Polymorphism and Fast Potassium-Ion Conduction in the T5 Supertetrahedral Phosphidosilicate KSi$_2$P$_3$

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Dedicated to Professor Peter Klüfers on the occasion of his 70th birthday

Abstract: The all-solid-state battery (ASSB) is a promising candidate for electrochemical energy storage. In view of the limited availability of lithium, however, alternative systems based on earth-abundant and inexpensive elements are urgently sought. Besides well-studied sodium compounds, potassium-based systems offer the advantage of low cost and a large electrochemical window, but are hardly explored. Here we report the synthesis and crystal structure of K-ion conducting T5 KSi$_2$P$_3$, inspired by recent discoveries of fast ion conductors in alkaline phosphidosilicates. KSi$_2$P$_3$ is composed of SiP$_4$ tetrahedra forming interpenetrating networks of large T5 supertetrahedra. The compound passes through a reconstructive phase transition from the known T3 to the new tetragonal T5 polymorph at 1020°C with enantiotropic displacive phase transitions upon cooling at about 155°C and 80°C. The potassium ions are located in large channels between the T5 supertetrahedral networks and show facile movement through the structure. The bulk ionic conductivity is up to 2.6×10$^{-4}$ Scm$^{-1}$ at 25°C with an average activation energy of 0.20 eV. This is remarkably high for a potassium ion conductor at room temperature, and marks KSi$_2$P$_3$ as the first non-oxide solid potassium ion conductor.

All-solid-state batteries (ASSB) with solid instead of liquid electrolytes are considered as the next generation energy storage devices because they provide higher energy densities and faster charging rates than conventional systems.[1–6] For the development of ASSBs, the solid electrolyte is a critical component and its ionic conductivity a key performance indicator. So far, several lithium ion-conducting materials are well investigated. Garnets such as doped Li$_x$La$_{2-x}$Zr$_2$O$_7$ and Li$_{1/2}$Al$_{1/2}$Ti$_{1/2}$PO$_4$ exhibit bulk ion conductivities up to 10$^{-3}$ Scm$^{-1}$ at room temperature. Similar and even higher lithium ion conductivities in the range of 1.6×10$^{-4}$ to 2.5×10$^{-2}$ Scm$^{-1}$ were found in ternary lithium thiophosphates,[7] halide argyrodites,[8,9] Li$_x$GeP$_2$S$_{12}$-type materials[10] and rare-earth halides.[11–13] Recently, it became apparent that phosphidosilicates may be promising candidates for solid electrolytes. These compounds contain SiP$_4$ tetrahedra, which are isolated in Li$_2$SiP$_4$[14] while in Li$_2$Si$_2$P$_3$ or Li$_2$Si$_3$P$_3$[15] the tetrahedra are condensed via edges or vertices to reduce the charge. The SiP$_4$ tetrahedra in Li$_2$SiP$_4$ form interpenetrating networks of T2 supertetrahedra,[14] while in Li$_2$Si$_2$P$_3$ fused T4 and T5 entities are present.[16] The lithium ion conductivities are between 4×10$^{-7}$ Scm$^{-1}$ (Li$_2$SiP$_4$)[14] and 1×10$^{-3}$ Scm$^{-1}$ (Li$_2$Si$_2$P$_3$)[17] with activation energies of 0.49 to 0.30 eV, respectively. NMR data of Li$_2$SiP$_3$ reveal an activation energy of about 0.1 eV indicating an even more facile ion transport in this compound. However, lithium batteries for large scale applications are restricted by the availability and cost of lithium.[18–22] Therefore, systems with earth abundant cheap alternatives such as sodium or potassium are requested. Solid sodium electrolytes like Na$_3$PS$_4$[23] or NaSICON-type Na$_2$Sc$_2$Si(SiO$_4$)$_3$(PO$_4$)$_2$[24,25] have conductivities on the order of 2×10$^{-4}$ Scm$^{-1}$ and 1×10$^{-3}$ Scm$^{-1}$, respectively. β-Alumina,[26] Na$_x$Sb$_2$S$_4$[27,28] or Na$_{11}$Sn$_2$PS$_{12}$[29,30] exceed these conductivities by about one order of magnitude. The phosphidosilicates Na$_3$Si$_2$P$_4$[24,25] have conductivities on the order of 4×10$^{-3}$ Scm$^{-1}$ with a low activation energy ($E_a$) of 0.25 eV. NMR data reveal an even lower activation energy of 0.11 eV, suggesting a facile Na hopping process. While sodium is much more abundant than lithium, it has a less negative electrode potential (−2.71 V) compared to lithium (−3.04 V). In contrast, potassium has a lower potential than Na (−2.93 V) that enables an improved cell output voltage.

