases Li₃SiO₄ (subcell) and γ-Li₄PO₄. Key: SiO₄ and PO₄ blue and red tetrahedra; lithium, green. Partially occupied Li sites are represented by partial shading. Unit cells are shown as solid lines.
Bloembergen—Purcell—Pound (BPP) fits and fitting of the linear regimes in Arrhenius plots (SI, Table S2). Due to the low natural abundance of $^{7}\text{Li}$ (7.59%) vs $^{6}\text{Li}$ (92.41%) and the significantly longer relaxation times, we focused on $^{7}\text{Li}$ NMR experiments in this study for the sake of higher sensitivity and shorter measurement times. $^{31}\text{P}$ MAS NMR experiments were performed at ambient temperature in a magnetic field of 16.4 T using a Bruker 1.3 mm triple-resonance MAS probe on an Avance III console. Pulse optimization was done using ammonium dihydrogen phosphate (ADP). A one-pulse sequence with high-power 1.8 $\mu$s pulses and a recycle delay of 3.0 s was applied to acquire the spectra for the line-shape measurements. The $^{31}\text{P}$ NMR signals were referenced to 85% H$_3$PO$_4$.

2.5. Atomistic Modeling. Interatomic potentials-based methods, which are well established and detailed elsewhere, were employed. The effective potentials describing the interatomic forces include a long-range Coulomb term, short-range Morse function, and repulsive contribution. The parameters were taken from the extensive library of potentials developed by Pedone et al., which have been shown to perform well in MD simulations of silicates and polyanion-type materials. Further details can be found in the SI, Table S3. Modeling of crystal structures and different defect ordering schemes was carried out using energy minimization methods (GULP code). For ion diffusion modeling we have used MD methods (DL_POLY 4 code). A time step of 1 fs for MD runs of up to 5 ns with supercells containing 20 000–30 000 ions was employed. Simulations were carried out at several temperatures (300–673 K). Each set of calculations was repeated three times to confirm good statistics. Such computational methods have been applied successfully to other Li-ion battery materials.

To facilitate comparison with experimental data, the calculated diffusion coefficients ($D$) were used to derive the ionic conductivity ($\sigma$) using the Nernst—Einstein relationship

$$\sigma = \frac{n q^2}{D kT}$$

where $n$ is the number of particles per unit volume, $q$ is the charge of an electron, $k$ is the Boltzmann constant, and $T$ is the temperature. $H_0$ is the correlation factor (or Haven ratio), defined as the ratio of the tracer diffusion coefficient to a diffusion coefficient dependent upon the ionic conductivity. In this work we have used the methods of Morgan and Madden to determine $H_0$. A Haven ratio of 1.0 suggests uncorrelated ion hopping, whereas high values ($>2$) are observed in fast-ion conductors with highly correlated ionic motion.

3. RESULTS AND DISCUSSION

3.1. Structures of (1−$z$)Li$_3$SiO$_4$−$z$Li$_3$PO$_4$ Solid Solutions. Our study confirms that the compositions Li$_3$SiO$_4$ and Li$_{1.75}$Si$_{0.75}$P$_{0.25}$O$_4$ can be indexed in space group P2$_1$/m, while Li$_{1.5}$Si$_{0.5}$P$_{0.5}$O$_4$ and Li$_{1.25}$Si$_{0.25}$P$_{0.75}$O$_4$ adopt the $\gamma$-Li$_3$PO$_4$ structure (Figure 2a). Lattice parameters refined from XRPD data are collected in Table 1.

To obtain deeper insights into the phase stabilities within the Li$_3$SiO$_4$–Li$_3$PO$_4$ system, we prepared several (1−$z$)Li$_3$SiO$_4$−$z$Li$_3$PO$_4$ compositions in steps of 0.25, where two phases coexist (Figure 2b; note that $c_0 \approx a_0$).

