

Na₂Ge₃P₃ and Na₅Ge₇P₅ Comprising Heteroatomic Polyanions Mimicking the Structure of Fibrous Red Phosphorus

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Dedicated to Professor Herbert W. Roesky on the Occasion of his 85th Birthday

Abstract. Recently lithium phosphidogermanates were discovered as fast lithium ion conductors for potential usage as solid electrolytes in all solid-state batteries. In this context we also studied sodium phosphidogermanates since sodium ion conductors are of equal interest. Na₂Ge₃P₃ and Na₅Ge₇P₅ both crystallize in the monoclinic space group *C2/m* with unit cell parameters of $a = 17.639(4)$ Å, $b = 3.6176(7)$ Å, $c = 11.354(2)$ Å, $\beta = 92.74(3)^\circ$ and $a = 16.168(5)$ Å, $b = 3.6776(7)$ Å, $c = 12.924(4)$ Å, $\beta = 91.30(3)^\circ$, respectively. Both show linearly condensed 9-atom cages of four Ge / five P and five Ge / four

P atoms, respectively. These cages contain Ge–Ge bonds and form one-dimensional tubes by sharing three atoms. The parallel tubes are paired through further Ge–Ge bonds. Both structures are closely related to the one of the fibrous type of crystalline red phosphorus. A comparison with other compounds such as NaGe₃P₃ and GeP reveals recurring structural motifs with a broad variety of connection patterns. According to the general formula Na_{4+x}Ge_{6+x}P_{6-x} with $x = 0$ and 1, the two novel structures hint for the possibility of a variable Na content which might allow Na ion mobility.

Introduction

An increasing interest in further evolved battery systems for various applications promotes the research on new materials. For stationary devices, the lower gravimetric power and energy density plays a minor role, and thus Na-based systems show a great potential. This is supported by the high abundance and affordability of Na, if compared to Li.^[1,2] Recently, a new class of materials, sodium phosphidosilicates, has been shown to exhibit good mobilities for Na ions up to 0.4 mS·cm⁻¹.^[3] The compounds Na₁₉Si₁₃P₂₅, Na₂₃Si₁₉P₃₃, Na₂₃Si₂₈P₄₅, Na₂₃Si₃₇P₅₇, *LT*-NaSi₂P₃, and *HT*-NaSi₂P₃ consist of supertetrahedra of SiP₄ units, which form three-dimensional channels for ion migration.^[3] Fast ion conduction has also been reported for the related Li phosphidosilicates, which could even be further increased by substitution of Si by Ge.^[4,5] The highest value for phosphide-based materials of 3 mS·cm⁻¹ was recently reported for Li₉AlP₄.^[6]

In the system Na/*Tt*/P a broader variety of connection patterns has been reported for the heavier homologues of Si (*Tt* = Ge, Sn) enabling the formation of *Tt*–*Tt* bonds and for-

mally negatively charged *Tt* atoms as found in NaGe₃P₃.^[7–10] These structures can provide alternative physical properties caused by the different bonding situation. Moreover, when comparing structural motifs of binary *A/Tt* (*A* = Li, Na; *Tt* = Si, Ge) compounds, a significantly larger tendency for the formation of low-dimensional building blocks is observed for the Na/Ge system. This is illustrated by the cluster-containing compounds Na₄Ge₄ and Na₁₂Ge₁₇,^[11,12] which are not reported for Li-containing systems. Such units result in a denser framework with short Na–Na distances, which are usually seen as beneficial for ion hopping. Following these ideas, the new compounds Na₂Ge₃P₃ and Na₅Ge₇P₅ have been prepared and characterized.

Experimental Section

All syntheses were carried out in an argon atmosphere in glove boxes (MBraun, 200B) with moisture and oxygen levels below 1 ppm or in containers, which were sealed in an argon atmosphere.

Syntheses: All compounds were synthesized in tantalum ampoules from the elements: Na (ChemPur, 99%), Ge (EVOCHEM GmbH, 99.999%) and red P (Sigma–Aldrich, 97%). The ampoules with a length of 30 mm and 10 mm in diameter were closed within the glove box via arc welding. The closed Ta ampoules were sealed in evacuated silica glass vessels and heated in muffle furnaces, and heating and cooling rates of 4 K·min⁻¹ and 1 K·min⁻¹ were applied, respectively.

