Defect-Mediated Conductivity Enhancements in Na$_{3-x}$P$_n$S$_{4}$ (P$_n$ = P, Sb) using Aliovalent Substitutions

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The sodium-ion conducting family of Na$_3$PnS$_4$, with P$_n$ = P, Sb, have gained interest for the use in solid-state batteries due to their high ionic conductivity. However, significant improvements to the conductivity have been hampered by the lack of aliovalent dopants that can introduce vacancies into the structure. Inspired by the need for vacancy introduction into Na$_3$PnS$_4$, the solid solutions with WS$_4^{2-}$ introduction are explored. The influence of the substitution with WS$_4^{2-}$ for PS$_4^{3-}$ and SbS$_4^{3-}$, respectively, is monitored using a combination of X-ray diffraction, Raman and impedance spectroscopy. With increasing vacancy concentration improvements resulting in a very high ionic conductivity of 13 ± 3 mS·cm$^{-1}$ for Na$_{2.9}$P$_{0.9}$W$_{0.1}$S$_4$ and 41 ± 8 mS·cm$^{-1}$ for Na$_{2.9}$Sb$_{0.9}$W$_{0.1}$S$_4$ can be observed. This work acts as a stepping-stone towards further engineering of ionic conductors using vacancy-injection via aliovalent substituents.

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Defect-Mediated Conductivity Enhancements in 

$\text{Na}_{3-x}\text{Pn}_{1-x}\text{W}_x\text{S}_4$ ($\text{Pn} = \text{P, Sb}$) using Aliovalent Substitutions

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Abstract

The sodium-ion conducting family of $\text{Na}_3\text{PnS}_4$, with $\text{Pn} = \text{P, Sb}$, have gained interest for the use in solid-state batteries due to their high ionic conductivity. However, significant improvements to the conductivity have been hampered by the lack of aliovalent dopants that can introduce vacancies into the structure. Inspired by the need for vacancy introduction into $\text{Na}_3\text{PnS}_4$, the solid solutions with $\text{WS}_4^{2-}$ introduction are explored. The influence of the substitution with $\text{WS}_4^{2-}$ for $\text{PS}_4^{3-}$ and $\text{SbS}_4^{3-}$, respectively, is monitored using a combination of X-ray diffraction, Raman and impedance spectroscopy. With increasing vacancy concentration improvements resulting in a very high ionic conductivity of $13 \pm 3 \text{ mS} \cdot \text{cm}^{-1}$ for $\text{Na}_{2.9}\text{P}_{0.9}\text{W}_{0.1}\text{S}_4$ and $41 \pm 8 \text{ mS} \cdot \text{cm}^{-1}$ for $\text{Na}_{2.9}\text{Sb}_{0.9}\text{W}_{0.1}\text{S}_4$ can be observed. This work acts as a stepping-stone towards further engineering of ionic conductors using vacancy-injection via aliovalent substituents.

TOC Graphic
Lithium and sodium thiophosphates are currently of high interest for solid-state battery applications due to their high ionic conductivity and ductile nature. A multitude of structural classes such as Li_{10}(Si/Ge/Sn)P_{2}S_{12}^{1–9} Li_{6}PS_{6}X^{10–15} in the case of Li\(^{+}\) conductors and Na_{11}Sn_{2}PS_{12}^{16–18} Na_{3}PS_{4} and Na_{3}SbS_{4} for Na\(^{+}\) conductors have attracted quite some interest.\(^{19–24}\) However, while most of these compounds possess vacant sites for the mobile carrier within the structure, a prerequisite for fast ionic conduction,\(^{25,26}\) Na_{3}PS_{4} and Na_{3}SbS_{4} are intrinsically hindered by fully occupied Na\(^{+}\) positions.