The XRPD pattern of Li$_3$SiO$_4$ was indexed and the lattice parameters were refined using the unit cell proposed by Völlenkle in the monoclinic space group P2$_1$/m. Most of the diffraction peaks of our sample could be indexed, but, as shown in Figure 3, many small-intensity contributions remained unidentified. These are signatures of lithium ordering within Li$_3$SiO$_4$ producing the supercell previously reported from single-crystal diffraction work and seen here for the first time in XRPD data.

Tranqui et al. described the structure of Li$_3$SiO$_4$ using the P2$_1$/m space group ($a = 11.546$ Å, $b = 6.090$ Å, $c = 16.645$ Å, $\beta = 99.5^\circ$, and $Z = 14$). The structure contains SiO$_4$ tetrahedra and LiO$_6$ ($n = 4, 5, 6$) polyhedra. The 19 fully occupied crystallographic sites for Li are distributed over 9 4f Wyckoff positions, while the other 10 are at 2e positions; this results in 56 lithium atoms per unit cell. A similar structure was proposed by de Jong, using results from single-crystal XRD and XPS measurements. Their structure was basically the same as that in previous work, with the main difference being the splitting of the Li(51) and Li(65) sites ($^\circ$) over two additional sites. It is noted that these sites in Tranqui’s work had thermal displacement parameters of 4.79 and 4.04 $\AA^2$, respectively, approximately twice as large as those for the other Li atoms. All four positions then have an occupancy of 0.5, which introduces a small degree of positional disorder over the Li sublattice. Careful inspection of our Li$_3$SiO$_4$ powder revealed that it contained single crystals of sufficient size (~20 $\mu$m) for precise structural analysis. Our refined structure contains 19 independent lithium sites. The corresponding Li(51) and Li(65) sites display isotropic thermal displacement parameters as high as 6.48 and 3.21 $\AA^2$, indicating that these two lithium
ions are loosely bound to their ideal positions. We carried out a second set of refinements by splitting the two sites. This resulted in occupancy factors for the sites split from Li(51) of 0.520(12) and 0.480(12).

The published atomic coordinates of each structure type (Li4SiO4 or Li3PO4 system, only the

Within the Li4SiO4−Li3PO4 system, only the Li3.75Si0.75P0.25O4 composition has been previously investigated by single-crystal XRD. The refinement converged to an overall composition of Li3.43Si0.75P0.25O4 after summation of individual Li site occupancy factors. We determined the crystal structures of the three solid solution compositions Li3.75Si0.75P0.25O4, Li3.5Si0.5P0.5O4, and Li3.25Si0.25P0.75O4 through Rietveld refinements of neutron powder diffraction data. Unlike Li3PO4, these three compositions do not exhibit long-range ordering of lithium ions at room temperature and therefore can be described using the original unit cells in Table 1.

The published atomic coordinates of each structure type (Li4SiO4 or γ-Li3PO4) were used as starting models for the refinements of Li3.75Si0.75P0.25O4, Li3.5Si0.5P0.5O4, and Li3.25Si0.25P0.75O4 compositions. The main challenge here was to localize the lithium atomic positions and occupancy factors. The refinement strategy can be illustrated using the original unit cells in Table 1.

Table 1. Cell Parameters Determined from X-ray Powder Diffraction for the (1−z)Li4SiO4−(z)Li3PO4 System

<table>
<thead>
<tr>
<th></th>
<th>Li4SiO4 (z = 0)a</th>
<th>z = 0.25</th>
<th>z = 0.50</th>
<th>z = 0.75</th>
<th>Li3PO4 (z = 1)</th>
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<tr>
<td>space group</td>
<td>P21/m</td>
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<td>Pnma</td>
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<tr>
<td>a (Å)</td>
<td>5.1504(3)</td>
<td>5.1094(2)</td>
<td>10.5990(7)</td>
<td>10.5356(3)</td>
<td>10.4763(3)</td>
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<tr>
<td>b (Å)</td>
<td>6.1012(4)</td>
<td>6.1135(4)</td>
<td>6.1155(3)</td>
<td>6.1169(2)</td>
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<tr>
<td>c (Å)</td>
<td>5.2998(3)</td>
<td>5.3002(4)</td>
<td>5.0114(3)</td>
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<td>β (deg)</td>
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<td>90</td>
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<td>90</td>
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<tr>
<td>V/Z (Å³)</td>
<td>83.268(3)</td>
<td>82.777(2)</td>
<td>81.207(2)</td>
<td>80.067(2)</td>
<td>78.924(2)</td>
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</table>

Subcell parameters of Li4SiO4 are used for ease of comparison.

