

On the Crystal Structure and Conductivity of Na₃P

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Dedicated to Professor Sven Lidin on the Occasion of His 60th Birthday

Abstract. As a potential material for Na-ion battery systems and on the basis of a structural discussion of compounds formerly believed to crystallize in the so-called Na₃As type the structure of Na₃P has been reinvestigated. Na₃P is found to crystallize in the Cu₃P type, analogous to Na₃As and is described by a three times larger unit cell [*P*6₃*cm*, *a* = 8.61224(10) Å and *c* = 8.81949(10) Å] compared to the former

model [*P*6₃/*mmc*, *a* = 4.9512(5) Å and *c* = 8.7874(13) Å]. As a structural manifestation of this symmetry reduction corrugated layers of Na and P atoms are observed which had formerly to be described as planar. The high purity of the material further enables the determination of its properties, showing mainly semiconducting behavior with a conductivity of 12 S·cm⁻¹ at room temperature.

Introduction

The ambition for renewable energy sources and the accompanied demand for affordable electrochemical energy storage systems encourages the research on available sodium-based batteries.^[1] For these systems novel compounds are needed, including new synthesis approaches as well as the re-evaluation of known materials. In this context, ternary sodium phosphides like NaSi₂P₃ have been shown to exhibit Na ion conductivities of up to 0.4 mS·cm⁻¹.^[2] Even the binary lithium phosphide Li₃P was reported to exhibit high ionic conductivities up to 0.1 mS·cm⁻¹.^[3] Li₃P and Na₃P chemically represent the lithiated or sodiated state, respectively, in high capacity phosphorus anodes^[4] and hence are interesting for battery applications. In addition, Na₃P has shown to be a decomposition product in solid-state batteries at the sodium metal anode^[5] and is often used as simple starting material in syntheses of ternary phosphides.

During our investigations we found significant discrepancies in the powder X-ray diffraction patterns, subsequently confirmed by X-ray single crystal diffraction measurements, with

respect to the previous structure reports.^[6,7] The structure is described to adopt the formerly so called Na₃As type with planar sheets of hexagons of alternating Na and P atoms stacked alternately with corrugated sheets formed exclusively by Na atoms (grey As-like). A hexagonal unit cell with lattice parameters of *a* = 4.9512(5) Å and *c* = 8.7874(13) Å and space group *P*6₃/*mmc* is proposed. At this time additional unassigned reflections have already been reported, that could not be removed by increased experimental accuracy.^[6] This led to a discussion about the certainty of the assumed structures of various *A*₃*B* compounds including the Na₃As type.^[8,9] However, *Dong and DiSalvo* confirmed the structural model of Na₃P containing large prolate ellipsoids for certain Na positions.^[7]

To match the experimentally observed additional reflections in the X-ray powder pattern of Cu₃P, a three times larger supercell with *anti*-LaF₃ structure (space group: *P*3̄*c*1) was suggested^[8] and this was applied to various compounds with *A*₃*B* composition, such as Na₃As and Na₃P (*a* = 8.626 Å, *c* = 8.797 Å). According to this structure type 2/3 of the Cu atoms are displaced from the formerly planar Cu–P sheet, while 1/3 of the Cu atoms remain coplanar to the P atoms. Later *Hafner and Range*^[9] revisited Na₃As on the basis of single crystal data and suggested the space group *P*6₃*cm* leading to a displacement of all Na atoms from the Na–As sheet, resulting in less prolate ellipsoids. They also recommended this space group and structure for related alkaline-pnictide systems; however no additional experimental evidence was provided. In this work, we use a combination of powder and single-crystal X-ray diffraction techniques to solve the crystal structure type of Na₃P and investigate the electronic transport properties.

