

A New Superionic Plastic Polymorph of the Na^+ Conductor Na_3PS_4

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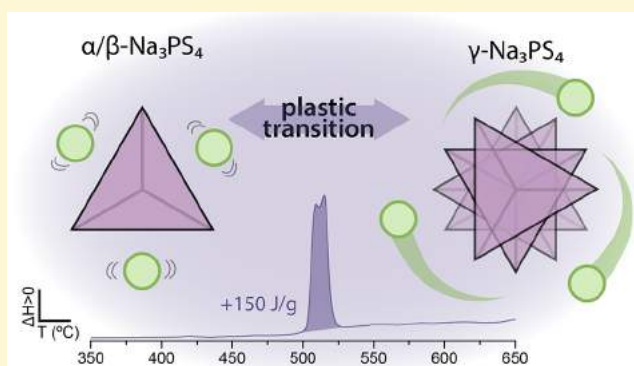
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Supporting Information

ABSTRACT: Na_3PS_4 is one of the most promising Na^+ conductors, relevant for applications that can leverage its high ionic conductivity, such as solid-state batteries. Currently, two crystalline phases of the material have been identified, and it has been thought to melt above 500 °C. In contrast, based on diffraction, *ab initio* simulations, impedance spectroscopy, and thermal analysis, we show that Na_3PS_4 remains solid above this temperature and transforms to a third polymorph, γ , exhibiting fast-ion conduction and an orthorhombic crystal structure. We show that the fast Na^+ -conduction is associated with rotational motion of the thiophosphate polyanions pointing to a plastic crystal. These findings are of major importance for the development and understanding of new polyanion-based solid electrolytes.



Sodium thio-orthophosphate (Na_3PS_4) has received considerable attention as a solid electrolyte material, especially for the development of sodium solid-state batteries.¹ Its crystalline structure and Na^+ ion-conduction properties were first explored by Jansen and Henseler and two polymorphs are currently known: the room-temperature tetragonal form (α), which transforms to a closely related cubic form (β) above 261 °C.² The ionic conductivity of crystalline Na_3PS_4 prepared by solid-state synthesis is of the order of 10^{-6} – 10^{-5} S/cm at 298 K,^{2–4} which limits its applicability to bulk solid-state battery applications.

A resurgence of interest in Na_3PS_4 came as a result of an improvement of its ionic conductivity achieved through mechanochemical synthesis, first reported by Hayashi et al.^{5,6} Such ball-milled, “glass-ceramic” Na_3PS_4 exhibits ambient ionic conductivities on the order of 10^{-4} S/cm,^{3–7} enabling its incorporation in solid-state batteries.^{5–11} The mechanochemical route is thought to stabilize the cubic polymorph (β), as

observed by Bragg diffraction, but there exist conflicting reports regarding its local and average structure.^{3,10,12} In addition, Jansen and Henseler hypothesized a pre-melting phase transition to a third phase, associated with rotational mobility of the PS_4^{3-} tetrahedra, which they were, however, unable to substantiate.² Such materials possessing significant rotational, conformational, and/or translational mobility of their constituent atoms, in combination with long-range order (crystallinity), are referred to as plastic crystals, with properties between those of classical liquids and solids.

These unanswered questions regarding the structure of Na_3PS_4 motivated us to pursue thorough investigations of the effect of its microstructure on ion conduction,¹³ as well as the evolution of its crystalline structure and electrical properties

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with temperature. We report here the observation of a previously unknown phase, which we attribute to a third polymorph of Na_3PS_4 that exhibits fast Na^+ conduction and plastic crystal characteristics, including rotational motion of the PS_4^{3-} anions.^{14–16}

First, we performed temperature-controlled synchrotron X-ray diffraction (XRD) experiments, which yielded results in agreement with published literature up to 500 °C, as shown in the contour plot of Figure 1a. The tetragonal polymorph (α -

