Towards Understanding the Different Influences of Grain Boundaries on Ion Transport in Sulfide and Oxide Solid Electrolytes

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Supporting Information Placeholder

ABSTRACT: Solid electrolytes provide a route to the development of all-solid-state batteries that can potentially surpass the safety and performance of conventional liquid electrolyte-based devices. Sulfide solid electrolytes have received particular attention as a result of their high ionic conductivities. One of the main reasons for such high ionic conductivity is the apparently reduced grain boundary resistance of sulfide solid electrolytes compared to their oxide counterparts, but this is not fully established. Using two model electrolyte systems, Na3PS4 and Na3PO4, we apply a novel microscale simulation approach to analyze ionic transport in polycrystalline materials with various grain volumes. For Na3PO4, high grain boundary resistance is found, with the Na-ion conductivity decreasing with decreasing grain volume. For Na3PS4, the overall influence of grain boundaries is significantly reduced compared to the oxide. Detailed analysis reveals a minimal change in the local structures and Na-ion conduction mechanism between bulk and polycrystalline Na3PS4, whereas the change is far more substantial for Na3PO4, with evidence of over-coordination of Na ions at the grain boundaries. Our microscale approach helps to explain the fundamentally different influences of grain boundaries on ion transport in phosphate and thiophosphate solid electrolytes.

KEYWORDS: Solid electrolytes, grain boundaries, ion transport, solid-state batteries, interfacial resistance

Research into solid electrolytes for high-performance all-solid-state batteries has seen a dramatic rise in recent years.1–9 By replacing the flammable liquid electrolytes currently employed in commercial Li- and Na-ion batteries with solid electrolytes, the safety of the devices can be significantly enhanced,10 as well as providing an avenue to potentially improve their energy and power densities. A multitude of structural classes, including garnet, NASICON, LISICON, thiophosphate, LIXICON and perovskite structures, have been considered as solid electrolyte materials.6,11–17 Amongst these families of materials, Li- and Na-ion conducting thiophosphates, including Li10MP2S12 (M = Ge, Si or Sn), Li3PS4, Na3PS4 and Na6Sn2PS12,6,18–24 have received significant interest due to their intrinsic soft mechanical nature and fast-ion conduction.1,2,5

In oxide-based solid electrolytes, grain boundaries (GBs) are generally considered to inhibit ion migration and therefore represent a substantial hurdle for fast-ion conduction.14,16 For sulfide-based solid electrolytes, the influence of GBs on the overall ion transport is not as clear, with conflicting reports of GBs that either hinder ionic conduction20,26,27 or have no significant effect on ionic conduction.20,21,28,29 In any case, it is frequently observed that oxides show larger GB resistance than sulfides.30–32 GBs are also important microstructural features that are linked to dendrite formation and penetration,33–35 and defect segregation.36 Furthermore, there is growing interest in glass-ceramic ion conductors, where the roles of nanocrystallite and GB effects are not clear.37–38 Although many reports discuss the influence of GB resistance on ionic conductivity, its origins and mechanisms are not entirely understood, particularly at the atomic scale.

Na3PS4 has recently experienced a resurgence in interest,21,39–47 primarily as a result of the work of Hayashi et al.46,48 who synthesized a stable glass-ceramic cubic phase at room temperature with an unprecedented Na-ion conductivity of 2×10−4 S cm−1.
Krauskopf et al.\textsuperscript{21} report that the influence of GBs appears to be small in these mechanically soft materials. Small GB resistances have also been reported for other well-known sulfide solid electrolytes, such as the argyrodite Li$_6$PS$_5$Br\textsuperscript{49} and Li$_{18}$GeP$_2$S$_{12}$.\textsuperscript{20,29,50} Conversely, earlier studies have speculated that the Na-ion conductivity of Na$_3$PS$_4$ is influenced by grain boundaries.\textsuperscript{26,27} Although Na$_3$PO$_4$ has been studied for over four decades as a solid electrolyte,\textsuperscript{55-57} its GB resistance has not been fully characterized.