Figure 3. Full pattern profile matching of XRPD pattern of Li4SiO4; red dots, experimental data; black line, profile matching; blue bar, Bragg positions of the small cell; green bar, Bragg positions of the 7-fold super cell.

Figure 4. Fourier-transformed scattering density difference maps (at z = 0.7) from refinements of Li3.75Si0.75P0.25O4 neutron diffraction data (a) in the absence of Li1, (b) in the absence of Li2, and (c) with both Li1 and Li2.

These maps clearly reveal sharp difference density peaks at the atomic positions of Li1 and Li2, which were then subsequently used to refine the overall structure, as well as other positions in the unit cell.

In order to determine the positions of the last two Li atoms in the unit cell, two models were used to refine the structure. The first straightforward ‘3Li’ model was based on the previous ‘2Li’ model, with a third Li crystallographic position added where the Fourier-transformed scattering density difference map had the sharpest peak. A second ‘6Li’ model was used as a starting configuration, based on the knowledge that the nonequivalent structure of Li3.75Si0.75P0.25O4 contains six crystallographically different lithium sites. In both cases, the refinements of cell parameters, atomic positions, and anisotropic thermal factors (B_aniiso) of Si, P, and O gave reasonable values. The refinement of the isotropic thermal factor Biso of Li(3) in the ‘3Li’ model or Li(6) in the ‘6Li’ model led to a divergence attributed to the low occupancy of the sites. Rietveld refinements resulted in a final value of the Bragg R-factor of 6.13% for the ‘3Li’ model and 4.92% for the ‘6Li’ model. The diffraction pattern and refinement results for
the “6Li” model, finally chosen as the most reliable one, are shown in Figure 5 and in SI, Table S4.

Similar studies were carried out to determine the crystal structures of Li₃₋ₓSiₓP₀.₇₅O₄ and Li₃₋ₓSiₓP₁₋ₓO₄ (data summarized in SI, Tables S5 and S6, respectively). All of these compositions show highly symmetrical XO₄ tetrahedra (Si₁₋ₓPₓO₄) with very small variation in the X−O bond lengths and O−X−O angles very close to 109.47°. Baur’s polyhedral bond length distortion indices⁵⁸ are 0.5% for x = 0.25, 0.2% for x = 0.5, and 0.2% for x = 0.75, which are close to the usual value of 0.5% found in orthophosphates. The variation of the average X−O bond length with x in Si₁₋ₓPₓO₄ tetrahedra is in excellent agreement with those obtained from linear interpolation between the average Si−O distance in Li₄SiO₄ and the average P−O distance in Li₃PO₄ (SI, Table S7). This further indicates that the experimental Si/P stoichiometry of the powders is very close to the nominal one. A detailed list of Li−O bond lengths can be found in SI, Table S4. The longer average Li−O distance around Li(6) (2.25 Å) is consistent with its lower occupancy factor (0.14). LiO₆ face- and edge-sharing polyhedra are interconnected so as to generate a 3D conducting network.

Variable-temperature (VT) ⁷Li NMR signal line shapes of Li₃₋ₓSiₓP₀.₇₅O₄, Li₃₋ₓSiₓP₁₋ₓO₄ show a significant change of the broadening and intensity of rotational sidebands as well as the CT’s fwhm (Figure 6 and SI, Figure S9). Different regimes of Li motion and Li−Li couplings are revealed for different temperatures.

Figure 5. Neutron powder diffraction pattern and Rietveld refinement of Li₃₋ₓSiₓP₀.₇₅O₄.