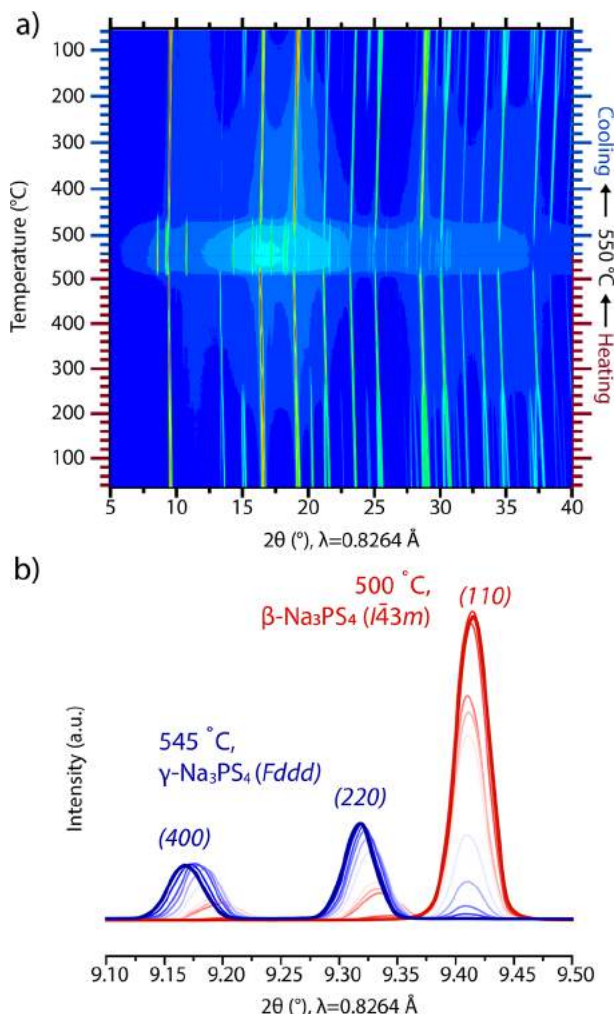


Figure 1. Temperature-controlled synchrotron X-ray diffraction (XRD) of Na_3PS_4 : (a) logarithmic contour plot of diffractograms in the range of 30–550 °C upon heating and cooling (the color code, from blue to red, indicates the range from low diffraction intensity to high diffraction intensity, respectively); (b) superimposed sections of the diffractograms at $9.1^\circ < 2\theta < 9.5^\circ$ and $500^\circ\text{C} < T < 545^\circ\text{C}$ every 5 °C.

Na_3PS_4) is observed at 25 °C and persists with heating up to 220 °C when it begins transforming to the cubic polymorph (β - Na_3PS_4); the transformation reaches completion at 275 °C. In turn, the diffraction peaks of β - Na_3PS_4 are observable until 500 °C.

Above 500 °C, new diffraction peaks appear, indicating the formation of another crystalline phase. Gradually, the intensities of the peaks attributed to β - Na_3PS_4 decrease and those of the new phase increase (Figure 1b). The transformation is complete at 545 °C and is accompanied by a

distinct wavelike rise in the baseline diffraction signal, typically associated with the diffuse scattering from amorphous or liquid samples.

Upon subsequent cooling, the crystallographic transformations are reversible with the reappearance of β - and α - Na_3PS_4 , respectively. Neutron diffraction experiments are consistent with the XRD observations (see Figure S1 in the Supporting Information), showing the same phase evolution with temperature, despite the stark differences in sample environment (~ 2 g of sample in vanadium container under secondary vacuum for neutrons; ~ 10 mg of sample in sealed quartz ampule under positive pressure of argon for synchrotron). These observations lead to the conclusion of the existence of a third polymorph of Na_3PS_4 , accessible above 500 °C, which we will refer to as γ .

The XRD pattern of γ - Na_3PS_4 can be fully indexed in an orthorhombic *Fddd* space group with lattice parameters of 6.6055(1), 11.7143(2), and 20.7378(3) Å at 550 °C (Figure 2). The $\beta \rightarrow \gamma$ transition is accompanied by an abrupt increase in the volume of the unit cell by $\sim 10\%$, from 180.8 Å³/f.u. to 198.8 Å³/f.u. (assuming $Z = 8$ for the orthorhombic cell). A direct structural solution of the γ -phase from the powder diffractogram is complicated by diffuse electronic density attesting to extensive disorder and by an apparent effect of preferential orientation: the relative intensities for the α - and β -phases are different on heating and cooling, respectively (see Figure 1a).

Based on the observed space group and mapping of the scattering (electronic) density of the high-temperature diffractograms, we deduce that the γ -phase is structurally related to thenardite (Na_2SO_4), which also crystallizes in *Fddd* (albeit with a much smaller unit cell). Using the structure of Na_2SO_4 as a starting point, we expanded its unit cell to our observed lattice parameters and replaced SO_4^{2-} tetrahedra with PS_4^{3-} to reach a hypothetical “ Na_2PS_4 ” structure (see Figure S2 in the Supporting Information). This treatment resulted directly in realistic P–S bond length, close to 2 Å, thereby validating the approach.