In this study, we elucidate the role of GBs in the transport of ions in solid electrolytes by proposing a novel microscale strategy based on large-scale molecular dynamics (MD) simulations. We apply this method to analyze these two well-known polycrystalline model systems, Na$_3$PS$_4$ and Na$_3$PO$_4$, with various grain volumes, in order to elucidate the different contributions of GB resistance in sulfide and oxide solid electrolytes. Our findings show high GB resistance for Na$_3$PO$_4$, but for Na$_3$PS$_4$, the relationship between ion transport and grain volume is weaker. Structural and mechanistic results reveal pronounced differences between the local environments of the ions at the GBs of Na$_3$PO$_4$, while for Na$_3$PS$_4$, these differences are minimized. This novel microscale approach illustrates the fundamentally different influences of grain boundaries on ion transport at the atomic scale in sulfide and oxide solid electrolytes.

RESULTS AND DISCUSSION

Structures and Na-ion conductivity of bulk Na$_3$PS$_4$ and Na$_3$PO$_4$. Two crystal polymorphs are known for Na$_3$PS$_4$: a tetragonal phase with space group $P4_{2}c$ and lattice parameters of $a = 6.952$ Å and $c = 7.076$ Å,\textsuperscript{54} and a cubic phase with space group $I4_3m$ and a lattice parameter of $a = 6.989$ Å.\textsuperscript{53} These polymorphs are very similar, with minor differences in the orientation of the PS$_4$ tetrahedra and the corresponding positions of the Na ions. Furthermore, they also exhibit similar Na-ion conductivities,\textsuperscript{21-39} although earlier studies have reported higher conductivities for the cubic phase.\textsuperscript{26,27} Similarly, a tetragonal phase with space group $P4_{2}c$ and lattice parameters of $a = 10.811$ Å and $c = 6.818$ Å,\textsuperscript{55} and a cubic phase with space group $Fm\overline{3}m$ and a lattice parameter of $a = 7.544$ Å\textsuperscript{55} also exist for Na$_3$PO$_4$. The tetragonal-cubic transition for Na$_3$PO$_4$ results in a sudden increase in Na-ion conductivity.\textsuperscript{55}

In this work, we focus on the cubic polymorphs as the crystallographic similarities between cubic Na$_3$PS$_4$ and Na$_3$PO$_4$ allow us to examine key GB effects. The calculated lattice parameters for cubic Na$_3$PS$_4$ and Na$_3$PO$_4$ are 6.992 and 7.524 Å, respectively, in excellent agreement with experimental data.\textsuperscript{20,55} The agreement between the experimental and calculated bond distances is also excellent, as shown in the supporting information.

Figure 1 shows the Arrhenius plots for the calculated Na-ion conductivity for bulk Na$_3$PS$_4$ and Na$_3$PO$_4$. Mean squared displacement (MSD) plots for Na-ion diffusion in bulk Na$_3$PS$_4$ and Na$_3$PO$_4$ are given in Figure S1. We find that the Na$_3$-ion conductivity is higher in the sulfide than the oxide, with calculated bulk conductivities of $3.42 \times 10^{-4}$ and $9.18 \times 10^{-3}$ S cm$^{-1}$ for Na$_3$PS$_4$ and Na$_3$PO$_4$, respectively, at 400 K.

Our conductivity measurements are in good agreement with the impedance measurements of Krauskopf et al.\textsuperscript{21} for tetragonal Na$_3$PS$_4$ obtained from a high-temperature solid-state synthetic route ($\sim 8 \times 10^{-5}$ S cm$^{-1}$ at 333 K) and Yu et al.\textsuperscript{57} for cubic and tetragonal Na$_3$PS$_4$ ($\sim 1 \times 10^{-4}$ and $\sim 1 \times 10^{-5}$ S cm$^{-1}$ at 300 K, respectively). The calculated activation energy of 0.27 eV for Na$_3$PS$_4$ agrees well with the value of 0.28 eV derived from impedance measurements.\textsuperscript{26}

![Figure 1. Na-ion conductivities ($\sigma$) and activation energies ($E_a$) for bulk Na$_3$PS$_4$ and Na$_3$PO$_4$.](image)