The structure of Na_{3}PnS_{4}, with Pn = P, Sb, is displayed in Figure 1, crystallizing either in the cubic \(I\bar{4}3m\) or tetragonal \(P\bar{4}2_{1}c\) space groups. The cubic polymorph features a body centered cubic arrangement of the PnS\(^{3−}\) units, whereas the tetragonal polymorph exhibits a rotation of PnS\(^{3−}\) around the [111] axis that goes along with a minor tetragonal distortion along the c-axis. In the cubic structure, only one fully occupied Na\(^{+}\) position exists, while in the tetragonal structure, two Na\(^{+}\) positions can be found due to this tetragonal distortion resulting from the PnS\(^{3−}\) rotation.\(^{22,27}\) The resulting, fully occupied Na\(^{+}\) diffusion pathways are illustrated in Figure 1.

Different isoelectronic substitutions, such as Se for S and Sb for P, have already been carried out toward improving our understanding of this material system.\(^{27–29}\) Substituting Se into the anion sublattice is possible over the whole stoichiometric range, leading to a stabilization of the
cubic polymorph and general expansion of the lattice.\textsuperscript{27,30} This Se substitution also leads to a lattice softening, which in turn decreases both the activation energy for ion migration and the Arrhenius prefactor.\textsuperscript{27,31} Interestingly, further improvement of the conductivity up to 0.74 mS⋅cm\textsuperscript{-1} can be achieved by mixing Na\textsubscript{3}PS\textsubscript{4} with small amounts of Na\textsubscript{3}SiS\textsubscript{4}, highlighting the potential of this material class.\textsuperscript{32} Furthermore, depending on the synthetic conditions, it is also possible to individually synthesize the cubic and tetragonal polymorphs. For example, while mechanical alloying leads to the cubic polymorph, the tetragonal structure can be obtained by classic high temperature synthesis.\textsuperscript{19,24,33} Compared to Na\textsubscript{3}PS\textsubscript{4}, Na\textsubscript{3}SbS\textsubscript{4} exhibits an even higher ionic conductivity due to the overall lower activation barriers found in both polymorphs.\textsuperscript{33} In line with the full occupancy of the Na\textsuperscript{+} positions, the transport properties seem to depend on the defect concentration and thus, the synthesis conditions, and less on the crystal structure itself.\textsuperscript{22,34} This assumption is further affirmed upon considering the exceptionally high conductivity of 3 mS⋅cm\textsuperscript{-1} of the ball-milled t-Na\textsubscript{3}SbS\textsubscript{4} (with 2.5 mol % Na vacancies).\textsuperscript{29}

The existence of the fully occupied positions of Na\textsuperscript{+} are the reason that has made it difficult to optimize the ionic conductivity. The typical aliovalent dopants within the PS\textsubscript{4}\textsuperscript{3-} and SbS\textsubscript{4}\textsuperscript{3-} units are often tetravalent such as Si\textsuperscript{4+}, Ge\textsuperscript{4+}, Sn\textsuperscript{4+}.\textsuperscript{35} However, while these dopants work well in systems with a high number of vacant sites, they introduce more Na\textsuperscript{+} as mobile carries and hence cannot be incorporated in the structures of Na\textsubscript{3}PS\textsubscript{4} and Na\textsubscript{3}SbS\textsubscript{4}. Only recently has vacancy-injection via substitution has been proposed.\textsuperscript{36,37} Thus, inspired by the need to create more vacancies in Na\textsubscript{3}PS\textsubscript{4} and Na\textsubscript{3}SbS\textsubscript{4}, this work explores aliovalent substitutions within Na\textsubscript{3-x}Pn\textsubscript{x}S\textsubscript{4}. Incorporation of W\textsuperscript{6+} on the tetrahedral site, forming WS\textsubscript{4}\textsuperscript{2-} tetrahedra, leads to the introduction of vacancies via charge compensation. It should be noted that, in addition to the substitution with W\textsuperscript{6+}, the substitution of Na\textsubscript{3}PnS\textsubscript{4} with Mo\textsuperscript{6+} was attempted but synthetically unsuccessful.
Figure 2. Obtained X-ray diffraction patterns of (a) Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and (b) Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ with changing W content. The grey bars highlight the reflections of WS$_2$. Refined lattice parameters of (c) Na$_{3-x}$P$_{1-x}$W$_x$Sb$_4$ and (d) Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$, showing the structural changes during substitution. In both solid solutions, changes in the lattice parameters can be found during substitution, leading to a decrease in the tetragonal distortion (c/a ratio) and ultimately a transition from the tetragonal into the cubic crystal structure.