Since the availability and low cost of potassium are comparable with those of sodium, the exploration of potassium ion batteries (KIBs) appears promising. So far, studies on KIBs employing potassium metal anodes, solid electrolytes and cathodes such as Prussian blue with remarkable capacities and cycling stabilities were reported.[32–35] Surprisingly, only a few solid potassium ion electrolytes are known...
indicates crystallization of the silica capillary. We show that the potassium ion migration in this compound is predominantly two-dimensional.[34] In this work, we address the family of potassium phosphidosilicates as possible solid electrolytes. Currently only the compounds K$_2$SiP$_2$[36] and the layered T3 KSi$_2$P$_3$[37] are known in this system. Both are not promising as ion conductors because of the lack of partial occupied potassium sites. Here we report three new polymorphs of KSi$_2$P$_3$ with T5 supertetrahedral structures related to the sodium ion conductor NaSi$_2$P$_3$.[31] The polymorphs are characterized by X-ray powder diffraction based on the single-crystal data of the high temperature polymorph. Electrochemical impedance and MAS-NMR spectra of the new monoclinic modification revealed a remarkably high $\sigma_{\text{bulk}}$ (K$^+$) up to 2.6 $\times$ 10$^{-4}$ S cm$^{-1}$ at 25°C, and a low activation energy of 0.20 eV. This material hence qualifies as the first non-oxide fast solid potassium ion conductor.

KSi$_2$P$_3$ with the space group $C2/c$ was first described by Feng et al.[37] and is denominated as KSi$_2$P$_3$-$tI960$ in the following. It contains SiP$_4$ tetrahedra which form T3 supertetrahedra according to the Yaghi nomenclature.[38] These T3 entities are fused by one common SiP$_4$ tetrahedron resulting in a layered structure with the K$^+$ ions located on two fully occupied general Wyckoff sites between T3 supertetrahedral layers (see inset of Figure 2). This structure is stable up to 1000°C.

We find a mixture of two phases at 1020°C before KSi$_2$P$_3$-$mC96$ is completely transformed to a tetragonal modification at 1040°C, denoted as KSi$_2$P$_3$-tI960. Figure 2 shows the high temperature diffraction patterns. The additional reflection at about 9.8° indicates crystallization of the silica capillary. We were able to solve and refine the structure of this metastable high temperature polymorph quenched to room temperature with single-crystals. For details we refer to the experimental section in the Supporting Information). Table 1 summarizes the single-crystal data of KSi$_2$P$_3$-tI960 in space group $I4_1/acd$ (No. 142).[39] Atom positions and displacement factors are given in Tables S1 and S2 of the Supporting Information. KSi$_2$P$_3$-tI960 is also built from SiP$_4$ tetrahedra, but now forming three-dimensional networks of T5 supertetrahedra as shown in Figure 3. Every T5 cluster has a missing silicon site in its center, affecting the adjacent four phosphorus atoms by shifting them slightly towards the vacancy. This leads to shorter average P-P distances of 3.2 Å compared to 3.7 Å of the phosphorus atoms not neighboring the missing site. This appears counter-intuitive but has been already observed in several T5 supertetrahedral compounds, such as B$_2$S$_3$[40] Li$_3$Si$_2$P$_3$[41] HT- and LT-NaSi$_2$P$_3$[31] or UCR-15[41]. A possible explanation could be the preservation of charge neutrality in the interior of the T5 entity, since the T5 cluster is a section of the sphalerite-type structure with silicon defects resulting in the sum formula of Si$_2$P$_4$. However, this binary compound has

![Figure 1](image1.png) **Figure 1.** K$^+$-ion conductivities of known materials and of KSi$_2$P$_3$-$mC96$ (sample 2c in Table S9). Asterisks indicate single-crystal data. References and activation energies are in Table S8.