A conductivity of $2.1 \times 10^{-3}$ S cm$^{-1}$ was found for Na$_3$PO$_4$ at 600 K. This is in agreement with the value of $\sim 1 \times 10^{-3}$ S cm$^{-1}$ obtained from impedance values at the same temperature.\textsuperscript{52,56} Our calculated activation energy of 0.34 eV is slightly lower than the experimental value of 0.42 eV.\textsuperscript{52,56}

Na-ion conductivity of polycrystalline Na$_3$PS$_4$ and Na$_3$PO$_4$. To assess the impact of GBs on the Na-ion conductivity of the model Na$_3$PS$_4$ and Na$_3$PO$_4$ systems, we investigated polycrystalline systems with different grain volumes. The grain volumes are characterized by the number of grains. Figures 2(a) and (b) shows the Arrhenius plots for the calculated Na-
ion conductivity for bulk and polycrystalline Na$_3$PS$_4$ and Na$_3$PO$_4$, respectively. Example MSD plots for Na-ion diffusion in polycrystalline Na$_3$PS$_4$ and Na$_3$PO$_4$ are given in Figure S2.

Second, the calculated activation energies are all similar for the polycrystals of Na$_3$PS$_4$ (0.28–0.30 eV) compared to the bulk value of 0.27 eV, which suggests that the overall influence of GBs on Na-ion transport in this material is minimal.

In contrast, Figure 2(b) shows a reduction in conductivity and a small increase in activation energy for all the Na$_3$PO$_4$ polycrystalline systems compared to the bulk. The lowest conductivities are obtained for the systems with the smallest grain volume, reaching 2.24×10$^{-5}$ and 6.20×10$^{-3}$ S cm$^{-1}$ at 400 and 800 K, respectively. These values are significantly lower than the bulk conductivities of 9.19×10$^{-5}$ and 1.58×10$^{-2}$ S cm$^{-1}$ at 400 and 800 K, respectively. Furthermore, there is a relationship between the activation energy and the grain volume, with a rising trend in activation energy from bulk Na$_3$PO$_4$ to the Na$_3$PO$_4$ polycrystal with the smallest grain volume of 2.16 nm$^3$.

We have previously demonstrated the important role of the GB resistance in the fast-ion conductor, Li$_3$OCl, which allowed us to provide accurate estimates of ionic conductivities and activation barriers in agreement with experimental data. The results from Figure 2(b) provide evidence of GB resistance in Na$_3$PO$_4$. Although we are not aware of any experimental characterization of GB resistance specifically in Na$_3$PO$_4$, significant GB resistance for the majority of oxide-based Li- and Na-ion fast conductors is well documented.

Figure 3 shows the activation energies for bulk and polycrystalline Na$_3$PS$_4$ and Na$_3$PO$_4$ as a function of grain volume. The activation energies decrease for Na$_3$PO$_4$, but increase for Na$_3$PS$_4$, as the grain volume becomes larger. These findings highlight the opposing influences of GBs on Na-ion transport in sulfide and oxide solid electrolytes.

Figure 2. Na-ion conductivities ($\sigma$) and activation energies ($E_a$) for bulk and polycrystalline (for three different grain volumes of 108, 21.6 and 2.16 nm$^3$) (a) Na$_3$PS$_4$ and (b) Na$_3$PO$_4$. Conductivity data for all five grain volumes is given in Figure S3.

The Arrhenius plots for Na$_3$PS$_4$ in Figure 2(a) reveal two important findings. First, the conductivities for the polycrystalline systems are higher than for bulk Na$_3$PS$_4$. The highest conductivities are found for polycrystals with the smallest grain volume of 2.16 nm$^3$, with values of 6.15×10$^{-4}$ and 1.38×10$^{-2}$ S cm$^{-1}$ at 400 and 800 K, respectively, compared to the bulk conductivities of 3.42×10$^{-4}$ and 1.97×10$^{-2}$ S cm$^{-1}$ at 400 and 800 K, respectively. Furthermore, when the conductivities of the polycrystals of Na$_3$PS$_4$ are extrapolated to room temperature, they are very similar to the bulk conductivity. These results suggest that GB resistance in Na$_3$PS$_4$ is indeed weak, as proposed in recent impedance experiments of this mechanically soft material.
In order to confirm the trends between conductivity, activation energy and grain volume discussed above, we also carried out a number of test simulations with 125×125×125 Å³ cells containing 80000–120000 ions, thereby increasing the grain volumes by almost an order of magnitude. Arrhenius plots for the conductivities obtained from these calculations with grain volumes of 976.56, 195.31 and 19.53 nm³ (equivalent to 2, 10 and 100 grains, respectively) at 400, 600 and 800 K are given in Figure S4. From these results, it is clear that the same trends are observed as in Figures 2 and 3, namely, decreasing conductivity and increasing activation energy with decreasing grain volume for the oxide and increasing conductivity with decreasing grain volume for the sulfide.