Single crystals of Na₂Ge₃P₃ with a nominal composition of “Na₂Ge₂P₃” were prepared from 161.9 mg (7.04 mmol) Na, 512.3 mg (7.04 mmol) Ge and 327.4 mg (10.56 mmol) P. The sample was heated to 700 °C for 72 h and cooled to room temperature. Single crystals of Na₅Ge₇P₅ were obtained from a sample with the nominal composition “Na₂Ge₅P₂” by reacting 29.3 mg (1.27 mmol) Na, 231.3 mg

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(3.18 mmol) Ge and 39.5 mg (1.27 mmol) P, which were heated to 700 °C for 120 h.

Bulk materials of $\text{Na}_2\text{Ge}_3\text{P}_3$ and $\text{Na}_5\text{Ge}_7\text{P}_5$ were synthesized from the elements with a reduced amount of Ge, “ $\text{Na}_2\text{Ge}_2\text{P}_3$ ” (compare single crystal preparation) and “ NaGeP ” [36.3 mg (1.58 mmol) Na, 114.7 mg (1.58 mmol) Ge and 48.9 mg (1.58 mmol) P, 24 h, 700 °C], respectively. The powder diffraction patterns are shown in the Supporting Information (Figure S1). $\text{Na}_2\text{Ge}_3\text{P}_3$ contains small amounts of Ge, while $\text{Na}_5\text{Ge}_7\text{P}_5$ was accompanied by a small amount of a yet unknown phase. The content of Ge was reduced in the synthesis, since in most of the samples elemental Ge was found in the product despite of the high temperature applied for the synthesis. Also longer reaction times did not lower the portion of Ge.

Powder X-ray Diffraction: Data were collected at room temperature on a STOE STADI P diffractometer equipped with a position-sensitive detector (Mythen 1 K) using $\text{Cu-K}\alpha_1$ ($\lambda = 1.54060 \text{ \AA}$) or $\text{Mo-K}\alpha_1$ ($\lambda = 0.70926 \text{ \AA}$) radiation and a curved Ge (111) monochromator in Debye–Scherrer geometry. The samples for the measurement were sealed in glass capillaries ($\varnothing 0.3 \text{ mm}$) in an argon-filled glove box. The STOE WinXPOW^[13] software was used for phase analysis.

Single Crystal X-ray Data Collection: Single crystals were sealed in glass capillaries ($\varnothing 0.3 \text{ mm}$). For diffraction data collection, the capillary was mounted on a STOE StadiVari diffractometer equipped with a DECTRIS PILATUS 300 K detector and a Xenocs Genix 3D Microfocus X-ray source ($\text{Mo-K}\alpha$) at room temperature. On the basis of systematic extinctions, both structures were solved in the space group $C2/m$ by Direct Methods (SHELXS-2014) and refined by full-matrix least-squares calculations against F^2 (SHELXL-2014).^[14a] Data reduction and multi-scan absorption correction were carried out with the X-Area (version 1.88, Stoe) and the STOE LANA (version 1.77.1, Stoe) software packages.^[14b] The thin needle-shaped crystal of $\text{Na}_5\text{Ge}_7\text{P}_5$ shows only weak diffraction scattering owing to a poor crystal quality, which leads to higher reliability factors. Crystallographic data and structure refinement results are summarized in Table 1, atomic coordinates with anisotropic displacement parameters and selected interatomic distances with angles – in Tables S1–S5 (Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CSD-2005288 ($\text{Na}_5\text{Ge}_7\text{P}_5$) and CSD-2005289 ($\text{Na}_2\text{Ge}_3\text{P}_3$) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Differential Scanning Calorimetry (DSC): For the investigation of the thermal behavior of the compounds a Netzsch DSC 404 Pegasus device was used. Niobium crucibles were filled with 50 to 100 mg of the samples and sealed by arc-welding. Empty sealed crucibles served as a reference. Measurements were performed in an argon flow of 75 mL min^{-1} and a heating/cooling rate of $10 \text{ K}\cdot\text{min}^{-1}$ up to a temperature of 750 °C. Data collection and handling was carried out with the Proteus Thermal Analysis program.^[15]