All experimental details on the solid-state syntheses and characterization can be found in the Supporting Information. Figures 2 a,b show the X-ray diffraction patterns of Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ from 0 $\leq x \leq$ 0.1. Rietveld refinements were performed, but deemed unreliable due to unphysically large thermal displacement parameters of Na$^+$ of $> 10$ Å$^2$. While these large displacement parameters serve as an indicator for fast ionic conduction, an accurate refinement of atomic positions and occupancies becomes impossible, underlining the need for future low-temperature, high-resolution scattering experiments.

Nevertheless, the lattice parameters obtained with Pawley refinements of the solid solutions Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ can be found in Figure 2c and 2d, respectively. All Pawley fits to the diffraction data, as well as a table containing the refined lattice parameters, can be
found in the Supporting Information. With increasing W content, interesting changes in the patterns and the lattice of Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ can be observed:

(1) A certain phase fraction of the precursor WS$_2$ can be found in all samples of W substituted Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and above $x > 0.075$ minor reflections of WS$_2$ can also be seen in Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$. As WS$_2$ is isotypic with the MoS$_2$ layered structure, all of these reflections are likely influenced by texturing of a minor impurity precursor phase fraction or suggest a limited solubility in the structure of Na$_{3-x}$P$_{1-x}$W$_x$S$_4$. It is therefore difficult to assess the real solubility limit in the structure, based on these phase fractions.

(2) However, a systematic shift of the lattice parameters can be found during the WS$_2^{2-}$ incorporation. With increasing W-content in Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ the lattice parameter $a$ increases while the lattice parameter $c$ decreases and an overall decrease of the tetragonal distortion can be found. The changes in the lattice parameters and lattice volume (see Supporting Information Figure S3) are small for Na$_{3-x}$P$_{1-x}$W$_x$S$_4$, indicating a rather limited solubility when compared to Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$, as a much stronger trend can be found for Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$. The solubility limit seems to have been reached above $x \geq 0.1$ within Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$. This is further supported by the changing unit cell volume of Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$, which remains constant for $x = 0.1$ and 0.125, as shown in the Supporting Information Figure S5.

At this point, the differences in the changing lattice between the solid solutions Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ remain unclear as the tetrahedrally-coordinated ionic radius difference between Sb$^{5+}$ vs. W$^{6+}$ is low, whereas P$^{5+}$ exhibits a much smaller ionic radius. The differences are likely due to different solubility limits of WS$_2$ in the phases. In addition, competing effects during the introduction of Na$^+$ vacancies may lead to an overall lattice volume contraction (see Supporting Information Figure S5) and changing tetrahedral distortion.

(3) In both solid solutions, the decreasing tetragonal distortion leads to a structural change from the tetragonal to the cubic polymorph around $x = 0.1$ and $x = 0.075$ in Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$, respectively.

Ultimately, while low-temperature X-ray diffraction will be needed to assess the vacancy concentration and the W-occupancy on the tetrahedral positions, these structural data suggest that the introduction of W$^{6+}$ in Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ is possible. As Rietveld refinements are not possible using the room temperature data, the exact W occupancy and solubility limits cannot be adequately assessed. However, Raman spectroscopy is quite reliable in detecting the local polyhedral species in thiophosphates and can be used to monitor the generation of WS$_2^{2-}$ tetrahedra within the structure. The Raman spectra of Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$, are
shown in Figure 3a and 3b, respectively. For comparison, representative Raman spectra of solid WS₂ and the WS₄²⁻ ion in solution are shown.⁴⁰⁻⁴²