In summary, our results show two distinct and opposing behaviors for the effect of GBs on Na-ion conduction in two model sulfide and oxide solid electrolytes. 

**Local structural insights into GB effects.** The analysis of ion transport presented here shows the distinctly different influences of GBs on ion conduction in Na₃PS₄ and Na₃PO₄; however, the underlying reasons for these differences are not fully understood. To probe the local structural factors, we analyze the radial distribution functions (RDFs) for Na-Na, Na-P and Na-S/O in the bulk materials and the polycrystals with the largest (108 nm³) and smallest (2.16 nm³) grain volumes. The RDFs for both Na₃PS₄ and Na₃PO₄ at 400 K are displayed in Figure 4.

First considering Na₃PS₄, the bulk and polycrystal systems show a sharp primary peak at ~3.3 Å in their Na-Na RDFs. For the polycrystals, these peaks are higher, marginally broadened and their distance reduced by ~0.1 Å, compared to the bulk. These features suggest that the GBs in Na₃PS₄ allow the Na ions to be closer to each other. It is noteworthy that the Na-Na RDFs for the Na₃PS₄ polycrystals with the largest and smallest grain volumes are almost identical, suggesting that the difference between the conductivities of these polycrystals is not a primary result of the Na distributions. This is in agreement with the ab initio MD results of de Klerk and Wagemaker. The Na-P RDFs for the bulk and polycrystals of Na₃PS₄ show comparable behavior. The Na-S RDFs for Na₃PS₄ are almost identical for each system, with similar trends to those previously observed for RDFs of successful Na-ion hopping.

Overall, the RDFs for bulk and polycrystalline Na₃PS₄ are strikingly congruent, which strongly suggests that there is no substantial change in the conduction mechanism as a result of the GBs. This is further corroborated by the fact that the RDFs of the polycrystals are almost indistinguishable. These results again advocate that it is the point defect concentrations and compositional changes between these sulfide structures that are responsible for the small changes in Na-ion transport characteristics and not the GBs themselves.

Figure 4. Na-Na, Na-P and Na-S/O RDFs for bulk and polycrystalline (grain volumes of 108 and 2.16 nm³) Na₃PS₄ (left) and Na₃PO₄ (right) at 400 K.

We now turn our attention to Na₃PO₄. The bulk RDFs are in excellent agreement with previous MD studies. In contrast to Na₃PS₄, the Na-Na RDFs for bulk and polycrystalline Na₃PO₄ show very different behavior. The Na-Na distances of the primary peaks are 3.15 Å for the bulk and 3.05 and 2.95 Å for the polycrystals with grain volumes of 108 and 2.16 nm³, respectively. This decrease in Na-Na distance is met with a corresponding increase in peak height for the polycrystal with the smallest grain volume of 2.16 nm³. With decreasing grain volume, a new peak appears at ~4.5 Å, in addition to reductions of the peaks at Na-Na distances greater than 5 Å.

For the Na-P RDFs in Na₃PO₄, the main peaks at 3.5 Å undergo substantial changes when moving from the bulk system to the polycrystals. The peaks become smaller and increasingly asymmetrical, particularly
for the polycrystal with the smallest grain volume of 2.16 nm\(^3\) where a second peak on the right shoulder of the first peak becomes visible. Similar peak deformation has been observed for Na-P RDFs in Na\(_3\)PS\(_4\), where de Klerk and Wagemaker\(^\dagger\) associated the formation of two peaks at ~3–5 Å with unsuccessful Na-ion migration, since it results in a contraction of the free volume around the Na ions. Given that such behavior is indicative of unsuccessful hops, these results help to explain the reduced Na-ion conductivity that we observed as a function of grain volume for Na\(_3\)PO\(_4\).