Results and Discussion

Upon synthesizing Na₃P, additional reflections are found in the X-ray powder diffraction pattern, which do not correspond to the structural model established by *Brauer and Zintl* [*P*6₃/

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mmc, $a = 4.9512(5)$ Å and $c = 8.7874(13)$ Å].^[6] Similar to their previous observations the relative intensities of these reflections did not alter with the synthesis conditions such as reaction temperature and time or an added excess of Na or P. Different from the early results the indexing of these additional reflections succeeded, leading to a three times larger unit cell [$a = 8.61224(10)$ Å and $c = 8.81949(10)$ Å; Figure 1], similar to results as proposed formerly.^[8,9] These findings were confirmed by X-ray single crystal measurements, in which the super structure reflections were clearly detected. Moreover, a structure refinement from single crystal data using the small unit cell and deliberately ignoring the super structure reflections lead to large U_{33} parameters for Na in the planar Na–P sheet, which can also be seen in structure refinements of Na_3P prior to this work.^[7] Attempts to identify a possible phase transition via differential scanning calorimetry in the temperature range of -150 °C to 750 °C measurements showed a weak reversible, endothermic signal during heating at ca. 665 °C. However, the high temperature phase could not be isolated or characterized and may originate from a transformation into a higher symmetric space group.

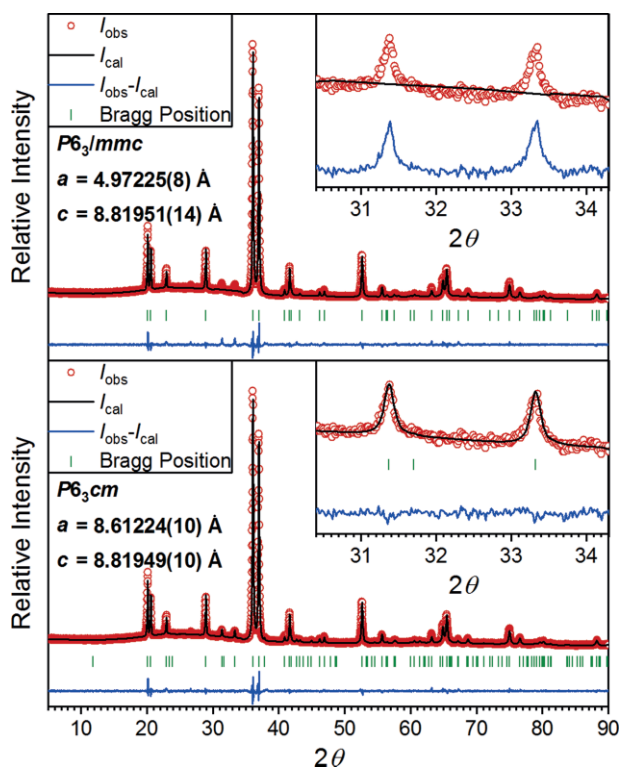


Figure 1. Rietveld refinement of Na_3P . Top: cell parameters $a = 4.97225(8)$ Å, $c = 8.81951(14)$ Å ($P6_3/mmc$, $R_{wp} = 3.81\%$, $R_{exp} = 3.70\%$, $R_{Bragg} = 2.66\%$, $GOF = 1.92$) and bottom: cell parameters $a = 8.61224(10)$ Å, $c = 8.81949(10)$ Å ($P6_3cm$, $R_{wp} = 3.23\%$, $R_{exp} = 3.69\%$, $R_{Bragg} = 1.79\%$, $GOF = 1.39$). I_{obs} and I_{cal} represent the observed and calculated intensity, respectively. The most intense reflections determining the unit cell are depicted as inset. A reflection with rather low intensity at ca. 27° was assigned to an unknown impurity by comparison with other samples.

As a reflection condition $h\bar{h}0l$: $l = 2n$ is observed in our single crystal data, in the hexagonal crystal system a set of

space groups consisting of $P6_3/mcm$, $P\bar{6}c2$ and $P6_3cm$ is obtained. Additionally, the trigonal space groups $P\bar{3}c1$, as found for the (*anti*-) LaF_3 type, and $P3c1$ were considered and finally the results were compared to a refinement in $P1$ to eliminate any possible restrictions from symmetry. In all investigated space groups, the structure solution resulted roughly in the same structure model, which is identical with the atomic arrangement proposed by Brauer and Zintl: more or less planar, hexagonal boron nitride-like sheets of P and Na atoms separated by corrugated layers of Na atoms, as shown in Figure 2a–e.

