Correlation of Structure and Fast Ion Conductivity in the Solid Solution Series Li₁₊₂xZn₁−xPS₄

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Supporting Information

Rechargeable all-solid-state batteries (ASSBs) using inorganic solid electrolytes (SE) have become one of the most promising alternatives to conventional Li-ion batteries that use flammable organic liquid electrolytes. Inorganic SEs have the potential to enable batteries that not only are safer but have a higher energy density, good low temperature performance and longer cycle life. 1–3 To realize the potential of ASSBs, new SE materials are sought that can adequately replace the current liquid electrolytes. These materials require fast lithium ion conduction (>10⁻⁴ S·cm⁻¹), a wide electrochemical stability window, and chemical compatibility with both the anode and the cathode. 4–8 While a range of various lithium-ion conductors exist and have been studied, 9 sulfides show the most promise in terms of ionic conductivity and processability. 1,5,8 Sulfides are very ductile, making them easily processed via cold-pressing. Notable sulfide type lithium-ion conductors that exhibit some of the highest ionic conductivities comparable to liquid electrolytes stem from the lithium thiophosphate family. These include the argyrodites, Li₅GeP₂S₁₂ (LGPS: 12 mS·cm⁻¹), 11 and its Si/Sn derivatives, Li₅PₓS₁₂ (17 mS·cm⁻¹), 15,16 and most recently LGPS-type Li₉S₄Sn₃P₄S₁₁-C₆S₆ (25 mS·cm⁻¹), 17 which exhibits the highest room temperature lithium ion conductivity to date.

Recently, Richards et al. 18 used density functional theory (DFT) and ab initio molecular dynamics (AIMD) to investigate the Li₁+ₓZn₁−ₓPS₄ (LZPS) system, which exhibits a body-centered cubic (bcc) sulfur sublattice. Theory suggests that this arrangement of sulfur atoms, which is also adopted by two other fast ion conductors (Li₅PₓS₁₁ and LGPS), is correlated to a low lithium migration barrier. 19 The stoichiometric parent phase LiZnPS₄ and its optical properties have been previously reported, but no ionic conductivity data was provided. 20,21 Its structure consists of a framework of PS₄ and ZnS₄ tetrahedra that house Li⁺ ions, where Li fully occupies the 2b site and Zn fully occupies the 2a site (Figure 1a). In the Li₁+ₓZn₁−ₓPS₄ nonstoichiometric phases (Figure 1b) the additional Li shares the 2a site with Zn as we show below, with the excess Li distributing equally between the 2a and an additional site, 2d. This 2d site is close to the “interstitial” site that was not explicitly identified in the theoretical work. 18 The stoichiometric phase was predicted to have extremely poor conductivity based on first-principles calculations (1.81 × 10⁻¹² S·cm⁻¹, E₉ = 1.07 eV), while the introduction of interstitial lithium defects is predicted to yield ionic conductivities greater than 5 × 10⁻² S·cm⁻¹ (with E₉ > 0.17 eV) at room temperature up to a solid solution solubility limit of x = 0.5, 18 i.e., Li₁.₅Zn₀.₅PS₄.

Here, we report the synthesis of the solid solution series and the structure of the member within the solubility limit with the highest predicted conductivity, derived from combined X-ray and neutron powder diffraction analysis.

The highest value of x (i.e., of lithium excess) in a well crystallized sample was x = 0.35, corresponding to Li₁.₃Zn₀.₆₅PS₄. We unequivocally identify lithium occupation of the 2d site, which is charge compensated by substitution of a Zn²⁺ ion in the 2a site with Li⁺ and is crucial for improving ionic transport. Experimental ionic conductivities (σ₉) measured by electrochemical impedance spectroscopy (EIS) show that the σ₉ of the most highly conductive phases are in the range of >10⁻⁴ S·cm⁻¹ at 25 °C: a very significant improvement over LiZnPS₄, albeit less than predicted. Phases with high values of x (>0.5) were experimentally unattainable as relatively pure crystalline phases, however. Our observations demonstrate that the enhancement in ionic conductivity observed in the x = 0.75 phase is likely due to a glass-ceramic matrix effect rather than from its inherent crystalline structure.
Li$_{1+x}$Zn$_{1-x}$PS$_4$ compositions were prepared at $x = 0.25$, 0.5, and 0.75 using solid-state synthesis consisting of ball-milling and annealing. Their synchrotron X-ray diffraction (XRD) patterns are shown in Figure 2. The compositions contain small impurities of Li$_2$P$_6$S$_8$ and ZnS which form upon slight decomposition of the LZPS solid solutions because of their metastable nature. As the lithium content increases (up to $x = 0.75$), the formation of significant Li$_2$P$_6$S$_8$ impurities becomes evident, in accord with the pseudobinary phase diagram calculated by Richards et al.\textsuperscript{18}