As with the Na-S RDFs for Na\(_3\)PS\(_4\), the Na-O RDFs for Na\(_3\)PO\(_4\) are all similar. Our structural analysis shows that the distributions of Na-S and Na-O distances are not crucial factors in determining the changes in conductivity when comparing bulk and polycrystalline systems.

Analysis of the integrated RDFs provides useful information on the local coordination of a species. The integration of the Na-Na, Na-P and Na-S/Na-O RDFs for bulk and polycrystalline Na\(_3\)PS\(_4\) and Na\(_3\)PO\(_4\) at 400 K are given in Figure 5.

The main feature revealed from the data in Figure 5 is the difference in the coordination of Na ions to neighboring Na ions between the polycrystals of Na\(_3\)PS\(_4\) and Na\(_3\)PO\(_4\). For Na\(_3\)PS\(_4\), the coordination number of Na ions to other Na ions is highest in the polycrystal with the largest grain volume of 108 nm\(^3\), whereas for Na\(_3\)PO\(_4\), the polycrystal with the smallest grain volume of 2.16 nm\(^3\) has the highest coordination number. This fundamental difference indicates that Na ions effectively become under-coordinated with decreasing grain volume in Na\(_3\)PS\(_4\), thereby providing potential for higher Na-ion diffusion in these polycrystals.

In contrast, the opposite is true for Na\(_3\)PO\(_4\), where the Na ions become over-coordinated with decreasing grain volume. These two opposing effects may help to explain the difference between the GB behavior of sulfide and oxide solid electrolytes. This under-/over-coordination effect is not seen for the Na-P and Na-S/Na-O integrated RDFs, which suggests that it is the Na-Na distributions at the GBs that play the major role in determining the Na-ion conductivity in these systems.

In summary, this local structural analysis has clearly shown different behavior for the Na\(_3\)PS\(_4\) and Na\(_3\)PO\(_4\) electrolytes. For the sulfide, the differences between the RDFs of the bulk and polycrystalline systems are small, suggesting that the structural changes induced by the GBs do not have a dramatic effect on Na-ion transport. Conversely, for the oxide, the differences are much more pronounced. The GBs have a significant impact on the short- and long-range atomic distributions, suggesting a fundamental change in the Na-ion conduction mechanism of Na\(_3\)PO\(_4\). These results help to explain the reasons why the impact of GBs on conductivity in sulfides is weaker than in oxides.

**Na-ion conduction mechanisms.** To clarify the underlying atomistic conduction mechanisms in these two materials and how the GBs affect these mechanisms, we produce density plots of the accumulated Na-ion trajectories over the simulated timescale, which are a powerful means of visualizing the migration pathways and all the positions in the lattice that are traversed.

Figure 6 shows the Na-ion diffusion density plots for selected regions of bulk Na\(_3\)PS\(_4\) and Na\(_3\)PO\(_4\) at 400 K. As expected, significant long-range three-dimensional Na-ion diffusion is observed in both systems. A greater density of Na-ion diffusion pathways is observed for Na\(_3\)PS\(_4\) compared to Na\(_3\)PO\(_4\), in agreement with the faster Na-ion diffusion of the sulfide system. The highest Na densities are observed
at the crystallographic Na sites with significant oscillation. Both materials exhibit the same vacancy diffusion mechanism, where the Na ions vibrate around their own sites before migration to a nearby vacant site. Vacancy migration has been proposed previously for both Na₃PS₄⁴⁹,⁴⁴,⁶⁰ and Na₃PO₄⁵¹,⁵₃,⁵₅.