Supporting Information (see footnote on the first page of this article): Figure of powder X-ray diffractograms of $\text{Na}_2\text{Ge}_3\text{P}_3$ and $\text{Na}_5\text{Ge}_7\text{P}_5$ compounds; Figure of DSC curves of $\text{Na}_2\text{Ge}_3\text{P}_3$ and $\text{Na}_5\text{Ge}_7\text{P}_5$; Tables with atomic coordinates and anisotropic displacement parameters of $\text{Na}_2\text{Ge}_3\text{P}_3$ and $\text{Na}_5\text{Ge}_7\text{P}_5$; Table with selected interatomic distances and angles for $\text{Na}_2\text{Ge}_3\text{P}_3$.

Results and Discussion

Synthesis

The compounds $\text{Na}_2\text{Ge}_3\text{P}_3$ and $\text{Na}_5\text{Ge}_7\text{P}_5$ were synthesized from the elements with various compositions close to the exact composition at 700 °C. The highest purity was obtained from samples with nominal compositions of “ $\text{Na}_2\text{Ge}_2\text{P}_3$ ” and “ NaGeP ”. Thermal analysis also showed reversible effects at 520 °C for $\text{Na}_2\text{Ge}_3\text{P}_3$ and 572 °C for $\text{Na}_5\text{Ge}_7\text{P}_5$ (Figure S2, Supporting Information). In $\text{Na}_2\text{Ge}_3\text{P}_3$ this effect was contributed to a decomposition or melting, whereas in $\text{Na}_5\text{Ge}_7\text{P}_5$ a solid-to-solid phase transition to an unknown phase was observed in PXRD measurements after fast cooling. In both cases single crystals of the corresponding compound are formed during cooling. Thus, for the preparation of large single crystals a slow cooling rate is beneficial, which is confirmed by the circumstance that all crystals are found in samples cooled with a rate of $1 \text{ K}\cdot\text{min}^{-1}$.

Crystal Structure of $\text{Na}_2\text{Ge}_3\text{P}_3$

$\text{Na}_2\text{Ge}_3\text{P}_3$ crystallizes as black needles in the monoclinic space group $C2/m$ with unit cell parameters of $a = 17.639(4) \text{ \AA}$, $b = 3.6176(7) \text{ \AA}$, $c = 11.354(2) \text{ \AA}$ and $\beta = 92.74(3)^\circ$ (Figure 1, left). The crystal structure consists of eight crystallographically independent positions, two Na, three Ge and three P sites. The Ge and P atoms build covalently bound $\frac{1}{2}[\text{Ge}_3\text{P}_3]^{2-}$ subunits separated by Na^+ . The polyanion

Table 1. Refinement data of the single-crystal X-ray diffraction analysis of $\text{Na}_2\text{Ge}_3\text{P}_3$ and $\text{Na}_5\text{Ge}_7\text{P}_5$ at 293 K.

	$\text{Na}_2\text{Ge}_3\text{P}_3$	$\text{Na}_{4.86(4)}\text{Ge}_{6.86(4)}\text{P}_{5.14(4)}$
Formula weight / $\text{g}\cdot\text{mol}^{-1}$	356.72	773.35
Space group	$C2/m$ (no. 12)	$C2/m$ (no. 12)
Crystal size / mm^3	$2.0 \times 0.10 \times 0.10$	$1.5 \times 0.03 \times 0.03$
Crystal color, shape	black, needle	black, needle
Cell parameters		
$a / \text{ \AA}$	17.639(4)	16.168(5)
$b / \text{ \AA}$	3.6176(7)	3.6776(7)
$c / \text{ \AA}$	11.354(2)	12.924(4)
$\beta / ^\circ$	92.74(3)	91.30(3)
Cell volume / \AA^3	723.7(2)	768.2(2)
Z	4	2
$\rho_{\text{calcd.}} / \text{g}\cdot\text{cm}^{-3}$	3.274	3.343
Abs. coeff. / mm^{-1}	13.046	13.934
$F(000)$ (e)	652	704
Temperature / K	293(2)	293(2)
Reflections collected	4260 ($R_\sigma = 0.0242$)	6185 ($R_\sigma = 0.0731$)
Unique reflections	747 ($R_{\text{int}} = 0.0536$)	931 ($R_{\text{int}} = 0.1176$)
Data / parameters / restraints	747/49/0	931/55/1
Reflections with $I > 2\sigma(I)$	671	683
Range in hkl	$\pm 20, \pm 4, \pm 13$	-20 to $17, \pm 4, \pm 16$
θ range / $^\circ$	$3.00 / 24.99$	$2.94 / 26.50$
GOF on F_o^2	1.166	1.093
R_1, wR_2 [$I > 2\sigma(I)$]	0.0362, 0.0903	0.0885, 0.2157
R_1, wR_2 (all data)	0.0428, 0.0796	0.1222, 0.2358
Largest diff. peak / hole / $\text{e}\cdot\text{ \AA}^{-3}$	1.266 / -1.116	2.713 / -2.883