The $a$ and $c$ lattice parameters were extracted by performing a Pawley full powder pattern fit of the synchrotron XRD patterns in the $I\bar{4}$ space group. The trends are shown in Figure 3 (with exact values given in Table S1), indicating that the cell volume increases with increased lithium content (293 Å$^3$ to 301 Å$^3$). The increase in cell volume stems from a significant increase in the $a$ lattice parameter (with a small decrease in the $c$ lattice parameter). Larger lattice volume often correlates to an improvement in ionic conductivity due to a reduced Li$^+$ ion migration barrier.\textsuperscript{19,22} Since the targeted Li$_1$Zn$_{0.25}$PS$_4$ phase is expected to have the highest ionic conductivity within the solid solution solubility limit, its crystal structure was refined against combined synchrotron powder X-ray diffraction data ($\lambda = 0.412$ Å) and time-of-flight (TOF) neutron diffraction data.

The reflections were assigned to a body-centered tetragonal cell (space group $I\bar{4}$, No. 82) with lattice parameters refined to $a = 5.7945(2)$ Å and $c = 8.8337(3)$ Å. The crystallographic details are summarized in Table 1 (we note that bond lengths, Table S2, are typical for all environments) while the fit for the synchrotron and neutron data is shown in Figure 4.

The results of the refinement indicate that the actual lithium content of the crystalline material is $x \approx 0.35$, lower than that targeted (i.e., $x = 0.5$). The crystalline Li$_{1.69}$Zn$_{0.69}$PS$_4$ (i.e., Li$_1$Zn$_{0.25}$PS$_4$) phase thus exists in an amorphous Li-rich thio phosphate matrix. The degree of crystallinity was estimated to be 69\% using Si as an internal reference (Figure S1). A proposed mixture of [77\% Li$_1$Zn$_{0.65}$PS$_4$ + 23\% a-Li$_2$PS$_4$] accounts for the overall Li$_{1.7}$Zn$_{0.6}$PS$_4$ target. The 8\% discrepancy may be attributed to the impurity phases (Figure 2). The refined structure of Li$_1$Zn$_{0.6}$PS$_4$ shows that the 2d sites are partially occupied by Li (34\%) and Zn (66\%) while the 2d site has partial occupancy of Li (34\%) as visually represented in the inset in Figure 4. Owing to the well-known difficulty in simultaneously refining thermal parameters and occupancies, the thermal parameters for the 2d and 2b site were fixed to average values from the literature.\textsuperscript{11,17,25,24} This resulted in congruence to site occupancies that yielded perfect charge balance of the compound and an equal distribution of excess Li on the 2d and 2a sites as expected. The results are in excellent accord with ab initio molecular dynamics studies that predict significant lithium ion density on an "interstitial site",\textsuperscript{18} which is similar to the 2d Wyckoff site we identify.

While Li$_{1.2}$Zn$_{0.9}$PS$_4$ ($x = 0.75$) was projected by theory to have the highest conductivity (1.14 × 10$^{-7}$ S·cm$^{-1}$),\textsuperscript{15} its structure could not be refined owing to the low quality of the X-ray and neutron data for this poorly crystallized compound. This is in accord with it lying just out of the predicted solubility limit.\textsuperscript{18} The structure of "Li$_1$Zn$_{0.6}$PS$_4"$ was refined from the synchrotron X-ray data owing to its low lithium content (a paucity of neutron time), and these results are shown in Table 2. The fit is shown in Figure 5; refined bond lengths (Table S2) correspond to typical values for all environments. The lattice parameters refined to $a = 5.7641(1)$ Å and $c = 8.8438(2)$ Å. Since lithium cannot be accurately refined from X-ray data, lithium occupations in the 2d and 2a sites were fixed to be equal, as determined by the Li$_{1.2}$Zn$_{0.9}$PS$_4$ formulation. The Zn occupancy was refined, and the vacant occupancy was assumed to be lithium given that the 2a site occupancy is constrained to 1. The refined composition of Li$_{1.2}$Zn$_{0.9}$PS$_4$ (with a 70\% degree of crystallinity determined by standard addition) shows that the target composition was also not achieved in this case. This may be due to slow kinetics of the reaction that prevents achievement of the targeted lithium contents, despite the employment of nanosized ZnS in the synthesis (see Supporting Information). However, synthesis at higher temperature or longer times is limited by thermodynamics: due to the metastability of the substoichiometric
phases, the LZPS structure partially decomposes to Li$_4$P$_2$S$_6$. The formation of such impurity phases can be prevented by heating at lower temperatures; however, this comes at the cost of a reduced degree of crystallinity.