In the case of Na₃₋ₓP₁₋ₓWₓS₄, all Raman modes of the PS₄³⁻ can be found, along with the main symmetric A₁ stretching mode at 413 cm⁻¹. In the Raman spectra of Na₃₋ₓSb₁₋ₓWₓS₄, three Raman signals can be noticed in the range of 340 cm⁻¹ to around 410 cm⁻¹ corresponding to the different modes of the SbS₄³⁻ tetrahedra in Na₃SbS₄.⁴³,⁴⁴ With increasing W-content, the intensity of the main modes decrease and additional Raman active modes can be found. Additionally, a different signal around 470 cm⁻¹ begins to evolve, corresponding to the vibrations of the WS₄²⁻ tetrahedra (shown in grey). A minor intensity corresponding to the WS₂ precursor can be found in the solid solution Na₃₋ₓP₁₋ₓWₓS₄, indicating a different and lower solubility limit of WS₄²⁻ in Na₃₋ₓP₁₋ₓWₓS₄ compared to Na₃₋ₓSb₁₋ₓWₓS₄. The assignment of all Raman modes for PS₄³⁻, SbS₄³⁻, WS₂ and WS₄²⁻ can be found in the Supporting Information, Table S3 as well as all Raman spectra including x = 0.025 and x = 0.075 in Figure S6. While minor shifts and differences in intensity are expected due to the reference spectrum stemming from thiometallocomplexes in solution, comparison of the reference spectra with the data corroborate the incorporation of WS₄²⁻ tetrahedra in Na₃₋ₓSb₁₋ₓWₓS₄, as well as Na₃₋ₓP₁₋ₓWₓS₄ to a minor extent.

![Raman spectra](image)

**Figure 3. Raman spectra of (a) Na₃₋ₓP₁₋ₓWₓSb₄ and (b) Na₃₋ₓSb₁₋ₓWₓS₄ for representative compositions, along with digitized Raman spectra of WS₄²⁻ polyhedra in solution⁴⁰⁻⁴¹ and single crystalline WS₂.⁴² In both cases, the Raman modes of the WS₄²⁻ polyhedra are visible and increase with increasing degree of substitution. In addition, WS₂ can be found in the compositional series of Na₃₋ₓP₁₋ₓWₓSb₄.**
In order to gain insight into how the increasing defect concentration by Na\(^+\) vacancies affect the ionic transport properties, AC impedance spectroscopy was performed on Na\(_{3-x}\)Pn\(_{1-x}\)W\(_x\)S\(_4\). Representative Nyquist-plots of the impedance response at -20 °C are shown for all compositions in the Supporting Information, Figure S7. In the more resistive samples of Na\(_3\)PS\(_4\) and Na\(_3\)SbS\(_4\), two semicircles can be found and the bulk and grain boundary contributions can be fully distinguished. However, in all other samples, only one process is visible followed by the blocking electrode. While the capacitances of the resolvable spectra are in the range of 38–64 pF·cm\(^{-2}\) for the high-frequency process, corroborating that predominantly bulk transport is observed,\(^{45}\) the bulk and grain processes of the highly conducting compositions cannot be distinguished. Therefore, all ionic conductivities and activation barriers presented here need to be considered as total conductivities.

The Arrhenius plots of all compositions can be found in Figure S7. It should be mentioned that for Na\(_{3-x}\)Sb\(_{1-x}\)W\(_x\)S\(_4\) with \(x = 0.05\) and \(x = 0.075\), a change in the Arrhenius behavior can be observed at temperatures slightly above room temperature (see Supporting Information, Figure S8). Typically, the cubic structure is the high-temperature polymorph. In Na\(_3\)SbS\(_4\), one would expect the phase transition from the tetragonal to the cubic structure at 170 °C.\(^{33}\) Considering the Arrhenius behavior during heating, as well as the structural changes in Figure 2, it seems that the W substitution not only lowers the tetragonal distortion in the structure, but also the phase transition temperature, similar to Na\(_3\)PS\(_{4-x}\)Se\(_x\).\(^{27}\) Therefore, with increasing W content, the phase transition temperature seems to decrease. For \(x < 0.05\), the phase transition is likely located above room temperature, whereas at \(x \geq 0.075\), the cubic phase seems to be the stable polymorph at room temperature.