The shortest interatomic contacts are found between the phosphorus atom and five sodium atoms which form a trigonal bipyramid, so alternatively the crystal structure can be described as built from $(\text{PNa}_2\text{Na}_{3/3})$ polyhedra which are connected via common corners to form layers (Figure 2f). Taking into account the slightly extended second coordination sphere around the P atom, all six faces of each bipyramid are capped by further Na atoms forming the apices of neighboring bipyramids, so each P atom is surrounded by eleven Na atoms (Figure 2g). Although the structure model is roughly the same after the refinements in all space groups, the residual factors differ considerably owing to several features of the crystal structure. Most strikingly, the quality factors of the refinements correlate with the planarity of the P/Na layers. While in $P6_3/mcm$ and in $P\bar{6}c2$, similar to the Brauer/Zintl model in $P6_3/mmc$, the P and Na atoms within these layers are restrained by symmetry to the same value for the z parameter and the residuals are outrageously high, in $P6_3cm$ and $P3c1$ the relevant atoms may be displaced from exact planarity resulting in considerably lower R-values (see Table 1 and Supporting Information, Table S2). In $P\bar{3}c1$ with two third of the relevant Na atoms having a free z parameter intermediate R values are obtained. The obvious inadequacies of the correct structure description are compensated by particularly large U_{33} parameters for the concerning Na atoms in $P6_3/mcm$ and in $P\bar{6}c2$ which are considerably larger than those with free z parameters in $P6_3cm$ and $P3c1$. As another feature the main axis of the trigonal PNa_5 bipyramid is slightly tilted with respect to the c axis which is not possible to constitute in $P6_3/mcm$ and in $P\bar{6}c2$ nor in $P6_3/mmc$ of the Brauer/Zintl model. Again, this deficiency is indicated by ellipsoids of Na atoms as those of atoms within the corrugated layers are elongated and strangely skewed ($P6_3/mcm$, $P\bar{6}c2$) or strongly flattened ($P6_3/mmc$) with respect to the c axis. After these considerations for the correct space group of Na_3P the higher symmetric groups ($P6_3/mcm$, $P\bar{6}c2$, $P\bar{3}c1$) can be closed out while applying lower symmetries no significant differences appear between $P6_3cm$, $P3c1$ and $P1$, and space group $P6_3cm$ is the clearly preferred choice (Table 2). Additionally, after refinements in all acentric space groups the Flack parameter was close to zero, therefore centrosymmetric groups should be less probable.

By describing the crystal structure in $P6_3cm$, Na_3P is indeed isostructural to Na_3As ^[9] and Cu_3P .^[10] With the symmetry degradation from the previously reported model ($P6_3/mmc$) to the new one ($P6_3cm$), including a larger number of occupied crystallographic sites (see Figure 3), several degrees of freedom are allowed. This is particularly expressed by the slightly,