Figure 6. ⁷Li VT MAS (4 kHz) NMR signals at 9.4 T. The middle graph shows the full spectra for Li₃₋ₓSiₓP₀.₇₅O₄ with a zoom of the first rotational sidebands at high temperatures (top). Temperature-dependent ⁷Li fwhm values of the CT signals are depicted at the bottom for all samples.
ments reveal a decrease of the coordination number with increasing P substitution. This indicates a disperse distribution of the Li atoms (“liquid-like”) with a mobile sublattice of the LiO4 polyhedra that is highly disordered.

31P high-speed MAS NMR data revealed one signal for the pure phosphate Li3PO4 with 145 Hz in fwhm of 8.9(1) ppm, which is in line with the crystal structure (SI, Figure S11). A significant broadening of the line shapes with fwhm of 666, 626, and 489 Hz for Li3.25Si0.25P0.75O4, Li3.5Si0.5P0.5O4, and Li3.75Si0.75P0.25O4, respectively, indicates atomic disorder due to the mixed occupancies of the Si/P sites.

Only slight shift variations with respect to the Si/P occupancy are found, in line with previous 31P NMR measurements.62 The highest shift and a pronounced asymmetry are found for Li3.5Si0.5P0.5O4, indicating local atomic ordering that is more complex than the spatially averaged picture derived from dihedral ordering. Here, the structural models and the interatomic potentials can be used reliably in the MD calculations.

Overall, the good reproduction of these complex structures of mixed compositions (for example, 4 × 10−8 cm2/s for Li3.25Si0.75P0.25O4). Calculated ionic conductivities are compared with experimental values from our AC impedance measurements in Figure 8 (the AC impedance spectra are shown in SI, Figure S13). The trends and magnitude of the ionic conductivities of all compositions are highly compatible and show that the formation of solid solutions increases the ionic conductivity by 3–4 orders of magnitude compared to the two end members; for example, at 573 K, the three intermediate compounds have conductivities of about 2.5 × 10−3 S/cm, while the ionic conductivity for pure phosphate Li3PO4 system at 573 K.

3.2. Li-Ion Conductivity and Dynamics. Examination of Li+ diffusion rates and conductivity is important for predicting battery charge/discharge rates, which we investigated using MD, AC impedance, and NMR spectroscopy. MD techniques are well suited to probing transport mechanisms at the atomic level, especially cooperative or correlated ion motion. Here, MD calculations over long simulation times of up to 5 ns were carried out over a temperature range covering typical battery operating temperatures for all compositions.

First, the mean-squared displacements (MSDs), \( \langle r^2(t) \rangle \), of all lithium ions (Figure 7) show that Li+ diffusion is significantly higher in the mixed PO4/SiO4 compositions than in the two end members. The Li+ diffusion coefficient \( D_{Li} \) can be derived from the MSD data according to \( \langle r^2(t) \rangle = 6D_{Li} t + B \). We calculate \( D_{Li} \) values of 2 × 10−9 and 2 × 10−12 cm2/s for Li3SiO4 and Li3PO4, respectively, at 573 K, with higher values for the fractional occupancies, numerous (>10 000) structure models were first energy minimized using random distributions of Li, Si, and P on their respective sites to find low-energy configurations. Calculated and observed structural parameters are given in Table 2 for the two end-member phases, Li3SiO4 and Li3PO4, and for Li3.25Si0.75P0.25O4 (data for Li3.75Si0.75P0.25O4 and Li3.25Si0.25P0.75O4 are listed in SI, Table S12). The calculated cell parameters and mean bond lengths deviate from experiment by at most 2%, and in most cases much less. Overall, the good reproduction of these complex structures of numerous different compositions gives us confidence that both the structural models and the interatomic potentials can be used reliably in the MD calculations.

Table 2. Comparison of Calculated Structural Parameters with Diffraction Data for (1−z)Li4SiO4−zLi3PO4

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<th>z</th>
<th>expt</th>
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<td>Li−O (Å)</td>
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<td>2.080</td>
<td>1.974</td>
<td>1.968</td>
<td>2.022</td>
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Figure 7. Mean-squared displacement (MSD) plots for Li+ for the different compositions at 573 K. Full lines indicate end members, while dashed lines represent intermediate compositions.