![Figure 2](image2.png) **Figure 2.** High temperature Mo-Kα X-ray powder diffraction pattern of a KSi$_2$P$_3$mC96 sample with a phase transition to KSi$_2$P$_3$-tI960 at about 1020°C (highlighted in green). Inset shows the crystal structure of the known KSi$_2$P$_3$-mC96 compound.

| Formula | KSi$_2$P$_3$-tI960 |
|---------|------------------|
| space group | $I4_1/acd$ (No. 142) |
| $a$ /Å | 21.922(2) |
| $c$ /Å | 39.868(3) |
| $V_{\text{cell}}$ /Å$^3$ | 19160(3) |
| $Z$ | 128 |
| $\rho_{\text{expt}}$ (g cm$^{-3}$) | 2.088 |
| $\lambda$ /Å | 0.71073 (Mo-Kα) |
| $\mu$ mm$^{-1}$ | 1.937 |
| $\theta$-range /° | 2.120-30.586 |
| reflections measured | 49579 |
| independent reflections | 7358 |
| parameters | 283 |
| $R_w$ | 0.0095 |
| $R_{\text{expt}}$ | 0.0452 |
| $R$ ($F^2 > 2\sigma(F^2)$)/all | 0.0391/0.0438 |
| $wR$ ($F^2 > 2\sigma(F^2)$)/all | 0.0919/0.0951 |
| Goof | 1.102 |
| restraints | 1 |
| $\Delta\rho_{\text{max/}}$ /e Å$^{-3}$ | 1.610/−1.374 |
not been confirmed experimentally, but predicted by DFT calculations.\[42,43\] The T5 clusters share one common SiP$_4$ tetrahedron resulting in a three-dimensional anionic network with giant voids interpenetrated by a second crystallographically equivalent network. These can be ascribed hierarchically to a diamond type network, resembling the structure of homeotypic HT-NaSi$_2$P$_3$.[31]

The potassium ions reside in big cavities of the supertetrahedral networks with large displacement factors and an average occupancy of 0.4. All eleven potassium positions are partially occupied and thus disordered (see Figure 4), similar to HT-NaSi$_2$P$_3$, which indicates mobility of potassium ions already at room temperature.

KSi$_2$P$_3$-tI$_{960}$ goes through displacive phase transitions upon cooling. As shown in Figure 5, KSi$_2$P$_3$-tI$_{960}$ exhibits a splitting of the most intense reflections at a diffraction angle range of 13.1 to 13.7° (Mo-K$_{α1}$) at 155°C. Two of these split reflections approach each other while the third moves towards a higher angle of about 14° beginning at 80°C, indicating a third phase transition. These phase transitions occur upon heating and cooling of a KSi$_2$P$_3$ sample making this T5 compound enantiotropic (see Figure 5). We were not able to synthesize suitable single-crystals of the two low temperature modifications mainly due to twinning. Therefore, we stabilized the different modifications for powder diffraction analysis at ambient conditions. While the room temperature modification is easily producible with conventional solid-state methods, small amounts of the other modification could only be obtained by a modified synthesis as described in the Supporting Information. The Cu-K$_{α1}$ diffraction patterns and Rietveld fits of the respective modifications are shown in Figure 6 (enlarged in the SI Figures S1–3) highlighting their most prominent differences consisting in the splitting, the intensity distribution, and the shifting towards higher diffraction angles of the indicated reflections. Acceptable refinements were obtained by translationsgleiche (t2) symmetry reductions from tetragonal KSi$_2$P$_3$-tI$_{960}$ (space group $I_4_1/acd$) to the orthorhombic and monoclinic subgroups of KSi$_2$P$_3$-oF$_{1952}$ ($Fddd$) and KSi$_2$P$_3$-mC$_{928}$ ($C_{2/c}$).

The potassium positions were calculated from the symmetry reduced single-crystal structure data of KSi$_2$P$_3$-tI$_{960}$. Therefore, these positions do not strictly follow the Bärnighausen tree while silicon and phosphorus do. The displacive phase transitions are mainly contractions of the crystal structure as visible in Table 2, thus increasing the crystallo-
graphic density along with the symmetry reduction (note that the cell parameters given in Table 2 appear dissimilar due to different space groups).

We have confirmed the composition and structure model of KSi$_2$P$_3$-mC$_928$ with EDX (Figure S4, Table S7) and MAS-NMR measurements. The $^{29}$Si spectrum (Figure S5) has broad signals between $\delta$(29 Si) = $C_0$ 12 to $C_0$ 26 ppm originating from 32 crystallographically inequivalent silicon atoms on general Wyckoff sites. Since the structure of KSi$_2$P$_3$-mC$_928$ is homeotypic to HT-NaSi$_2$P$_3$, the 31P spectra are comparable as shown in Figure 7. KSi$_2$P$_3$-mC$_928$ exhibits four broad signals within almost the same chemical shift range compared to the tetragonal sodium phase. Integration of these signals in the KSi$_2$P$_3$-mC$_928$ spectrum yields the same intensity distribution of 4:4:3:1 as in HT-NaSi$_2$P$_3$.[31]

The resonance pattern of KSi$_2$P$_3$-mC$_928$ is more complicated than that of HT-NaSi$_2$P$_3$ due to the symmetry reduction from tetragonal to monoclinic, which leads to splitting of all resonances and impeding a simple intensity assignment to the respective phosphorus atoms. Assuming that the upfield signal at $\delta$(31 P) = $C_0$ 298.7 ppm is the result of only one phosphorus atom, a sectional intensity integration of the whole spectrum is possible. It results in 49 distinct atoms being very close to the number of 48 atoms as predicted by X-ray diffraction. Hence, the NMR measurements are in line with the crystal structure.