We then performed static density functional theory (DFT) calculations to attempt to locate the additional Na position(s). The expansion of the thenardite unit cell from Na_2SO_4 to γ - Na_3PS_4 creates ample “interstitial” space for Na around the structure-forming tetrahedra. Indeed, our simulation analysis resulted in multiple structures with varying Na positions but very close energetically (within 15 meV/atom), indicating a high level of disorder of Na atoms among multiple positions. When relaxed, these structures all present formation energies only slightly higher (< 70 meV/atom) than the cubic β -phase. This difference is very small considering that the true average structure would feature partially occupied atoms, and it is also reasonable to expect high entropic contributions from pronounced atomic mobilities. Both of the above effects are not explicitly captured in the static DFT calculations and result in an overestimation of the free energy for the γ -phase.¹⁷

Combining the multiple possible positions for Na determined above, we propose an approximate crystal structure for γ - Na_3PS_4 , shown in Figure 3. This rigid model can still not fully explain the diffractogram, because it corresponds to a single conformation of the PS_4^{3-} tetrahedra and is constrained by the *Fddd* long-range symmetry. Instead, our ab initio simulations and scattering density mapping show two features: (i) multiple S positions are possible around the central P atom (i.e., multiple conformations of the PS_4^{3-} tetrahedra, each

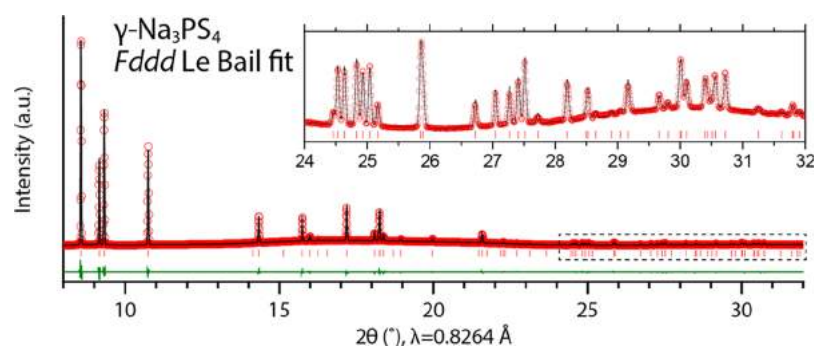


Figure 2. Le Bail (profile) fit of the synchrotron X-ray diffractogram of Na_3PS_4 at 550 °C.

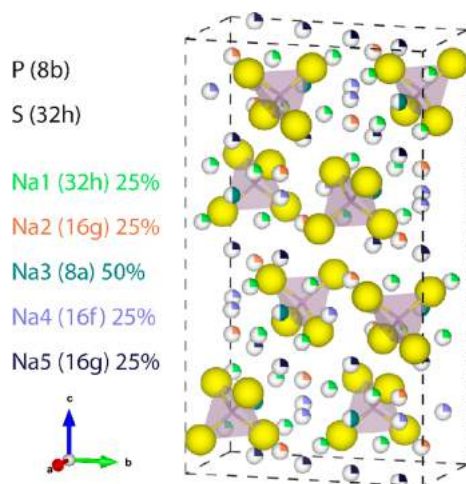


Figure 3. Proposed structure of $\gamma\text{-Na}_3\text{PS}_4$ from static *ab initio* calculations. P and S in purple and yellow, respectively, were fixed into perfect PS_4^{3-} tetrahedra. Relative occupations of Na sites were approximated from the relative calculated energies of different configurations. Crystallographic information file (.cif) provided as Supporting Information.

surrounded by its associated stable Na positions), and (ii) these are not locally constrained by the long-range symmetry. Diffraction probes an average structure; i.e., a superposition of all different possible conformations of PS_4^{3-} and further analysis of the diffuse scattering is needed to unambiguously elucidate the complete average structure. We present our attempts to that end and propose a preliminary structure solution consistent with both the diffractogram and the DFT calculations in the Supporting Information (Figures S3 and S4).

