High-Temperature High-Pressure Synthesis of the Highly Condensed Nitridophosphates NaP_4N_7, KP_4N_7, RbP_4N_7, and CsP_4N_7 and Their Crystal-Structure Determinations by X-ray Powder Diffraction

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Dedicated to Professor Wolf-Peter Fehlhammer on the occasion of his 60th birthday

Abstract: The nitridophosphates NaP_4N_7, KP_4N_7, RbP_4N_7, and CsP_4N_7 were synthesized by the reaction of the respective alkali metal azides with P_3N_5 in a belt apparatus at 40 kbar and 1800 – 2000 °C. The products were obtained as colorless crystalline powders. As compared to all other nitridophosphates obtained so far the temperature of synthesis could be raised by 1000 °C. Thus a convenient crystallization of the novel highly condensed nitridophosphates was achieved. The crystal structures were solved by direct methods on the basis of X-ray powder diffraction data and refined by the Rietveld method (NaP_4N_7: $C2/c$, $Z = 4$, $a = 1233.45(4)$, $b = 852.30(3)$, $c = 513.97(1)$ pm, $\beta = 102.572(2)°$; KP_4N_7: $Pnma$, $Z = 4$, $a = 1223.87(2)$, $b = 984.85(2)$, $c = 466.51(1)$ pm; RbP_4N_7: $a = 1231.07(2)$, $b = 989.46(1)$, $c = 468.44(1)$ pm; CsP_4N_7: $a = 1242.05(6)$, $b = 997.82(5)$, $c = 471.62(3)$ pm). NaP_4N_7 is isotypic with the oxides $M(M')_4O_7$ (M = Ca, Sr; M' = Al, Ga). The crystal structure of KP_4N_7, RbP_4N_7, and CsP_4N_7 is the aristotype of the mineral barylite, $BaBe_2Si_2O_7$.

Keywords: alkali metals · high-pressure chemistry · nitridophosphates · phosphorus · solid-state structures

Introduction

Phosphorus – nitrogen compounds have been discussed in the literature for more than 150 years.[1] However a detailed structural investigation of alkaline and alkaline earth nitridophosphates(v)[2, 3] and transition metal nitridophosphate sodalites[2, 4] was achieved only in the last few years. The binary nitride P_3N_5 represents the parent compound of the nitridophosphate class of compounds, and its crystal structure has only recently been determined after long-lasting efforts.[5]

With respect to their structures the nitridophosphates exhibit analogies to the nitridosilicates.[2, 6] However both classes of compounds significantly differ concerning their chemistry and stability. Nearly all nitridosilicates have been synthesized under high-temperature conditions and they are stable up to 1600 °C. Usually they are obtained as coarsely crystalline materials. In contrast, the thermal stability of P_3N_5 and the nitridophosphates seems to be limited to a maximum temperature of around 900 °C.[2, 5] For these reasons predominantly lower condensed PN compounds (molar ratio P:N ≤ 1:2) have been investigated, which usually are accessible at 600 – 800 °C.[2] However the synthesis of highly condensed PN compounds (molar ratio P:N > 1:2) is specifically challenging because improved materials properties are anticipated for these compounds.[2]

The synthesis of highly condensed single-phase nitridophosphates is rather difficult and the crucial point seems to be the formation of amorphous and polymeric phosphorus – nitrogen network structures during the condensation reactions. Because of the high kinetic stability of the P – N bonds the crystallization of these networks is prevented. Raising the temperature above 900 °C does not activate the desired reconstructive transformation to a long-range ordered and crystalline structure, but it causes an irreversible thermal dissociation under evolution of N_2.

The synthesis and investigation of highly condensed phosphorus nitrides has so far only been achieved for some rare examples. In order to avoid the described preparative problems, ammonothermal high-pressure conditions (e.g. $K_3P_6N_{11}$[3]) or the pyrolysis of suitable precursor compounds (e.g. P_3N_5[5] and HP_4N_7[7]) were applied. However, both concepts do not allow a broad synthetic approach to highly condensed nitridophosphates.

Thermally labile oxides have been synthesized in the past by oxygen high-pressure techniques using autoclaves.[8] The application of this procedure to the synthesis of nitrides seems to be technically difficult, because the evolution of N_2 by

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dissociation of the nitrides is not reversible below 900 °C for kinetic reasons. Recently Weller et al. obtained the nitrides Ca_2AuN and $Li_{3-x}Cu_xN$ under a pressure of 200 bar using autoclaves.[9] However the functional range of currently available autoclave systems seems to be limited to a maximum temperature of around 1100 °C.