Figure 4 shows the ionic conductivity and activation barriers for Na\(_{3-x}\)Pn\(_{1-x}\)W\(_x\)S\(_4\). With increasing W content, and with-it increasing vacancy concentration, the activation barriers for ionic transport decrease in both series of compositions. While the structural data suggests a low solubility of W\(^{6+}\) in Na\(_{3-x}\)P\(_{1-x}\)W\(_x\)S\(_4\), the Raman data show the incorporation of WS\(_{4}^2-\) and the transport properties are affected. As the overall lattice volume within the solid solution is decreasing, the decreasing activation barriers are likely related to changing defect formation enthalpies due to the incorporation of vacancies, rather than changing widths of the diffusion pathways. Theoretical work also suggests that incorporation of vacancies should lead to lower activation barriers.\(^{34}\) With these changes in the activation barriers and the changing carrier densities from the vacancy-injection, the ionic conductivity of both series increases significantly. While the W-substituted samples immediately exhibit a sharp increase of the conductivity and then a steadily rising conductivity with increasing W-content, the solid
solution Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ shows a much steeper jump at the tetragonal to cubic transition. As previously mentioned, the values presented here represent total conductivities and, especially in the pristine compositions, a large grain boundary contribution can be observed. Nevertheless, in the case of Na$_{3-x}$P$_{1-x}$W$_x$S$_4$, the unsubstituted compound exhibits a total conductivity of 0.04 ± 0.01 mS·cm$^{-1}$ and achieves 13 ± 3 mS·cm$^{-1}$ for $x = 0.1$, representing an increase of the conductivity exceeding three orders of magnitude. In the case of Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$, the pristine compound exhibits a conductivity of 0.01 ± 0.002 mS·cm$^{-1}$ and achieves 41 ± 8 mS·cm$^{-1}$ for $x = 0.1$. To the best of our knowledge, this is the highest ionic conductivity measured in the class of thiophosphate ionic conductors to date, showing the drastic influence of vacancy injection in Na$_{3-x}$Pn$_{1-x}$W$_x$S$_4$.

![Graph](image-url)

**Figure 4.** (a) Activation barriers of Na$_{3-x}$Pn$_{1-x}$W$_x$S$_4$ with Pn = P, Sb. and (b) room-temperature conductivities With increasing vacancy content, the conductivity changes drastically alongside with a continuous decrease of the activation barrier. Dashed lines represent guides-to-the-eye.

In conclusion, this work reports the aliovalent substitution in the solid solution series Na$_{3-x}$Pn$_{1-x}$W$_x$S$_4$ with Pn = P and Sb. X-ray diffraction and Raman spectroscopy corroborate that solid solutions can be formed and that WS$_4^{2-}$ polyhedra are incorporated into the structure. With increasing W content, the structures become less distorted leading to a structural transition from the tetragonal to the cubic phase. The increasing vacancy concentration leads to orders of magnitude improvements in the ionic conductivity, exhibiting a very high ionic conductivity of 13 ± 3 mS·cm$^{-1}$ for Na$_{2.9}$P$_{0.9}$W$_{0.1}$S$_4$ and 41 ± 8 mS·cm$^{-1}$ for Na$_{2.9}$Sb$_{0.9}$W$_{0.1}$S$_4$.

Future work needs to further explore the structural changes and occupancies during the substitution using low-temperature, high-resolution diffraction methods, as well as elucidating
the real defect concentration and changing phase transition temperatures. Overall, this work shows that aliovalent substitutions toward increasing vacancy content is possible by introducing WS$_4^{2-}$ in the thiophosphates and thioantimonates, thereby opening up a new and very promising route for optimization of these classes of superionic conductors, beyond Na$_3$PS$_4$ and Na$_3$SbS$_4$.

Supporting Information.