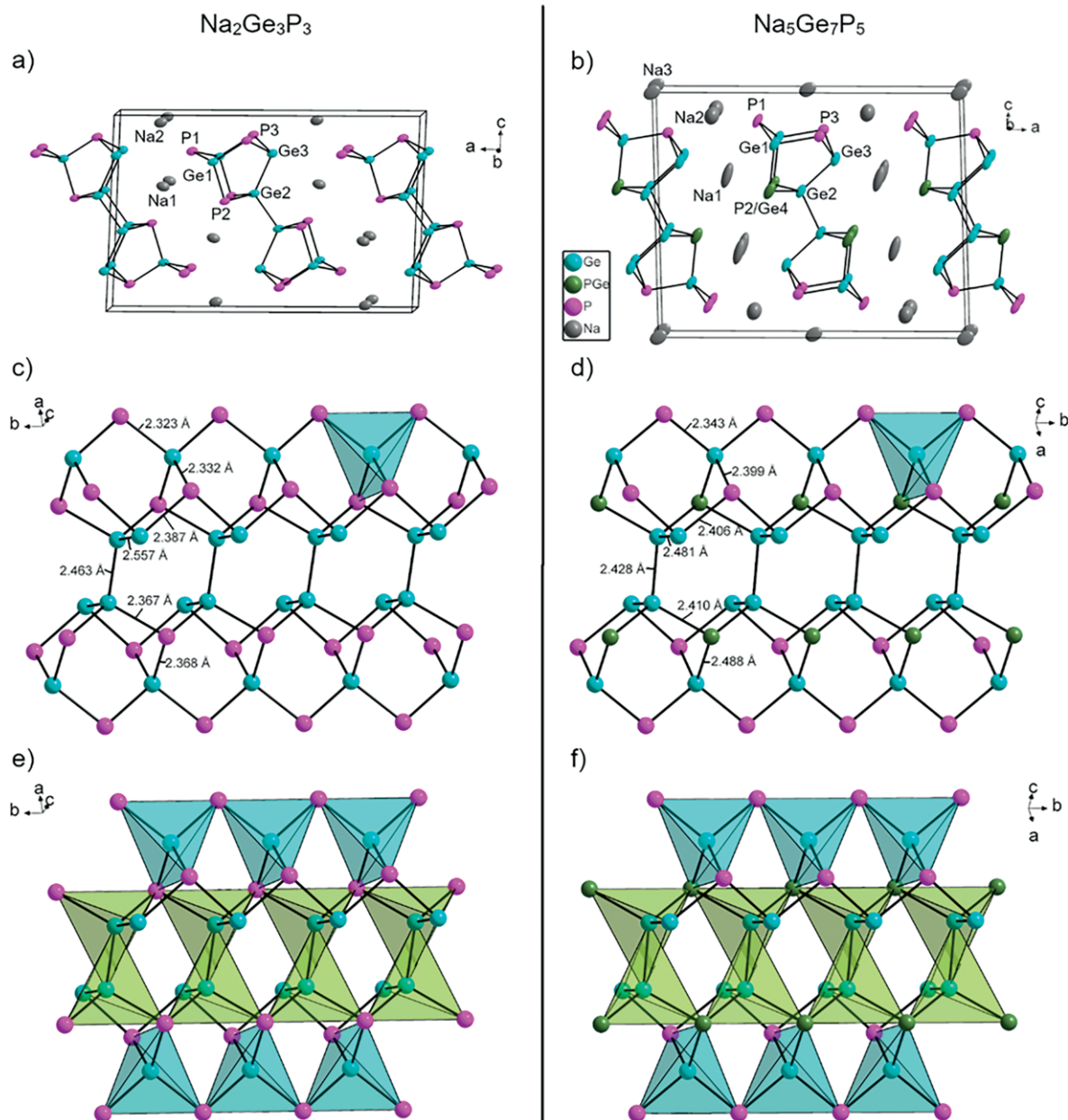


Figure 1. Structural motifs in $\text{Na}_2\text{Ge}_3\text{P}_3$ (left) and $\text{Na}_5\text{Ge}_7\text{P}_5$ (right). (a) and (b) Unit cells with atom labeling. (c) and (d) Enlarged anionic building blocks with bond lengths. A $\text{GeP}_4/\text{GeP}_3\text{Ge}$ tetrahedron is highlighted in light blue. (e) and (f) Connectivity of the tetrahedral building blocks. Tetrahedra around Ge1 are highlighted in light blue, tetrahedra around Ge2 are highlighted in green. Within one tube one Ge1 and two Ge2 tetrahedra share a P2/(Ge4) vertex and are connected via two Ge3–P3 bonds each. The Ge2 tetrahedra of connected tubes are interpenetrating each other.

consists of uniform nine-atom cages $[\text{Ge}_4\text{P}_5]$ composed of two five- and two six-membered rings (Figure 1). The five-membered rings are fused via a common Ge–Ge bond. The cages are connected to a linear tube with a pentagonal cross section by sharing three atoms on two opposing sides (Ge1, P2, P3). The tubes are connected via bonds between Ge atoms (Ge2) that are part of the Ge–Ge bond of the cage, resulting in a Ge_4 unit.

Due to the presence of several fourfold connected atoms, the tubes can also be described as a chain of condensed GeP_4 and $\text{Ge}(\text{P}_2\text{Ge}_2)$ tetrahedra. The GeP_4 tetrahedra are formed by