Using a high-pressure belt apparatus we have now succeeded in synthesizing the novel highly condensed nitridophosphates NaP_4N_7, KP_4N_7, RbP_4N_7, and CsP_4N_7 at 40 kbar by a straightforward synthetic procedure which easily seems to be applicable to other nitrido compounds. Under these high-pressure conditions the temperature of synthesis for the nitridophosphate was raised up to 2000 °C.

Experimental Section

P_3N_5: Phosphorus(v) nitride (P_3N_5) was synthesized[10] from hexachlorocy-clotriphosphazene (($PNCl_2)_3$, p. a., Fluka) by reaction with dried gaseous ammonia (99.8 %, Linde) in a quartz flow-through tube placed in a furnace. In the first reaction step (($PNCl_2)_3$) was heated to 100 °C for 10 h under flowing ammonia, then cooled down to room temperature and powderized. The procedure then was repeated at 115, 175, and 265 °C. The crude product then was heated to 600 °C under evacuation (10^2 Pa) and finally it was heated to 950 °C for 2 h under flowing ammonia.

MN_3, (M = K, Rb, Cs): An anion exchange resin (30 g, Ionenaustauscher III(OH⁻), Merck) was loaded with N_3^- ions using the column technique and an 0.1N aqueous solution of NaN_3 (extra pure, Merck). The respective metal chloride (2 g, p. a., Merck) was dissolved in H_2O (150 mL) and the solution was transferred onto the ion-exchange resin. After the solution had passed through the column, the solvent was evaporated in vacuum and pure MN_3 (checked by X-ray powder diffraction) was obtained.

MP_4N_7 (M = Na, K, Rb, Cs): A mixture of the respective azide MN_3 and P_3N_5 was mixed thoroughly in the molar ratio M:P = 0.25 under argon in a glove box and placed in a hexagonal BN (hBN) capsule. The sealed capsule was subjected to the conditions of 40 kbar and 1800 to 2000 °C using a belt apparatus.[11] After the desired high-temperature and high-pressure conditions had been maintained for 15 min, the sample was quenched to room

Abstract in German: *Die Nitridophosphate(v) NaP_4N_7, KP_4N_7, RbP_4N_7 und CsP_4N_7 wurden durch Umsetzung der jeweiligen Metallazide mit P_3N_5 in einer Belt-Apparatur bei 40 kbar und 1800 - 2000 °C als feinkristalline, farblose Pulver erhalten. Im Vergleich zu allen bislang bekannten Nitridophosphaten konnte die Synthesetemperatur um etwa 1000 °C erhöht werden, was zu sehr günstigen Kristallisationsbedingungen der sonst nur schwierig zu erhaltenen hochkondensierten Nitridophosphate(v) führt. Die Kristallstrukturen wurden mittels Direkter Methoden auf der Grundlage von Pulver-Röntgenbeugungsdaten aufgeklärt und nach dem Rietveld-Verfahren verfeinert (NaP_4N_7: C2/c, Z = 4, a = 1233.45(4), b = 852.30(3), c = 513.97(1) pm, β = 102.572(2)°; KP_4N_7: Pnma, Z = 4, a = 1223.87(2), b = 984.85(2), c = 466.51(1) pm; RbP_4N_7: a = 1231.07(2), b = 989.46(1), c = 468.44(1) pm; CsP_4N_7: a = 1242.05(6), b = 997.82(5), c = 471.62(3) pm). NaP_4N_7 ist isotyp mit den Oxiden M(M')$_4O_7$ (M = Ca, Sr; M' = Al, Ga). Die Kristallstrukturen von KP_4N_7, RbP_4N_7 und CsP_4N_7 können als Aristotyp des Minerals Barylith, $BaBe_2Si_2O_7$, beschrieben werden.*

temperature before the applied pressure was released. This process led to the formation of MP_4N_7 as a crystalline air-stable white powder [Eq. (1)].

$$4 P_3N_5 + 3 MN_3 \xrightarrow[\text{belt apparatus, 40 kbar}]{1800-2000 °C, 15 min} 3 MP_4N_7 + 4 N_2 \qquad (1)$$