Figure 8. Experimental (blue squares) and calculated (red circles) ionic conductivities for the Li3SiO4−Li3PO4 system at 573 K.
conductivity is $2.5 \times 10^{-6}$ S/cm for Li$_4$SiO$_4$ and $1.2 \times 10^{-8}$ S/cm for Li$_3$PO$_4$.

For the intermediate compositions, conductivity values obtained from MD calculations (red circles in Figure 8) show good agreement with experimental values. For the end members, the calculated ionic conductivities are higher than those observed experimentally, especially for Li$_4$SiO$_4$. This difference is most likely due to these materials being poor ionic conductors with very slow lithium-ion diffusion, which did not reach the fully equilibrated state during the long MD simulations. Nevertheless, the trend in ionic conductivities across the composition range is well reproduced.

$^7$Li MAS NMR reveals much smaller spin–lattice relaxation times ($T_1$) of 3.60, 2.07, and 1.37 s for Li$_{3.75}$Si$_{0.75}$P$_{0.25}$O$_4$, Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$, and Li$_{3.25}$Si$_{0.25}$P$_{0.75}$O$_4$, respectively, compared to 42.4 s for Li$_3$PO$_4$ and 21.2 s for Li$_3$SiO$_4$; these results suggest enhanced Li-ion dynamics in the solid solutions, in agreement with the impedance and modeling results. $^7$Li VT $T_1$ measurements for the solid solution samples show a high temperature $T_1$ minimum that is in line with literature data for samples of similar composition (Figure 9 and SI, Figure S14). Furthermore, the asymmetry of the slopes below and above the $T_1$ minima are in agreement with previous results for fast ion conductors. A determination of the respective activation energies via a BPP fit gives 0.18(3), 0.23(2), and 0.21(2) eV for Li$_{3.75}$Si$_{0.75}$P$_{0.25}$O$_4$, Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$, and Li$_{3.25}$Si$_{0.25}$P$_{0.75}$O$_4$, respectively (Figure 11, and SI, Tables S2 and S15). These values are lower than those from previous NMR measurements, which is likely due to their slightly different compositions as well as the alternative synthesis routes.

Activation energies have also been derived from MD simulations (SI, Figure S16) and AC impedance measurements from Arrhenius plots (SI, Figure S17); a representative example is shown in Figure 10. Their values are listed together with BPP fitted values in SI, Table S15, and the results from the three techniques are summarized in Figure 11. In general, the results for the mixed compositions from all techniques demonstrate the same trends with much lower activation energies than the two end members. The absolute values of the activation energies, however, are sensitive to different length scales and degrees of long-range order probed by each technique. NMR $T_1$ data is highly sensitive to local ion hopping such as the rapid oscillation over the low energy barrier between the split Li sites. In MD this local oscillatory behavior is averaged out and only long-range ionic transport in the bulk contributes, whereas AC impedance contains contributions from the entire sample, including grain boundary resistance.

On the basis of the BPP fit of the VT $^7$Li NMR data and the respective correlation times $\tau_C$ at 573 K, we derived average jump rates for the Li atoms of 0.76, 1.49, and 1.18 GHz for Li$_{3.75}$Si$_{0.75}$P$_{0.25}$O$_4$, Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$, and Li$_{3.25}$Si$_{0.25}$P$_{0.75}$O$_4$, respectively. Using the Einstein–Smoluchowski equation and the Li–Li jump distance of 1.76 Å (derived via MD hopping analysis) the respective diffusion coefficients $D^\parallel$ (at 573 K) are calculated to be $3.9 \times 10^{-8}$, $7.7 \times 10^{-8}$, and $6.1 \times 10^{-8}$ cm$^2$/s for Li$_{3.75}$Si$_{0.75}$P$_{0.25}$O$_4$, Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$, and Li$_{3.25}$Si$_{0.25}$P$_{0.75}$O$_4$, respectively. These values are again in line with the data and trends from the MD simulations.