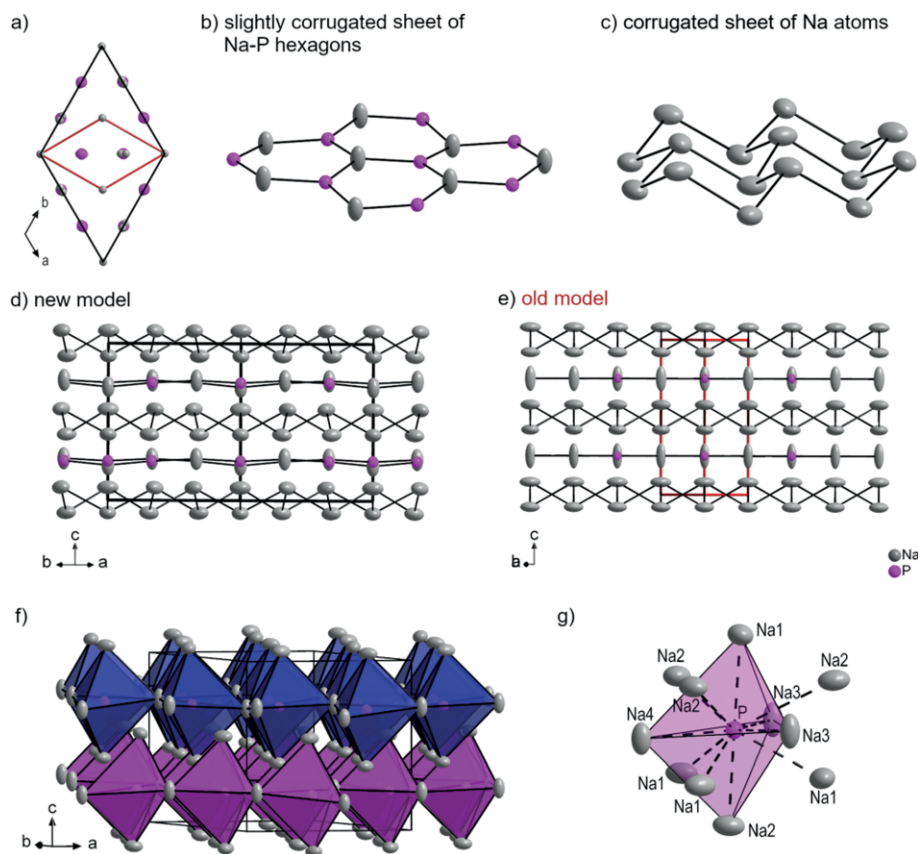


Figure 2. Illustration of the crystal structure of Na_3P . (a) Relative unit cell edges a and b of the new ($P6_3cm$, black) and previously reported structure model ($P6_3/mmc$, red) with view along the $[001]$ direction. (b) and (c) Illustration of the different layers occurring in the structure (new model). (d) and (e) Comparison of the projection of the extended unit cell along the $[110]$ direction of the new model with the reported model. Some Na–P bonds are drawn to indicate the corrugated NaP sheets. (f) Polyhedral representation of Na_3P emphasizing two layers of corner-connected trigonal PNa_5 bipyramids. (g) Coordination polyhedron of phosphorus, a distorted six times capped trigonal bipyramid.

Table 1. Comparison of the structure refinement results of single crystal data in different space groups, illustrated by selected significant structure parameters. The previously reported and the new structural model are highlighted in bold and suspicious parameters are colored in red.

	$P6_3/mmc$	$P6_3cm$	$P\bar{3}c1$	$P3c1$	$P1$
$wR_2(\text{all})$	0.0667	0.0653	0.0880	0.0640	0.0793
$z(\text{P})$	$\frac{1}{4}$	0.2500(6)	$\frac{1}{4}$	0.2500(5)	0.2500(1)
$z(\text{Na}_{\text{eq}1})$	$\frac{1}{4}$	0.2225(7)	$\frac{1}{4}$	0.2375(6)	0.2231(3)
$z(\text{Na}_{\text{eq}2})$		0.2646(8)	0.2271(2)	0.2373(6)	0.2653(4)
$z(\text{Na}_{\text{eq}3})$				0.2794(6)	0.2653(4)
$U_{33}(\text{Na}_{\text{eq}1})$	0.096(2)	0.053(3)	0.094(2)	0.064(2)	0.053(2)
$U_{33}(\text{Na}_{\text{eq}2})$		0.063(2)	0.0509(9)	0.063(2)	0.060(2)
$U_{33}(\text{Na}_{\text{eq}3})$				0.052(2)	0.062(2)
$U_{11}(\text{Na}_{\text{cap}1})$	0.0625(9)	0.0399(7)	0.0441(6)	0.0369(8)	0.0386(11)
$U_{22}(\text{Na}_{\text{cap}1})$	0.0625(9)	0.0399(7)	0.0550(7)	0.0481(10)	0.0376(12)
$U_{33}(\text{Na}_{\text{cap}1})$	0.0239(8)	0.0235(12)	0.0239(5)	0.0236(9)	0.0242(10)