It has been proposed that Na-ion diffusion in Na₃PO₄ can occur through the coupling of Na ions with the reorientation of their neighboring phosphate anions, i.e., the so-called “paddle-wheel” effect.⁶¹ In agreement with earlier MD studies,⁴⁹,⁵₃,⁶² we find no strong evidence of this effect for either Na₃PO₄ or Na₃PS₄. As shown by the images in Figure S5, we do not observe any significant rotation of the PS₄ and PO₄ tetrahedra. Furthermore, correlated motions have been excluded for Na₃PO₄ on the basis of high-resolution neutron backscattering studies.⁶³

We now turn our attention to Na-ion diffusion in the polycrystals. Figures 7 and 8 show the diffusion density plots of Na ions in Na₃PS₄ and Na₃PO₄ polycrystals with a grain volume of 108 nm³ (two grains), respectively, at 400 K. Both grains (labelled 1 and 2) of the polycrystals are shown in separate images in order to better visualize Na-ion diffusion at the GBs. Significant areas of intergranular diffusion (diffusion between different grains) are highlighted for Na₃PS₄. Figure 7 shows a higher level of Na-ion diffusion at the GBs for Na₃PS₄ compared to Na₃PO₄ (Figure 8), as can be observed by the dense blue areas located at the edges of the grains of Na₃PS₄.

In Na₃PO₄, the majority of Na-ion diffusion takes place within the grains, with very few Na ions hopping across the GBs from one grain to another. In contrast, intergranular diffusion is far more prevalent in Na₃PS₄, as highlighted by the red circles in Figure 7.
These results strongly suggest that GBs in Na$_3$PS$_4$ do not restrict ion transport to the same extent as those of Na$_3$PO$_4$. Such findings are in complete agreement with our conductivity and structural analysis.

On this basis, it can be proposed that the undercoordination of conducting ions at the GBs of mechanically soft sulfides can be beneficial for conductivity, whereas for oxides, the overcoordination is detrimental for ion transport. These results help to explain the opposing effects of GBs in solid electrolytes reported in the literature.\textsuperscript{36,37,69}

**CONCLUSIONS**

Grain boundary resistance is one of the key challenges that must be overcome for the successful utilization of all-solid-state batteries. It is generally accepted that grain boundary resistance is higher in oxides than sulfides; however, the underlying reasons for this are not fully understood. In this work, we have used a novel microscale simulation approach to identify and explain the fundamentally different influences of grain boundaries on ion transport in two model solid electrolytes, Na$_3$PS$_4$ and Na$_3$PO$_4$, with the following key results:

(a) High grain boundary resistance is found for Na$_3$PO$_4$, in which the Na-ion conductivity decreases with increasing grain volume.

(b) In contrast, the relationship between Na-ion transport and grain volume is far weaker for Na$_3$PS$_4$. This suggests that for the sulfide it is the composition and point defect concentrations that are more important, in agreement with recent experimental findings.

(c) The local structures in bulk and polycrystalline Na$_3$PS$_4$ are very similar and help to explain the weak trend between its Na-ion transport and grain volume. In contrast, the local structure of Na$_3$PO$_4$ exhibits distinct changes, including overcoordination around Na ions at the grain boundaries, indicative of a fundamental change in the ion conduction mechanism.

Our results help to clarify the opposing behavior of grain boundaries in phosphate-and thiophosphate-based solid electrolytes and their impact on ion conduction. Given the importance of interfaces in all-solid-state batteries, we propose that the microscale approach taken in this work can be widely applied to other solid electrolyte materials.

**METHODS**

The MD simulations are based on established techniques and have been widely used to determine the ion transport properties in a wide variety of Li- and Na-ion battery materials.\textsuperscript{16,36,37,68} A new potential model was developed for cubic Na$_3$PS$_4$ (Table S1) using the empirical derivation procedure of the General Utility Lattice Program (GULP).\textsuperscript{69} For Na$_3$PO$_4$, we used the proven potential model of Tilocca et al.\textsuperscript{70} (Table S2) that was developed for MD calculations of phosphosilicate glasses, augmented here with a Na-Na interatomic potential from Harding.\textsuperscript{71} Formal valence charges for all ions and a potential cut-off of 12 Å were used. A full description of the potential models is available in the Supporting Information (Tables S1–S4).