3.3. Atomistic Conduction Mechanism. Of great interest to our present discussion is the question of the underlying
atomic-scale mechanism in the solid solutions that promotes enhanced conductivity. MD density plots of the accumulated lithium ion trajectories over the simulated time scale are a useful means of visualizing the migration pathways and the regions in the lattice which are most frequently traversed by the mobile Li+ ions.

Lithium diffusion density plots are shown in Figure 12 for Li3PO4, Li3SiO4, and Li3.5Si0.5P0.5O4 at 573 K. First, it can be seen that the trajectories in the mixed composition form a continuous 3D network of conduction pathways; this suggests that there is significantly greater Li+ diffusion in the mixed composition than in the two end members. The 3D nature is important since the dimensionality of the Li+ diffusion can have a major impact on the battery charge/discharge rate. For example, LiFePO4 is a 1D conductor, and the presence of blocking defects in the 1D channels can severely impede the diffusion and the capacity.43 In contrast, 3D diffusion behavior allows lithium access through all surfaces of the particles, irrespective of their crystallographic orientation, and would be less affected by blocking defects.

In previous studies64,65 on the related Na3PO4 material, the contribution of tetrahedral rotation to ion conduction (termed the “paddle wheel” effect) has been discussed. To examine if such effects also operate in the Li3SiO4−Li3PO4 system, the movement of oxygen ions in the SiO4/PO4 tetrahedra during the MD simulation were plotted (Figure 13); it can be seen that the tetrahedra undergo only slight displacements, but with no major rotational motion to aid Li+ conduction.

This result is in line with the findings of the 31P NMR experiments. During the applied high-speed MAS experiments at 60 kHz using ambient temperature bearing and drive gas migration snapshots are presented, and shows the migrating interstitial Li ion displacing an adjacent Li ion into an interstitial position within the neighboring polyanion layer. Such a cooperative mechanism facilitates lithium-ion diffusion and promotes high ionic conductivity in these mixed Si/P compositions.

NMR studies69,67 have reported lithium site exchange between different coordination environments, which is consistent with the mechanism presented here. Previous ab initio studies68 of off-stoichiometric Li1-xPO4 set up with lithium interstitial defects find a low energy barrier for a Li+ interstitialalcy mechanism. Similar cooperative mechanisms have been suggested in other lithium-ion conductors46,69 and may be important in related framework-structured materials.70

As noted earlier, we have also analyzed the Haven ratio values to obtain a more quantitative assessment of the degree of correlated motion. For Li3PO4 a Haven ratio close to 1.0 at all temperatures is found (SI, Figure S18) suggesting uncorrelated ion motion, and consistent with the observed low conductivity. For Li3SiO4 correlated motion is not found at low temperatures (373 K) with a Haven ratio of 1.03; at elevated temperatures (473 K), as more lithium ions become mobile, some correlated motion is indicated with a Haven ratio reaching a value of 1.6. Given these results and the greater Li content of Li3SiO4, a high conductivity may be expected. However, the observed activation energy for lithium migration in Li3SiO4 is as high as 0.84 eV (Figure 11) indicating low mobility. For the mixed Si/P compositions we find higher Haven ratios in the range 2.3 to 3.6 (at 473 K) indicating significantly more correlated motion than in Li3SiO4 and consistent with the enhanced ionic conductivity that is experimentally observed.

flows the sample temperature is increased up to 70 °C.56 However, the decrease of the MAS speed to 30 kHz (ca. 35 °C) and below does not affect the 31P NMR signal line shape (SI, Figure S11), which indicates no significant movement of the anionic tetrahedra in this temperature regime.