All experimental details on synthesis, X-ray diffraction and impedance spectroscopy can be found here. All structural data as obtained from Pawley refinements can be found here. In addition, assignments of the Raman modes and all Raman spectra are given. Further, the impedance data and Arrhenius plot, as well as information on the Arrhenius behavior and phase transitions.

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Notes

The authors declare no competing financial interests.

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Supporting Information - Defect-Mediated Conductivity Enhancements in $\text{Na}_{3-x}\text{Pn}_{1-x}\text{W}_x\text{S}_4$ ($\text{Pn} = \text{P, Sb}$) using Aliovalent Substitutions

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Experimental:

Synthesis. The following precursors were used: Na$_2$S (Sigma Aldrich), S$_8$ (Acros Organics, 99.999%), WS$_2$ (chemPur, 99.98%) and P$_4$S$_{10}$ (Merck Millipore, for synthesis), as well as Sb$_2$S$_3$. The latter precursor was synthesized beforehand using antimony Sb (chemPur 99.99 %) and S$_8$ (Acros Organics, 99.999%).

All used precursors were hand ground using an agate mortar in stoichiometric amounts for 20 minutes. Afterward, the homogenous mixtures were pressed into pellets via a hand press and loaded into quartz ampoules (10 mm diameter). The ampoules were thoroughly cleaned and dried by 800 °C under dynamic vacuum beforehand. Filled ampoules were then sealed and placed into an oven with a defined heating procedure. Figure S1 shows the heating procedure used for the different synthesized products. Obtained samples were ground to a homogeneous powder again for further characterization. All steps were carried out under argon atmosphere (<0.1 ppm O$_2$, <1.0 ppm H$_2$O). Sintering of the pellets was also carried out in an evacuated quartz ampoule. The ampoule was placed directly into a pre-heated oven at reaction temperature (550 °C for Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$) for ten minutes. Since the Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ samples were partially molten after reacting at 550 °C, these samples are sintered at 500 °C to not distort the pellet geometry. Afterward, the ampoules underwent rapid cooling in air to room temperature.

![Figure S1](image)

*Figure S1: Scheme of the heating procedure to synthesize either a) Na$_{3-x}$P$_{1-x}$M$_x$S$_4$ (with Pn = P, Sb and M = W, Mo) or b) Sb$_2$S$_3$.*

X-Ray Diffraction. PANanalyticals Empyrean was used for laboratory X-Ray diffraction measurements. To keep prepared samples under argon atmosphere while measuring Kapton Foil (7.5 µm) was used as well as a Si(911) no-background sample holder. A 2Θ range of 10 – 90 ° was analysed with a step size of 0.026 ° with 150 s to 250 s per degree. The utilized radiation was the Cu-K$_\alpha$ line (0.15418 nm). A 1 mm slit as well as a 10 mm beam mask was used in combination with a spinning sample holder.

Electrical Characterization. Impedance measurements were carried out using an SP300 potentiostat from Biologic in a range from 100 mHz to 7 MHz in temperature range from
-40 °C to 60 °C. The temperature was controlled by the WKL 64 climate chamber from Weiss. For the measurements the samples were pressed isostatically with 380 MPa to obtain dense pellets (> 80% relative density), which then have a 200 nm thick gold layer deposited on both sides as electrical contacts. Afterward, aluminium current collectors were fixated on the pellets using Kapton tape. To ensure avoiding contact with air, this whole setup was pouched in under argon atmosphere. Measurements were controlled using the software EC-Lab V 13.0, while the obtained spectra were analysed with RelaxIS 3.