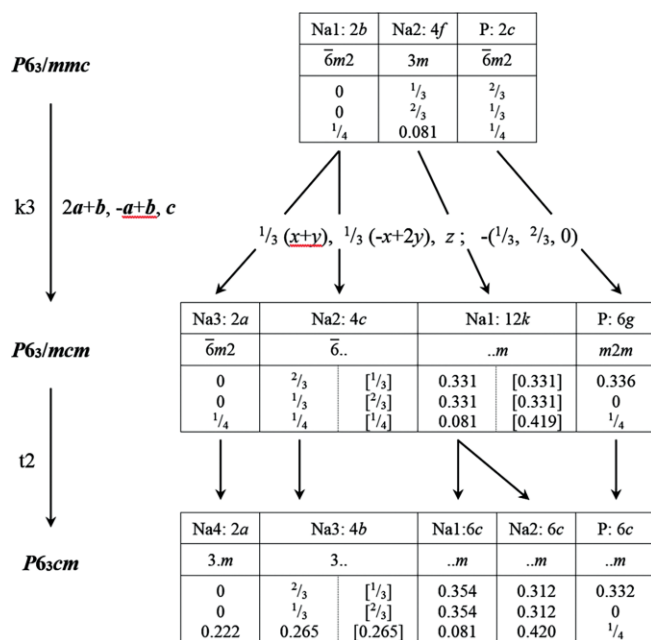
but unambiguously corrugated P–Na sheets which were restrained to be planar in the former model, and the deviation of the Na atoms from perfect planarity in z direction is 0.129(1) Å and 0.2423(1) Å for Na3 and Na4, respectively (Figure 2).

Nevertheless, each P atom is in plane with the surrounding almost regular triangle of Na atoms forming the equatorial plane of the trigonal PNa_5 bipyramid with an Na–P–Na angle sum of 360.00(8)°. The closest interatomic distances are nearly not affected by the changes in symmetry, and the P–Na distances within the PNa_5 bipyramid [2.8701(13)–2.928(7) Å] are

almost identical with the latest values presented by *Dong and DiSalvo* [2.874–2.920 Å].^[7] This polyhedron is just slightly distorted, indicated by the linear main Na1–P–Na2 axis [179.58(9)°] and the equatorial PNa_3 plane mentioned above, the axis direction deviates from the plane normal by 8.48°. The polyhedron is slightly tilted with respect to the unit cell, e.g. the angle between the main axis of the polyhedron and the crystallographic c axis is 3.53°, that between the equatorial plane and the ab plane is 4.94°. The P–Na distances within the second coordination sphere are not changed in average but are

Table 2. Data collection and refinement parameters of a single crystal structure determination of Na₃P.

Chemical formula	Na ₃ P
Crystal system	hexagonal
Space group	<i>P6₃cm</i> (no.185)
<i>M_r</i>	99.94
Temperature /K	293
<i>a</i> /Å	8.6216(2)
<i>c</i> /Å	8.8285(2)
<i>V</i> /Å ³	568.32(2)
<i>Z</i>	6
Radiation type	Mo- <i>K_α</i>
<i>μ</i> /mm ⁻¹	0.80
Crystal size /mm	0.17 × 0.16 × 0.12
Diffractometer	
Absorption correction	
No. of measured reflections	31731
No. of independent reflections	619
No. of observed reflections	582
<i>R_{int}</i>	0.046
No. of reflections	619
No. of parameters	25
No. of restraints	1
<i>R</i> (<i>F</i> ²)[<i>I</i> > 2σ(<i>I</i>); <i>R_w</i> (<i>F</i> ²)[<i>I</i> > 2σ(<i>I</i>)]	0.020; 0.063
<i>R</i> (<i>F</i> ²)(all); <i>R_w</i> (<i>F</i> ²)(all)	0.022; 0.065
Goodness of Fit	1.147
Absolute structure parameter	0.1(3)
Δρ _{max} , Δρ _{min} /e Å ⁻³	0.162; -0.269

**Figure 3.** Symmetry degradation according to *Bärnighausen*.^[11]

more irregular [3.094(4)–3.418(3) Å, comp. to 6×3.239 Å in *P6₃mmc*].