Detailed analysis of ion transport from the MD simulations reveals that Li+ diffusion takes place by a cooperative interstitial or knock-on type mechanism involving the concerted motion of interstitial and lattice Li+ ions. This is illustrated in Figure 14 for Li3.5Si0.5P0.5O4 where continuous

![Figure 12](Image)

**Figure 12.** MD density plots of mobile lithium ions (green) overlaid on the tetrahedral framework structure (PO4, red; SiO4, blue) of Li3PO4, Li3SiO4, and Li3.5Si0.5P0.5O4.

![Figure 13](Image)

**Figure 13.** Density plots of oxygen atoms (orange) during the MD simulation overlaid on the tetrahedral framework structure of Li3.5Si0.5P0.5O4 (PO4, red; SiO4, blue).

![Figure 14](Image)

**Figure 14.** MD simulation snapshots of Li-ion positions in Li3.5Si0.5P0.5O4 showing the cooperative knock-on like mechanism: the migrating interstitial Li+ (green) displaces another Li+ (purple) toward a neighbor site which in turn leads to further Li+ (blue) migration (PO4, red; SiO4, blue).
On the basis of these insights, we suggest that further conductivity enhancement may be possible by disordered the lithium sublattice via mixing or doping of the polyanion framework. We are currently exploring such solutions as well as synthesizing $^6$Li-enriched samples of the solid solution to perform 1D and 2D exchange $^6$Li NMR experiments.

4. CONCLUSIONS

This investigation of the Li$_4$SiO$_4$–Li$_3$PO$_4$ solid electrolyte system has used a powerful multi-technique approach of diffraction, AC impedance, NMR spectroscopy, and atomistic modeling to obtain new information concerning the crystal structures and lithium-ion conduction mechanisms. Several key features emerge:

(a) An immiscibility zone has been found for (1−$z$)Li$_4$SiO$_4$–$z$Li$_3$PO$_4$ compositions around 0.35 < $z$ < 0.45. Lower $z$ compositions can be indexed to Li$_3$SiO$_3$P$_2$O$_7$ structures, while higher $z$ compositions are γ-Li$_3$PO$_4$-like. The crystal structures of the mixed compositions Li$_{3.5}$Si$_{0.5}$P$_{0.5}$O$_4$ and Li$_{3.25}$Si$_{0.25}$P$_{0.75}$O$_4$ have been determined for the first time, and can be described as isolated SiO$_4$ or PO$_4$ tetrahedra with a distribution of lithium atoms on multiple crystallographic sites. Such a disordered lithium sublattice is supported by $^6$Li NMR results.

(b) Both AC impedance and MD simulation results for the (1−$z$)Li$_4$SiO$_4$–$z$Li$_3$PO$_4$ system reveal appreciable ionic conductivities ($10^{-3}$ S/cm at 573 K) in the mixed compositions ($z$ = 0.25, 0.5, 0.75), which are orders of magnitude higher than those of the end members. $^7$Li and $^{31}$P NMR results on local structure are in line with these findings and reveal the sensitivity of the activation energies to the local Li-ion dynamics.

(c) New fundamental understanding of the microscopic conduction mechanism is found. The MD simulations of the mixed Si/P compositions reveal Li-ion conduction pathways through 3D networks; they also show a cooperative-type interstitial mechanism, which is consistent with the Haven ratio values and the Li-ion dynamics from NMR. Such correlated motion is a key factor in promoting high ionic conductivity.

These insights are of great significance in developing strategies for optimizing the Li-ion conductivity of this system, as well as identifying new solid electrolytes.

ASSOCIATED CONTENT

Supporting Information

Single-crystal measurement results for Li$_4$SiO$_4$: BPP fit parameters and results; interatomic potentials; crystallographic data for solid solution compositions; comparison of calculated and experimental structural parameters; $^7$Li ambient and high-temperature NMR signal line shapes and fwhm analysis; $^6$Li and $^{31}$P NMR signals; comparison of experimental and simulated structural parameters; AC impedance plots; $^7$Li(1/T$_1$) vs T and Arrhenius plots; activation energies derived from NMR, AC impedance, and MD simulation; Arrhenius plots from MD and AC impedance; and Haven ratio values. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.0b04444.

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Notes

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