Ge1 surrounded by two P1, one P2 and one P3 atom and are connected via P1 into chains. The $\text{Ge}(\text{P}_2\text{Ge}_2)$ tetrahedra (Ge2 surrounded by two P2, Ge2, Ge3) are connected to the GeP_4 unit by shared P3 atoms. The bond angles at all atoms are in the range of $99.68(9)$ to $113.30(7)^\circ$ and thus deviate from the ideal tetrahedral angle of 109.47° . Ge1 coordinates to four P atoms, whereas Ge2 shows three Ge–P and one Ge–Ge bond. Ge3 is threefold connected forming two bonds to P3 and one to Ge2. Three Ge atoms coordinate each P2 and P3, while P1 is only bound to two Ge atoms. Ge–P bond lengths in the slightly distorted GeP_4 tetrahedra are in the narrow range be-

tween 2.323(2) and 2.368(3) Å and are in good agreement with Ge–P bonds found in GeP, NaGe₃P₃ and α -/ β -Li₈GeP₄.^[15] The Ge2–Ge3 bond within the cage is significantly longer [2.557(1) Å] than in elemental Ge (2.450 Å)^[16] or than the intertube Ge2–Ge2 bond [2.463(1) Å], and shorter than the Ge–Ge bonds found in NaGe₃P₃ (2.626 Å) that contains similar structural motifs.^[18]

Regarding the connectivity of the atoms of two 4b-Ge, one 3b-Ge, two 3b-P and one 2b-P atoms (3b = three-bonded, 2b = two-bonded atom), negative charges according to the 8-N rule are formally placed at the 3b-Ge (Ge3) and 2b-P (P1) atoms. These charges are counterbalanced by two Na⁺, which is placed in distorted octahedral voids (P₅Ge) between the paired tubes.