The importance of excess phonon free energy in stabilizing defect-type ionic conductors with highly mobile Li$^+$ ion lattices has been previously invoked, for example, in Li$_{7}$P$_{3}$S$_{11}$, and especially in Li$_{1+2x}$Zn$_{1-x}$PS$_{4}$. We note that the limiting composition Li$_{1.7}$Zn$_{0.65}$PS$_{4}$ ($x = 0.35$) is approximately halfway between the predicted solubility limit for the solid solution series without phonon contributions ($x = 0.15$) and with phonon contributions ($x = 0.5$). Clearly Li$_{1.7}$Zn$_{0.9}$PS$_{4}$ ($x = 0.1$) falls within the regime where phonon contributions are not necessary to stabilize the material. All experimental attempts to increase the degree of lithium substitution to attain $x = 0.5$ were unsuccessful—irrespective of temperature, time, and processing conditions—and resulted in significant levels of impurity phases. These results confirm that phonon contributions do play a vital role in stabilizing these defect structures but likely to a lower degree than presumed.

Partial occupancy of Li in the 2a and 2d site in the LZPS structure should facilitate the ion conduction by creating low energy percolating pathways through the structure. The Li$^+$ ion conductivity of the various LZPS compositions was studied using electrochemical impedance spectroscopy (EIS) on pressed pellets at variable temperatures. The impedance spectra in Nyquist form showed classic semicircles at high frequency and a linear Warburg component in the low-frequency range (Figure 6a). Fitting the data (see inset for equivalent circuit and Table S3 for fit parameters) resulted in experimental conductivities at 25 °C plotted in Figure 6b as a function of lithium content. The conductivities range from 5.40 $\times$ 10$^{-8}$ S cm$^{-1}$ at $x = 0$ to 8.4 $\times$ 10$^{-4}$ S cm$^{-1}$ at $x = 0.75$. The conductivity of the refined phase Li$_{1.7}$Zn$_{0.65}$PS$_{4}$ was 1.30 $\times$ 10$^{-4}$ S cm$^{-1}$, which is lower than predicted for either Li$_{2.0}$Zn$_{0.5}$PS$_{4}$ (5.38 $\times$ 10$^{-2}$ S cm$^{-1}$) or Li$_{1.5}$Zn$_{0.75}$PS$_{4}$ (2.77 $\times$ 10$^{-2}$ S cm$^{-1}$) as shown in Figure 6. The amorphous content may be responsible, although temperature-dependent conductivity measurements exhibit Arrhenius behavior with a low activation energy of 0.22 eV. This value is close to the range predicted by MD simulations for the defect phases, namely, 0.165 eV (Li$_{1.7}$Zn$_{0.3}$PS$_{4}$) and 0.181 eV (Li$_{1.5}$Zn$_{0.7}$PS$_{4}$). While the possible amorphous phase (i.e., a-Li$_{4}$PS$_{4}$, $\sigma$ = 2.8 $\times$ 10$^{-4}$ S cm$^{-1}$) may contribute to the overall

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Table 1. Atomic Coordinates, Wyckoff Symbols, and Isotropic Displacement Parameters for the Targeted Li$_{2.0}$Zn$_{0.5}$PS$_{4}$ Phase in the Space Group $I$4 (No. 82)

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Table 2. Atomic Coordinates, Wyckoff Symbols, and Isotropic Displacement Parameters for the Targeted Li$_{1.5}$Zn$_{0.75}$PS$_{4}$ Phase in the Space Group $I$4 (No. 82)

Figure 4. Combined Rietveld refinement of "Li$_{2.0}$Zn$_{0.5}$PS$_{4}$" based on synchrotron X-ray diffraction and neutron diffraction data. Visual representation of the refined crystal structure (refined to a composition of Li$_{1.7}$Zn$_{0.65}$PS$_{4}$) is shown as an inset. Excluded regions correspond to impurity phases, mainly Li$_{4}$P$_{2}$S$_{6}$, which comprises <5% of the total (see Figure 2).

Figure 5. Rietveld refinement of "Li$_{1.5}$Zn$_{0.75}$PS$_{4}$" synchrotron X-ray diffraction data only. Excluded regions correspond to impurity phases, mainly Li$_{4}$P$_{2}$S$_{6}$, which comprises <10% of the total (see Figure 2).

Table 3 for fit parameters resulted in experimental conductivities at 25 °C plotted in Figure 6b as a function of lithium content.