**Raman.** Raman spectroscopy measurements were carried out using Brukers Senterra with a laser wavelength of 532 nm. A few grains of powder of the analysed material were sealed under argon atmosphere in an air-tight cuvette and multiple spectra were measured for different grains. A spectral range of 270 cm\(^{-1}\) to 1700 cm\(^{-1}\) was analysed with a power of 0.2 mW. The investigated area is around 50 \(\mu\)m x 1000 \(\mu\)m. Data was collected with the program OPUS V. 7.
Figure S2: X-ray diffraction data and Pawley fits to obtain the lattice parameters of Na$_{3.3}$P$_{1-x}$W$_x$S$_4$. 
Table S1: Summary of the obtained lattice parameters of Na$_{3-x}$P$_{1-x}$W$_x$S$_4$

| $x_N$ in Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ | lattice par. a / Å | lattice par. c / Å | unit cell V. |
|-------------------------------------|---------------------|---------------------|--------------|
| 0.0 %                               | 6.9546(2)           | 7.0944(3)           | 343.16(2)    |
| 2.5 %                               | 6.9571(3)           | 7.0888(3)           | 343.02(3)    |
| 5.0 %                               | 6.9664(2)           | 7.0745(3)           | 343.04(3)    |
| 7.5 %                               | 6.9662(3)           | 7.0840(4)           | 343.67(3)    |
| 10.0 %                              | 6.9973(4)           | -                   | 342.56(2)    |

Figure S3: Unit cell volume of Na$_{3-x}$P$_{1-x}$W$_x$S$_4$
Figure S4: X-ray diffraction data and Pawley fits to obtain the lattice parameters of Na$_3$-xSb$_{1-x}$W$_x$S$_4$. 
Table 2: Summary of the obtained lattice parameters of Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$

| $x_N$ in Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ | lattice par. a / Å | lattice par. c / Å | unit cell V. / Å$^3$ |
|-------------------------------------|---------------------|---------------------|---------------------|
| 0.0 %                               | 7.1650(1)           | 7.2963(1)           | 374.57(2)           |
| 2.5 %                               | 7.1725(2)           | 7.2752(2)           | 374.28(3)           |
| 5.0 %                               | 7.1824(1)           | 7.2480(2)           | 374.08(2)           |
| 7.5 %                               | 7.2024(1)           | -                   | 373.78(1)           |
| 10.0 %                              | 7.2013(1)           | -                   | 373.50(1)           |

Figure S5: Unit cell volume of Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$, showing the solubility limit for $x \geq 0.1$. 
Figure S6: Raman spectra for a) Na$_{3-x}$P$_x$W$_x$S$_4$ and b) Na$_{3-x}$Sb$_x$W$_x$S$_4$.

Table S3: Summary of measured vibrational signals compared to their literature values.

| Vibration mode       | Wave number (measured) / cm$^{-1}$ | Wave number (literature) / cm$^{-1}$ |
|----------------------|------------------------------------|-------------------------------------|
| $v_{\text{symm}}$ (SbS$_4^{3-}$) | 364                                | 366 Ref. [1]                        |
| $v_{\text{asymm},1}$ (SbS$_4^{3-}$) | 386                                | 389 Ref. [1]                        |
| $v_{\text{asymm},2}$ (SbS$_4^{3-}$) | 406                                | 410 Ref. [1]                        |
| $v_{\text{symm},1}$ (PS$_4^{3-}$)   | 413                                | 413 Ref. [2]                        |
| $v_{\text{deform},4}$ (PS$_4^{3-}$) | 278                                | 280 Ref. [3]                        |
| $v_{\text{asymm},3}$ (PS$_4^{3-}$)  | 569 / 536                         | 569 / 536 Ref. [4]                 |
| $v_{\text{symm}}$ WS$_4^{2-}$       | ca. 470                            | 482 Ref. [5]                        |
| $v_{\text{asymm}}$ WS$_4^{2-}$      | ca. 460                            | 469 / 460 / 450 Ref. [5]           |
| $v$ WS$_2$               | ca. 350                            | 350 Ref. [6]                        |
Figure S7: Impedance spectra of a-c) Na$_{3-x}$P$_{1-x}$W$_x$S$_4$ and d-f) Na$_{3-x}$Sb$_{1-x}$W$_x$S$_4$ as well as the corresponding Arrhenius plots. Two processes are visible in the spectra with lower W contents, indicating grain boundary processes. At higher values of x, the spectra can no longer be resolved.
Figure S8: Selected Arrhenius Plots to showcase the phase transition in the material.

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