Crystal Structure of Na₅Ge₇P₅

Na₅Ge₇P₅ crystallizes as black needles in the monoclinic space group *C2/m* with unit cell parameters of $a = 16.168(5)$ Å, $b = 3.6776(7)$ Å, $c = 12.924(4)$ Å and $\beta = 91.30(3)^\circ$ (Figure 1, right). The similarity to Na₂Ge₃P₃, which is already indicated by the unit cell dimensions and the space group, is confirmed by the presence of covalently bound, paired tubes with identical atom connectivity. However, differences are found in the number of atom positions. For Na₅Ge₇P₅ one additional partially occupied Na site occurs, and the P2 site is mixed occupied with Ge4, leading to a total of nine independent sites: three Na, three Ge, two P, and one Ge/P site. The occupation of Ge4 and P2 on the mixed position is 0.43(2) and 0.57(2), respectively. Partial defects were tested for all Na positions, which led to lower occupation factors of 0.89(5) for the Na2 site, suggesting a correlation between the Na content and the mixed Ge/P position, resulting in the refined composition Na_{4.76(10)}Ge_{6.88(6)}P_{5.12(6)}, which is very close to the charge balanced composition Na_{4+x}Ge_{6+x}P_{6-x}. Therefore, in the final refinement these correlated occupancies have been restrained. The final composition Na_{4.86(4)}Ge_{6.86(4)}P_{5.14(4)} differs only slightly from the ideal formula, and thus in the following discussion we will for the sake of simplicity refer to the compound as Na₅Ge₇P₅. The ratio Ge:P = 1:1 on this position leads to the polyanion with the formula $\frac{1}{2}[\text{Ge}_3\text{P}_3]^{2-}$. In case the mixed position is occupied only with P, the building blocks are identical to the one of the cages in Na₂Ge₃P₃ described above. GeP₄ and Ge(P₂Ge₂) tetrahedra have bond length and angles in the range as discussed above [2.3429(4) to 2.4885(8) Å and 103.41(2) to 113.662(13)°, respectively]. The Ge2–Ge3 bond within the cage of 2.4807(8) Å is only slightly longer than the *exo*-cage bond connecting the tubes [2.4288(7) Å].

Substitution of the three-bonded P atom [(3b-P)⁰] in the polyanion $\frac{1}{2}[\text{Ge}_3\text{P}_3]^{2-}$ in Na₂Ge₃P₃ by Ge requires an extra negative charge to conserve the valency of the atoms [(3b-Ge)⁻]. In Na₅Ge₇P₅ 50% of a three-bonded P atom position is replaced by Ge, thus by doubling the formula unit in Na₂Ge₃P₃ the polyanion $2 \times \frac{1}{2}[\text{Ge}_3\text{P}_3]^{2-} = \frac{1}{2}[\text{Ge}_6\text{P}_6]^{4-}$ is replaced by $\frac{1}{2}[\text{Ge}_7\text{P}_5]^{5-}$. Therefore, one extra Na atom per two formula units is required for charge compensation, resulting in Na₅

Ge₇P₅. The added Na₃ is located in a distorted octahedral void of six P atoms at the origin of the unit cell. The cavity arises by a rotation of the anionic units if compared to Na₂Ge₃P₃. The angle between Ge2–Ge2 and the *c* axis is reduced from 37.56(3)° in Na₂Ge₃P₃ to 23.91(6)° in Na₅Ge₇P₅. This orientational change of the polyanion results in a shorter *a*, but longer *c* axis and additionally affects the coordination of the other Na sites. While Na1 is octahedrally coordinated by P_{4-x}Ge_{2+x} (0 ≤ *x* ≤ 3), Na2 is surrounded by a rectangular pyramid of five P atoms.

Discussion

The polyanions consist of two inter-connected parallel tubes with a pentagonal cross section and show an intriguing structural similarity to the strands of fibrous red phosphorus.^[17] In the latter, the tubes are built from P₈ and P₉ cages connected via P₂ dumbbells and are interconnected through a two-connected P atom of the P₉ cage. The polyanions exclusively comprise nine-atom cages Ge₄P₅ and Ge₅P₄ for Na₂Ge₃P₃ and Na₅Ge₇P₅ (dark grey atoms in Figure 2b), respectively, that are fused to linear strands by sharing three atoms [Ge1, P2/(Ge4), P3] with neighboring cages. In fibrous red phosphorus the strands are interconnected via the two-connected P atom of the P₉ cage, whereas the strands in the ternary phases bind through the Ge atom of the Ge–Ge unit, leading to four-connected Ge atoms (Figure 2b). This difference is of course induced by the presence of Ge atoms, allowing for four-connected atoms. However, since the bridging P2 atoms of the E₉ cage (E = P, Ge) remains two-bonded, a formal negative charge is attributed to P2.