As a consequence, the Na1 and Na2 atoms which are surrounded by distorted tetrahedra of P atoms, are situated closer to a tetrahedron face (Na2) and a tetrahedron edge (Na1) in *P6₃cm*, respectively. While the Na–P distances are only slightly affected the repulsive interactions between cations might have a higher importance for the symmetry reduction

because 75% of all atoms are cations. The average Na–Na distances are significantly larger in *P6₃cm* (see Table 4), e.g. the closest Na–Na distances, which are found between two apices of bipyramids belonging neighboring layers, are increased by the symmetry change [3.0136(12) Å in *P6₃cm* vs. 2.988 Å in *P6₃mmc*].

Other important structural indications for an incorrect symmetry in this compound are several large anisotropic displacement parameters of Na atoms, i.e. particularly the *U*₃₃ of the equatorial and those parallel to *ab* of the apex Na atoms (Table 3). As another expression of this the standard deviations of the *z* coordinates of the equatorial Na3 and Na4 are increased. These vibration directions may be expected due to their orthogonality to the strongest Na–P interactions, obviously these atoms are effectively fixed, e.g. Na3 and Na4 by three P neighbors within the *ab* plane while interactions in *c* direction are considerably weaker. This is observed after all the structure refinements in different symmetries; however, in the new structure model in *P6₃cm* they are significantly smaller than in the Brauer/Zintl model.

Conductivity Measurements

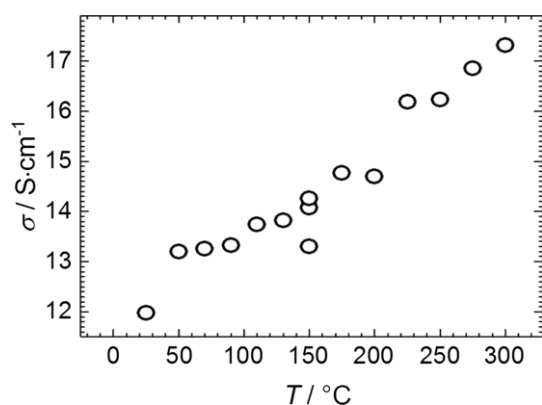
Since the material is interesting for application in sodium-ion batteries and has been shown as a decomposition product at the anode in all-solid-state batteries,^[5] we investigated its electrical conductivity. Therefore, impedance spectra were recorded in a temperature range of 25 °C to 300 °C. A total conductivity of $\sigma = 12$ S·cm⁻¹ at room temperature was found to be mainly electronic of nature and we were not able to resolve the partial ionic conductivity. A slight increase of the conductivity with temperature up to 300 °C (Figure 4) to 17 S·cm⁻¹ is observed.

Conclusions

A close inspection of powder and especially single-crystal X-ray diffraction data of Na₃P revealed several superstructure reflections which lead to a three times larger unit cell (*a* = 8.61224(10) Å and *c* = 8.81949(10) Å) compared to the formerly reported one [*a* = 4.9512(5) Å, *c* = 8.7874(13) Å]. Na₃P crystallizes in space group *P6₃cm* and differs slightly from the previously reported model by additional degrees of freedom for some refinement parameters which allow an increased shortest distance between neighboring cations and lead to decreased anisotropic displacement parameters. The higher reliability of the new structure model as compared to the hitherto accepted model of *Brauer and Zintl*^[6] was shown by comparison of some relevant structure parameters resulting from refinements in different space groups. With the presented structure model and symmetry, Na₃P is isotypic to Na₃As (which underwent a similar transformation of its generally accepted crystal structure^[9]) as well as to Cu₃P,^[10] and support the assumption of *Hafner and Range* that more trialkaline pnictides adopt this structure type.^[12] These authors also provided the hypothesis of ternary compounds crystallizing with the small unit cell and the higher symmetric space group *P6₃/mmc*. This

Table 3. Wyckoff positions, atom coordinates, isotropic and anisotropic displacement parameters of Na₃P after the structure refinement in *P6₃cm*.