Differential scanning calorimetry (DSC) data, shown in Figure 4a and performed at the same heating rate as the diffraction experiments (5 °C/min), correspond well with the observed diffraction behavior and previous differential thermal analysis results.² No thermal signature is observed for the $\alpha \rightarrow \beta$ phase transition, consistent with the very small difference in formation energy between the two polymorphs, amounting to ~ 5 meV/atom, as calculated by DFT,^{12,18,19} and with the minor atomic rearrangements required for this transition.

In contrast, an intense doublet thermal signature is observed upon heating, centered at 509.5 and 515 °C with an onset at 503.5 °C, collectively amounting to ~ 150 J/g. Jansen and Henseler, who also observed this doublet, attributed it to pre-melting and melting.² Their assignment was likely based on earlier investigations of the $\text{Na}_2\text{S}\text{--P}_2\text{S}_5$ phase diagram, which

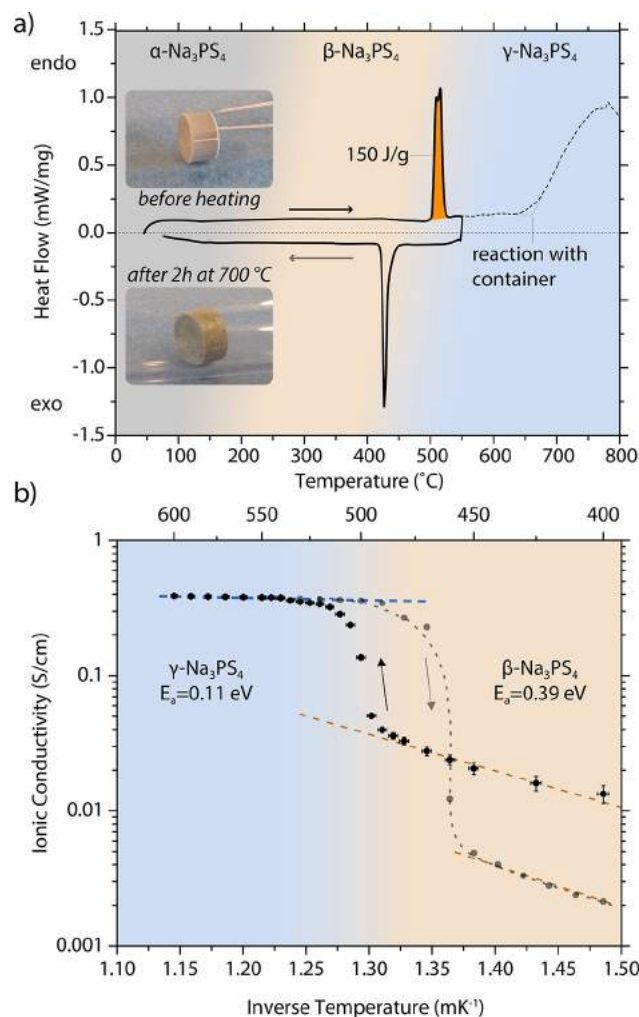


Figure 4. (a) Differential scanning calorimetry (DSC) curve of Na_3PS_4 (inset shows photographs of Na_3PS_4 pellets before and after heating to 550 °C for 2 h). (b) Evolution of ionic conductivity in Na_3PS_4 , as measured by impedance spectroscopy.

had proposed a melting point of 790 K (517 °C) for Na_3PS_4 .²⁰ Interestingly, the same authors reported on the “mechanical stability” of pelletized Na_3PS_4 up to and above the reported melting point of 517 °C. Indeed, we confirm that pellets of Na_3PS_4 maintain their shape after 2 h at 700 °C, significantly above the proposed melting temperature (Figure 4a, inset). In attempting to determine the actual melting point through DSC, a further broad endothermic effect was observed with an onset of 661.7 °C. We associate the latter with reactivity of γ -