The MD calculations were performed using LAMMPS.\textsuperscript{72} Long MD runs of 10 ns were completed using a time step of 1 fs and supercells of 9000–13000 ions for both the bulk (single crystal) and polycrystalline systems. Larger polycrystals of 8000–12000 ions were also tested in order to verify the trends determined for the smaller polycrystalline cells. Simulations were carried out for a temperature range of 400–800 K at intervals of 100 K using the NVT ensemble with a Nose-Hoover thermostat,\textsuperscript{73} with initial equilibration performed using the NPT ensemble for ~2 ns. We note that our calculations were carried out at elevated temperatures to improve computational efficiency.

Disorder was introduced to the bulk systems to promote long-range diffusion using Na vacancies (compensated by S or O vacancies) that were randomly distributed throughout the supercells at a concentration of 10%. A lower Na vacancy concentration of 3% was also tested (see Figure S6), with only a minor reduction in Na-ion conductivity below 800 K and a minor increase in activation energy observed compared to the 10% Na vacancy bulk systems. Such disorder was not introduced into the polycrystals as point defects were already present as a result of the GBs. The average stoichiometries of the polycrystals are given in Table S5. Self-diffusion data for Na were obtained from a mean squared displacement (MSD) analysis according to:

\begin{equation}
\langle r_i^2(t) \rangle = 6D_{Na}t
\end{equation}

where $\langle r_i^2(t) \rangle$ is the MSD, $D_{Na}$ is the diffusion coefficient for Na and $t$ is time. The diffusion data were then converted to conductivities ($\sigma$) using the Nernst–Einstein relationship:

\begin{equation}
\frac{1}{D_{Na}} = \frac{H}{kT} \frac{nq^2}{\sigma}
\end{equation}
where \( n \) is the number of Na ions per unit volume, \( q \) is the electron charge, \( k \) is the Boltzmann constant, \( T \) is the temperature and \( H_R \) is the Haven ratio, which is set to 1 in our calculations.

The polycrystal models used in this study were constructed using Voronoi tessellations, as employed in the Atomsk program,\(^7\) in which nodes are introduced at given positions inside the simulation box that are then linked with their neighboring nodes. The normals to these links are then found and these define the contours of the randomly orientated grains, i.e., the GBs in this study. Unit cells are then placed at the nodes and are expanded in three dimensions. The final polycrystal is then obtained after the unit cells have been expanded and cut into the respective grains. The unit cell structures and example polycrystals for cubic Na\(_3\)PS\(_4\) and Na\(_3\)PO\(_4\) are given in Figure 9. Further details regarding the setup of the polycrystals for the MD simulations are given in the supporting information.

![Figure 9. Example polycrystals containing two grains (grain volume of 108 nm\(^3\)) for (a) Na\(_3\)PS\(_4\) and (b) Na\(_3\)PO\(_4\). The top images show the three-dimensional polycrystals, while the bottom images indicate the approximate positions of the two grains. Na ions and PS\(_4\) and PO\(_4\) tetrahedra are given in blue, yellow and red, respectively.](image)

Cubic polycrystals with dimensions of 60×60×60 Å\(^3\) were used. Polycrystals with 2, 5, 10, 20 and 100 grains (equivalent to grain volumes of 108, 43.2, 21.6, 10.8 and 2.16 nm\(^3\), respectively) were used to investigate the effects of GBs on Na-ion transport in these systems. Example polycrystals with 2, 10 and 100 grains for Na\(_3\)PS\(_4\) are illustrated in Figure 10. MD simulations were carried out on three different random polycrystals for each grain volume and the data were averaged. The variance in conductivity between the random three polycrystals for each grain volume was minimal, as detailed in Tables S6 and S7, which show the activation energy of each polycrystal for Na\(_3\)PS\(_4\) and Na\(_3\)PO\(_4\), respectively.

![Figure 10. Polycrystals of Na\(_3\)PS\(_4\) containing (a) 2, (b) 10 and (c) 100 grains (equivalent to grain volumes of 108, 21.6 and 2.16 nm\(^3\), respectively). Each color represents a unique grain.](image)

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

(A) Potential model for Na\(_3\)PS\(_4\); (B) Potential model for Na\(_3\)PO\(_4\); (C) MD simulation procedure for polycrystals; (D) Activation energies; (E) Na-ion diffusion and conductivity; (F) PS\(_4\) and PO\(_4\) orientations; (G) Influence of Na vacancy concentration.

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