	Wyckoff position	x	y	z	U_{iso}	
P	6c	0.33171(13)	0	0.2500(6)	0.0164(2)	
Na1	6c	0.3539(2)	0.3539(2)	0.0810(2)	0.0384(6)	
Na2	6c	0.3121(2)	0.3121(2)	0.4199(2)	0.0375(6)	
Na3	4b	2/3	1/3	0.2646(8)	0.0344(7)	
Na4	2a	0	0	0.2225(7)	0.0315(9)	
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0.0160(3)	0.0162(4)	0.0170(3)	0	0.00058(14)	0.0081(2)
Na1	0.0399(7)	0.0399(7)	0.0235(12)	-0.0023(9)	-0.0023(9)	0.0110(6)
Na2	0.0489(9)	0.0489(9)	0.0224(12)	-0.0022(10)	-0.0022(10)	0.0304(8)
Na3	0.0204(4)	0.0204(4)	0.063(2)	0	0	0.0102(2)
Na4	0.0205(5)	0.0205(5)	0.053(3)	0	0	0.0103(3)

**Figure 4.** Total electrical conductivity in the temperature range from 25 °C to 300 °C derived from impedance spectroscopy measurements.

might explain the earlier findings of *Dong and DiSalvo*^[7] whose Na₃P crystals were isolated from a reacted mixture of NaN₃, TiN, P and KI and, thus, could contain impurities stabilizing the higher symmetry. The conductivity of Na₃P was found to be mainly semiconducting of nature, with a total room-temperature electrical conductivity of $\sigma = 12 \text{ S}\cdot\text{cm}^{-1}$. These electric properties differ from those reported for Li₃P. A possible explanation for these distinctions are better overlapping *p* orbitals in Na₃P leading to a smaller bandgap. However, to clarify the reason for these differences more investigations of the structure and conductivity of the interesting class of alkaline pnictides are desirable.

Experimental Section

Synthesis: Na₃P was synthesized as black crystalline powder from stoichiometric mixtures of Na (960 mg, 99%, Chempur) and P (310 mg, 97%, Sigma–Aldrich) in Ta ampoules. The sample was heated to 700 °C for 1 h, cooled to 500 °C, annealed for 24 h, reground and reheated to 400 °C for 36 h. Temperature rates were 4 K·min⁻¹ for heating and 1 K·min⁻¹ for cooling. Samples were synthesized and prepared under an inert argon atmosphere inside a glovebox.

Differential Scanning Calorimetry: Phase transitions were investigated using two different DSC devices. Low temperature DSC measurements were conducted with a Netzsch DSC 200 F3 Maia in the temperature range from -150 °C to 300 °C. The samples (ca. 10 mg) were filled in aluminum crucibles and closed via cold welding. For

DSC measurements from 200 °C to 750 °C a Netzsch DSC 404 Pegasus was used, for which the samples (ca. 50 mg) were filled into a niobium crucible and sealed by arc welding.

Single Crystal X-ray Diffraction: A black crystal was isolated and sealed in a fused silica capillary (diameter 0.3 mm). Data were collected on a single-crystal X-ray diffractometer equipped with a FR591 rotating anode with Mo-*K*_α radiation ($\lambda = 0.71073 \text{ \AA}$), a Montel optic, a APEX II, κ -CCD detector and the APEX 2 software package.^[13] The structure was solved via direct methods with ShelXS97.^[14] For structure refinement the program package SHELX-2014 was used.^[15] De-

Table 4. Selected interatomic distances (Å) for Na₃P after structure refinements in space groups *P6₃cm* and *P6₃/mmc*.