We have identified possible migration pathways of all polymorphs of KSi$_2$P$_3$ from geometrical calculations yielding four large channels through the structure, which are connected by short passages along every supertetrahedral face. This indicates a 3D ion conduction similar to NaSi$_2$P$_3$. The calculated migration paths are visualized in Figure S6–S8 in the Supporting Information.

We have shown recently that ionic conductivity in supertetrahedral phosphidosilicates increases with increasing cluster size.[31] In view of the T5 structure of KSi$_2$P$_3$, high K-ion mobility seems more likely than in the T3 structure. We applied electrochemical impedance spectroscopy (EIS) and potentiostatic polarization measurements as described in the SI on several samples from different batches to assess the ionic and electronic conductivity. All results are listed in Table S9 and S10, and a representative impedance spectrum at $C_0$ 208 $C_0$ is shown in Figure 8. The measurements were performed at low temperatures to deconvolute the bulk properties of the material and to avoid phase changes that already occur at $\approx 80 \, ^{\circ}C$, which may influence the performance. The spectrum contains high and low frequency contributions followed by a spike resulting from the polarization of K$^+$ ions at the blocking electrodes at low frequencies. The spectrum is fitted with the equivalent circuit model depicted in the inset in Figure 8. For the high frequency semicircle modelled by R1-CPE1, an effective capacitance $C_{\text{eff}} = (Q(R_{\text{a}}/C_0)^{1/2})$ of 8 pf is calculated that corresponds to a relative permittivity of 24. This is a typical value for the bulk contributions of a solid inorganic mate-

Table 2: Rietveld refinement results of the T5 KSi$_2$P$_3$ modifications.

| Modification | KSi$_2$P$_3$-tlf960 | KSi$_2$P$_3$-oF1952 | KSi$_2$P$_3$-mC928 |
|--------------|-------------------|-------------------|-------------------|
| space group  | I4/mcm (No. 142)  | Fddd (No. 70)     | C2/c (No. 15)     |
| $a$ /Å       | 21.8826(3)        | 31.529(1)         | 31.8337(4)        |
| $b$ /Å       | 21.8826(3)        | 30.5475(5)        | 30.4796(3)        |
| $c$ /Å       | 40.2923(8)        | 39.961(1)         | 25.2909(2)        |
| $\beta$ $^\circ$ | 90                | 90                | 90                |
| $V_{\text{cell}}$ /Å$^3$ | 19293.8(6) | 38487(2) | 19150.3(4) |
| $\rho_{\text{ray}}$ /($g$ cm$^{-3}$) | 2.07651(6) | 2.0842(1) | 2.11092(5) |
The partial electronic conductivity was measured by a potentiostatic polarization experiment over several hours at 0.25 and 0.5 V for several samples (cf. Table S10). A representative plot is shown in Figure 8 (right). The electronic conductivity ranges from $0.09 \times 10^{-8}$ to $1.1 \times 10^{-8}$ S cm$^{-1}$, resulting in a transferance number $\tau_e = \sigma_{ion}/(\sigma_{ion} + \sigma_{con})$ of 0.9998. This suggests that this material can be classified as a predominantly ionic conductor.

In summary, we have identified three new polymorphs of KSi$_2$P$_3$ with T$_5$ supertetrahedra and K$^+$-ion conductivities up to $2.6 \times 10^{-4}$ S cm$^{-1}$ at 25°C. The hitherto known modification consists of T$_3$ supertetrahedra without partially occupied K sites, which hampers ion conduction. We demonstrate fast potassium ion conduction through three-dimensional connected voids between large T$_5$ supertetrahedra. KSi$_2$P$_3$ contains low cost, non-redox active and abundant elements. As the first non-oxide solid material, KSi$_2$P$_3$ extents the compositional space of solid potassium ion conductors, which is key for the rational design of further potassium solid electrolytes. Further investigations must show whether these compounds are suitable for use in batteries.

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**Conflict of interest**

The authors declare no conflict of interest.

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