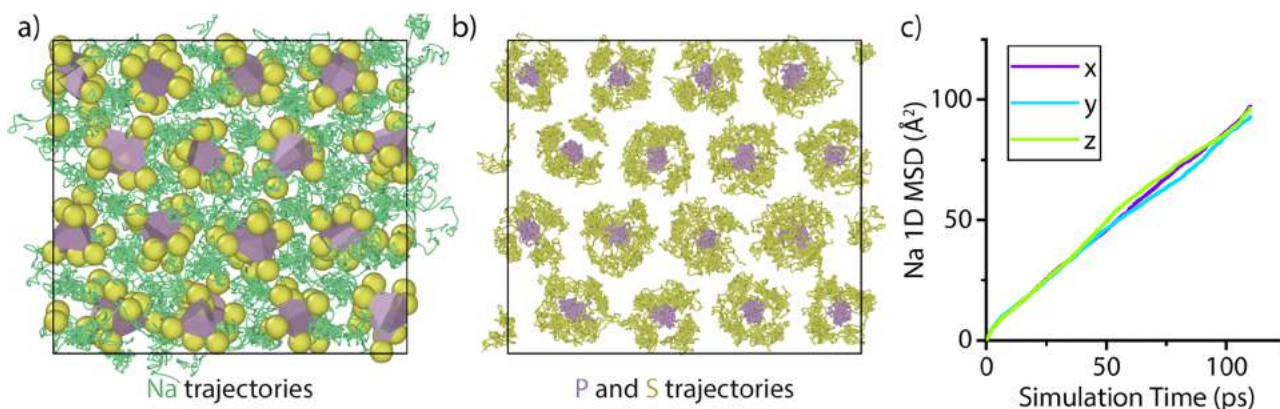


Figure 5. Atomic mobility results from ab initio molecular dynamics of γ - Na_3PS_4 . Atomic trajectories of (a) Na and (b) P and S (green, purple and yellow lines, respectively) shown in projection through the bc plane for 50 ps after equilibration of a 900 K simulation without extrinsic vacancies. (c) Na^+ mean-squared displacements (MSD) in each spatial dimension.

Na_3PS_4 with the alumina sample container; given that pellets heated in quartz at 700 °C still maintain their shape (Figure 4a, inset) and orthorhombic diffraction characteristics (not shown). Thus, we associate the thermal effects at ~ 500 °C with the $\beta \rightarrow \gamma$ phase transition and re-evaluate the melting point of Na_3PS_4 to >700 °C. Furthermore, an increase in the DSC baseline allowed us to determine an increased heat capacity of the γ -phase (1.19 J/(g/K) at 550 °C), compared to that of the α - and β -phases (1.03 J/(g/K) at 100 °C).

The ionic conductivity of the samples was extracted from impedance spectra measured as a function of temperature (see Figure S5 in the Supporting Information) and is presented in the Arrhenius plot of Figure 4b. For β - Na_3PS_4 (400–480 °C), we observe an activation energy of 395 ± 10 meV, in good agreement with the value reported by Jansen and Henseler (402 meV).² The $\beta \rightarrow \gamma$ transition at 500 °C causes a sudden increase in the ionic conductivity of Na_3PS_4 of about an order of magnitude, from ~ 40 mS/cm to ~ 400 mS/cm. The activation energy for ion conduction in the γ -phase is evaluated as 110 ± 10 meV. The electrical behavior is reversible with a hysteresis on cooling, consistent with diffraction and thermal analysis. The hysteresis is likely linked to kinetic limitations for the transformation back to the β -phase. Upon cooling, an order of magnitude decrease in absolute conductivity of the β -phase was observed, which could be ascribed to crystallographic texturation, as evident in the diffractograms of Figure 1a and the creation of porosity in the pellet upon the sudden, significant ($\sim 10\%$) crystallographic contraction upon the $\gamma \rightarrow \beta$ transition.

Extrapolating the high-temperature electrical behavior to room temperature, the conductivity of γ - Na_3PS_4 would be ~ 50 mS/cm, significantly higher than any known solid electrolyte for Na or Li. Of course, exploitation of γ - Na_3PS_4 for room-temperature applications, such as solid-state batteries, would necessitate its stabilization at lower temperatures than those presented here. Quenching²¹ and/or chemical substitutions (e.g. Cl doping or polyanion mixing)^{18,22–29} might prove useful to that effect, similar to what has been observed, for example, in analogous borohydride plastic crystal electrolytes.^{30–33} The results of our preliminary unsuccessful efforts are outlined in the Supporting Information (Figure S6).