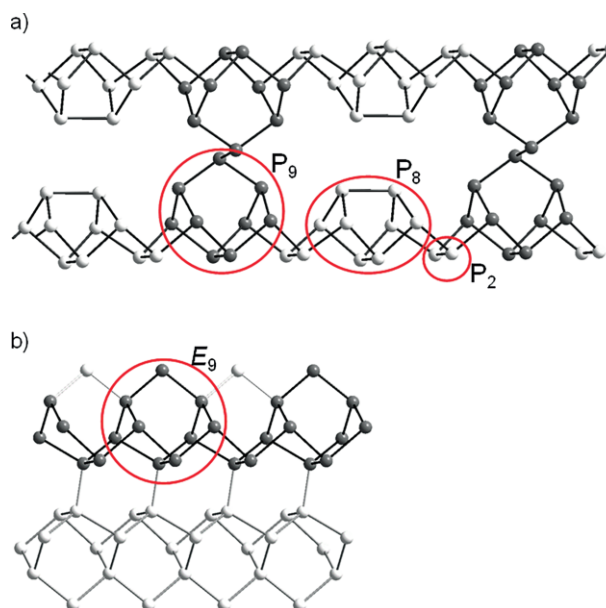


Figure 2. (a) In fibrous red phosphorus two strands consisting of P₉, P₈ and P₂ units are connected through the bridging P atom. (b) Arrangement of the analogous E₉ cages in Na₂Ge₃P₃ highlighted as dark grey atoms. The E₉ cages are connected through Ge atoms of the Ge₂ unit (cp. Figure 1c).

Comparison with other Ge- and P-containing species with different amounts of Na reveals an interesting trend. Keeping

the Ge:P ratio in $\text{Na}_2\text{Ge}_3\text{P}_3$ constant and reducing the Na content leads to NaGe_3P_3 .^[18] This compound consists of slabs formed by tubes identical to the ones found in $\text{Na}_2\text{Ge}_3\text{P}_3$. Contrary to the situation in the latter, these slabs are not connected through the Ge_2 units with formation of Ge_4 , but the Ge dumbbells of the five-membered ring are attached through one Ge atom to the two-connected P atom of the E9 cage, allowing the formation of a two-dimensional slab.

The complete removal of Na leads to the binary compound GeP ,^[18] in which Ge_2 dumbbells are connected by three-connected P atoms into two-dimensional slabs of four- and three-connected Ge and P atoms, respectively.

Conclusions

A comparison with other compounds from that phase system reveal a modular construction pattern. By different connectivities the building blocks can be combined to one-dimensional units, or more or less condensed two-dimensional structures in GeP ^[18] and NaGe_3P_3 .^[8] The two new phases $\text{Na}_2\text{Ge}_3\text{P}_3$ and $\text{Na}_5\text{Ge}_7\text{P}_5$ illustrate the flexibility of the structures in the Na/Ge/P phase system by retaining basic structural polyanionic units. Both compounds represent the first examples with a new connection mode for a known building block, leading to pairs of parallel, one-dimensional Ge–P tubes. Additionally, the connection via Ge–Ge bonds leads to the formation of Ge_n chains in $\text{Na}_5\text{Ge}_7\text{P}_5$. The compounds also give a descriptive example for pnictide-tetrel substitution. The two compounds can be regarded as examples of the general formula $\text{Na}_{4+x}\text{Ge}_{6+x}\text{P}_{6-x}$ with $x = 0$ and 1 arising in $\text{Na}_4\text{Ge}_6\text{P}_6$ (= $\text{Na}_2\text{Ge}_3\text{P}_3$) and $\text{Na}_5\text{Ge}_7\text{P}_5$, respectively. Substitution of P by Ge and addition of a corresponding amount of Na forces the rotation of the polyanions to provide space for the additional cations. This results in an increasing c and a decreasing a parameter, but the symmetry of the structure remains unchanged. The structures thus allows for a variable Na content, which might influence Na ion mobility. Therefore, the synthesis of phase-pure materials and subsequent determination of their electric properties are highly desirable.

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