	<i>P6₃cm</i>	<i>P6₃/mmc</i>
P–Na4	2.870(1)	2.874(1) (3×)
P–Na3	2.884(1)	
P–Na3 ⁱ	2.884(1)	
P–Na2 ⁱⁱ	2.920(6)	2.920(1) (2×)
P–Na1 ⁱⁱⁱ	2.928(6)	
P–Na1	3.315(3)	3.239(1) (6×)
P–Na1 ^{iv}	3.094(3)	
P–Na1 ^v	3.315(3)	
P–Na2	3.158(3)	
P–Na2 ^{iv}	3.418(3)	
P–Na2 ^v	3.158(3)	
Na1–Na2	3.014(1)	2.988(3)
Na1–Na2 ⁱⁱ	3.219(2)	3.208(1) (3×)
Na1–Na2 ^{vi}	3.219(2)	
Na1–Na2 ^{vii}	3.212(2)	
Na1–Na4	3.297(3)	3.239(1) (3×)
Na1–Na3	3.227(4)	
Na1–Na3 ^{viii}	3.227(4)	
Na3–Na1	3.227(4)	3.239(1) (6×)
Na3–Na1 ^{iv}	3.227(4)	
Na3–Na1 ^{ix}	3.227(4)	
Na3–Na2	3.271(4)	
Na3–Na2 ^{iv}	3.271(4)	
Na3–Na2 ^{ix}	3.271(4)	
Na4–Na1	3.297(3)	3.239(1) (6×)
Na4–Na1 ^v	3.297(3)	
Na4–Na1 ^x	3.297(3)	
Na4–Na	3.206(4)	
Na4–Na ^v	3.206(4)	
Na4–Na ^x	3.206(4)	

Symmetry operations for *P6₃cm*: (i): $y, x-1, z$; (ii): $y, y-x, z-0.5$; (iii): $y, y-x, z+0.5$; (iv): $-y+1, x-y, z$; (v): $y-x, -x, z$; (vi): $x-y, x, z-0.5$; (vii): $-x+1, -y+1, z-0.5$; (viii): y, x, z ; (ix): $y-x+1, -x+1, z$; (x): $-y, x-y, z$.

tails on crystal data, data collection and structure refinement are summarized in Table 1. Selected interatomic distances are given in Table 4. All atom positions are fully occupied. During the refinements in $P6_3cm$ and $P3c1$ the z parameter of the P atom has been restrained to $1/4$, and in $P1$ additionally the x and y parameters to 0, to ensure optimal comparability between the structure parameters in the different space groups. In the final refinement cycles they were released to obtain e.s.d.'s.

X-ray Powder Diffraction: The sample was sealed in a fused silica capillary (diameter 0.3 mm). Data collection was performed in Debye–Scherrer geometry on a STOE Stadi P diffractometer [Ge(111)] monochromator, Cu- $K_{\alpha 1}$ radiation, $\lambda = 1.54056 \text{ \AA}$ with a Dectris MYTHEN 1 K detector. Raw data were processed with the WinXPOW software package^[16] and for Rietveld refinements the FullProf software package^[17] was used.

Crystallographic data (excluding structure factors) for the structure 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 number CSD-2006662 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Conductivity Measurements: Prior to impedance spectroscopy measurements the sample was densified within a hot press setup^[18] at 150 °C and 2 tons (\varnothing 12 mm). Within the setup electronic impedance spectroscopy was performed at different temperatures between 25 °C and 300 °C using a frequency response analyzer (BioLogic SP-150) with a frequency range of 1 MHz to 10 Hz and an amplitude of 20 mV. The pellet height was extrapolated at room temperature after hot pressing. Impedance measurements at higher temperature yielded decreased ionic conductivities, most likely caused by a reaction between Na_3P and the electrode material.

Supporting Information (see footnote on the first page of this article): Details of the single crystal structure determination and of the Rietveld refinement, symmetry degradation via alternative paths, results of the structure refinements in different space groups and of the DSC measurements.

Note added in proof: The space group $P6_3cm$ for Na_3P has been reported also on the basis of PXRD data.^[19]

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Keywords: Sodium phosphide; Crystal structure; Phosphorus; Conductivity; Impedance spectroscopy

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