We further probed the atomic-scale ionic diffusion characteristics of the γ -phase by means of ab initio molecular dynamics (MD) simulations for a range of temperatures (600–1050 K), using, as a starting point, the derived thenardite structure

(Figure 3). The atomic trajectories show clear signs of fast ion conduction, with delocalized Na^+ ions attesting to the effective “melting” of the Na sublattice (see Figure 5a). All Na^+ ions are mobile, with some notable long-range displacements across the simulation cell, indicative of fast ion conduction. The Na^+ -ion translational mobility is accompanied by distinct motion of the S atoms about the central P atoms of the thiophosphate tetrahedra (see Figure 5b). Despite their rotational motion, the (barycenters of the) PS_4^{3-} units remain translationally fixed to their starting position, confirming the macroscopically solid nature of the phase. The diffusion coefficients derived from the mean-squared displacement of the Na^+ ions are approximately an order of magnitude higher than any previously calculated for the β - and α -phases (shown in Figures S7 and S8 in the Supporting Information).^{18,19} Furthermore, the calculated mean-squared displacements shown in Figure 5c show that the Na-ion diffusion is isotropic in three dimensions, despite the orthorhombic long-range symmetry. The calculated activation energy for Na diffusion is 161 ± 13 meV, in good agreement with the values extracted from impedance spectroscopy.

The ensemble of our observations points to a plastic nature^{34–36} for the γ - Na_3PS_4 phase, based on the following:

- The latent heat for the $\beta \rightarrow \gamma$ transition is unusually high for a simple crystallographic phase transition. The measured value of 150 J/g (34.2 kJ/mol) is closer in magnitude to a typical heat of melting. Other known plastic phase transitions also exhibit such high latent heats, for example, 214 J/g (24.8 kJ/mol) for Li_2SO_4 at 577 °C.³⁷ The increase of heat capacity upon the $\beta \rightarrow \gamma$ transition is also consistent with the increased average kinetic energy of the atoms in γ - Na_3PS_4 .
- In the diffractograms of the γ -phase, the sharp Bragg peaks rapidly diminish in intensity at high angles and are accompanied by diffuse scattering. This is also a hallmark of plastic crystal phases, stemming from high mobility and short-range atomic correlations, also observable, e.g., in Li_2SO_4 ³⁷ and $\text{LiCB}_{11}\text{H}_{12}$ and $\text{NaCB}_{11}\text{H}_{12}$.³⁸ Furthermore, Li_2SO_4 also presents preferential orientation upon cooling from the plastic phase, similar to our observations for Na_3PS_4 (Figure 1a).
- The measured ionic conductivity increases ~ 10 -fold and the corresponding activation energy decreases sharply by

a factor of 4 upon transition from the β - to the γ -Na₃PS₄ phase.

- (d) There is a sizeable stepwise increase in unit-cell volume associated with the $\beta \rightarrow \gamma$ transition, which is further correlated with the sharp increase in ionic conductivity. Such behavior has been observed in other fast-ion-conducting plastic crystal phases, e.g., Li₂SO₄ (~3.2% volume increase,³⁹ associated with one to four orders of magnitude conductivity increase⁴⁰ for the monoclinic to cubic transition at 575 °C⁴¹).
- (e) A distinct softening is evident when handling Na₃PS₄ samples above 500 °C, which are very easily deformable under minimal pressure, attesting to the namesake of “plastic crystals”.⁴²
- (f) Our MD simulations clearly demonstrate both fast Na⁺ conduction and PS₄³⁻ rotational motion.

In conclusion, we report a new polymorph (γ) of Na₃PS₄ with an orthorhombic crystal structure that exhibits fast ion conduction and plastic crystal characteristics. Our combined experimental and *ab initio* modelling investigation shows that isotropic Na⁺ conduction with a very low activation energy of ~0.1 eV is associated with rotational motion of the thiophosphate polyanions. Such concomitant motion could be a key factor in promoting high ionic conductivity and we believe that this study will stimulate further work on γ -Na₃PS₄ and plastic crystal solid electrolytes in general.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00322.

Approximate structure of γ -Na₃PS₄ from DFT calculations (CIF)

Approximate structure of γ -Na₃PS₄ from Rietveld refinements (CIF)

Experimental and computational methods and additional figures. (PDF)

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Author Contributions

T.F. coordinated the work, performed experiments, and prepared the manuscript. J.A.D. performed the *ab initio* calculations. F.F. performed the synchrotron diffraction experiments. E.S. assisted with the neutron diffraction. B.F. assisted with impedance spectroscopy. M.C. performed the thermal analysis. O.C. and J.-N.C. assisted with analysis of diffraction data. M.S.I. and C.M. supervised the work.

Notes

The authors declare no competing financial interest.

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