The conductivities range from 5.40 $\times$ 10$^{-8}$ S cm$^{-1}$ at $x = 0$ to 8.4 $\times$ 10$^{-4}$ S cm$^{-1}$ at $x = 0.75$. The conductivity of the refined phase Li$_{1.7}$Zn$_{0.65}$PS$_{4}$ was 1.30 $\times$ 10$^{-4}$ S cm$^{-1}$, which is lower than predicted for either Li$_{1.7}$Zn$_{0.9}$PS$_{4}$ ($x = 0.1$) falls within the regime where phonon contributions are not necessary to stabilize the material. All experimental attempts to increase the degree of lithium substitution to attain $x = 0.5$ were unsuccessful—irrespective of temperature, time, and processing conditions—and resulted in significant levels of impurity phases. These results confirm that phonon contributions do play a vital role in stabilizing these defect structures but likely to a lower degree than presumed.
Communication

which is known to have very high conductivities of \( >10^{-4}\) S cm\(^{-1}\), and the activation energy is 0.25 eV, quite close to theory (0.252 eV\(^{18}\)).

The highest ionic conductivity of 8.4 \( \times 10^{-4}\) S cm\(^{-1}\) was achieved when the \( x = 0.75\) glassy precursor was heated at lower temperatures (230 °C) to form a very poorly crystallized material. An SEM image of its featureless morphology is shown in Figure S2. Heating above that temperature results in a lower conductivity of 2.4 \( \times 10^{-4}\) S cm\(^{-1}\) and clear phase separation of the LZPS solid solution and \( \gamma\)-Li3PS4. The high conductivity in the glassy phase formed at low temperature is exclusive to the \( x = 0.75\) compound (Table S3).

Postulating that the improvement in ionic conductivity arises from the glass-ceramic nature of the material, we probed the local structure of Li\(_{2.5}\)Zn\(_{0.25}\)PS\(_4\), via Raman spectroscopy and compared it to the other two phases (Figure S3). While Li\(_{2.5}\)Zn\(_{0.25}\)PS\(_4\) and Li\(_{1.75}\)Zn\(_{0.65}\)PS\(_4\) show predominantly PS\(_4^−\) moieties characteristic of the crystalline structure (along with LiP\(_2\)S\(_4\) impurity), the more highly conductive Li\(_{2.5}\)Zn\(_{0.25}\)PS\(_4\) synthesized at low temperature contains an additional peak in the Raman spectrum not present in the other two compositions. It corresponds to P2S\(_7^−\) and clear phase separation of the LZPS solid solution and \( \gamma\)-Li3PS4. Predicted values are close to the targeted Li\(_{2.0}\)Zn\(_{0.5}\)PS\(_4\) and Li\(_{1.5}\)Zn\(_{0.75}\)PS\(_4\) were successfully synthesized. Their structures were elucidated via refinement of diffraction data. The obtained phases, Li\(_{1.75}\)Zn\(_{0.65}\)PS\(_4\) and Li\(_{1.25}\)Zn\(_{0.9}\)PS\(_4\), respectively, demonstrated ionic conductivities of 1.30 \( \times 10^{-4}\) S cm\(^{-1}\) and 1.65 \( \times 10^{-5}\) S cm\(^{-1}\). These values are more than 4 orders of magnitude higher compared to that of the parent LiZnPS\(_4\) phase, owing to occupation of the 2d interstitial site in the lattice as predicted by theory. This represents a good demonstration of how information from ab initio molecular dynamics can augment experiment, similar to Li\(_{10}\)GeP\(_2\)S\(_{12}\), where early reports using powder diffraction alone could not locate a lithium site important to 3D mobility, but a combination of theory and single crystal diffraction enabled full structure resolution.\(^{15,26−28}\)

While our experimental lithium ion conductivities were lower than predicted, this can be ascribed to a combination of not fully accessing the targeted lithium defect concentrations (owing to the limitations of kinetics and thermodynamics) and the accompanying reality of the presence of amorphous and potentially poorly conductive materials. The fact that we can synthesize solid solutions close to the predicted superionic phases is encouraging, however, and suggests that alternate highly nonequilibrium synthetic routes may be required to access pure phases. This should provide further inspiration for future endeavors. Moreover, LZPS compositions at high lithium contents—Li\(_{2.5}\)Zn\(_{0.25}\)PS\(_4\)—exhibit conductivities up to 8 \( \times 10^{-4}\) S cm\(^{-1}\), showing that a glassy matrix can play a key role in governing fast lithium ion conduction.

### ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b05108.

Experimental details, lattice parameters for different compositions, bond lengths, SEM images, and Raman spectra (PDF)

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**Notes**

The authors declare no competing financial interest.

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**Figure 6.** (a) Activation energy plot of Li\(_{1.5}\)Zn\(_{0.5}\)PS\(_4\) and Li\(_{1.25}\)Zn\(_{0.9}\)PS\(_4\) along with an inset of the Nyquist plots at each temperature plus the equivalent circuit used to fit the impedance data and (b) Li\(^+\) ion conductivity at 25 °C versus x in Li\(_{1+2}\)Zn\(_{−}\)PS\(_4\). Predicted values are taken from ref 18.
at ORNL’s Spallation Neutron Source were sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. We thank Yan Chen for his assistance with the neutron powder diffraction data collection on VULCAN.

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