X-ray diffraction investigations: The X-ray diffraction measurements of NaP_4N_7, KP_4N_7, and RbP_4N_7 were carried out with a conventional transmission powder diffractometer in Debye–Scherrer geometry with $Cu_{K\alpha1}$ radiation. Because of the higher absorption coefficient of cesium, CsP_4N_7 was investigated with $Mo_{K\alpha}$ radiation. From the diffraction patterns (Figure 1 and 2) it was obvious that KP_4N_7, RbP_4N_7, and CsP_4N_7 are isotypic, while NaP_4N_7 has a different structure. Indexing of the diffraction
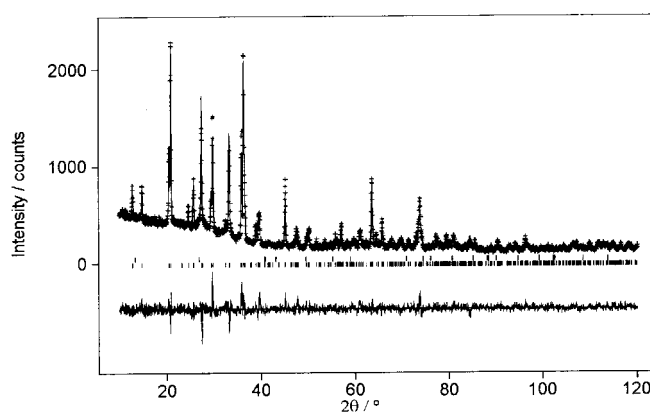

Figure 1. Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as difference profile of the Rietveld refinement of NaP_4N_7. The lower row of vertical lines indicates possible peak positions of NaP_4N_7 (upper row: BN). The powder pattern was obtained with a STOE Stadi P powder diffractometer ($Cu_{K\alpha1}$, $\lambda = 154.05$ pm).
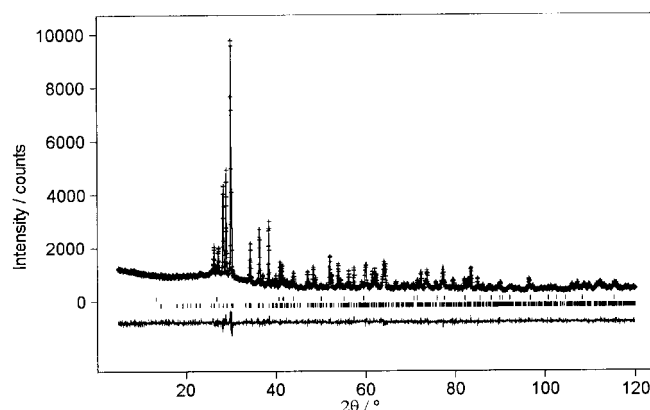

Figure 2. Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as difference profile of the Rietveld refinement of RbP_4N_7. The lower row of vertical lines indicates possible peak positions of RbP_4N_7 (upper row: BN). The powder pattern was obtained with a STOE Stadi P powder diffractometer ($Cu_{K\alpha1}$, $\lambda = 154.05$ pm).

patterns was achieved with the program ITO.[12] From the systematic absences the space groups Cc or C2/c for NaP_4N_7 and $Pn2_1a$ or Pnma for the three other compounds were considered. The integrated intensities of NaP_4N_7 and RbP_4N_7 were extracted by using the program EXTRA.[13] These intensities were used for an ab initio crystal structure determination with the program SIRPOW.92.[14] By assuming the respective centrosymmetric space groups the positions of all atoms were determined by direct methods. The Rietveld refinement of the crystal structures of the four title compounds was performed with the program GSAS.[15] For the crystal structure refinement of KP_4N_7 and CsP_4N_7 the atomic coordinates of RbP_4N_7 were used as starting values. Analysis of the diffraction patterns of KP_4N_7 and CsP_4N_7 revealed an amount of approximately 5 % wt of cubic

Table 1. Crystallographic data for MP$_4$N$_7$ (M = Na, K, Rb, Cs).

formula	NaP$_4$N$_7$	KP$_4$N$_7$	RbP$_4$N$_7$	CsP$_4$N$_7$
M_r [g mol^{-1}]	244.88	261.04	307.42	354.79
crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$C2/c$ (no. 15)	$Pnma$ (no. 62)	$Pnma$ (no. 62)	$Pnma$ (no. 62)
diffractometer	Stoe STADI P	Stoe STADI P	Stoe STADI P	Siemens D5000
λ [pm]	154.050	154.050	154.050	70.926
T [°C]	25(2)	25(2)	25(2)	25(2)
a [pm]	1233.45(4)	1223.87(2)	1231.07(2)	1242.05(6)
b [pm]	852.30(3)	984.85(2)	989.46(1)	997.82(5)
c [pm]	513.97(1)	466.51(1)	468.44(1)	471.62(3)
β [°]	102.572(2)			
cell volume [10^6 pm^3]	527.37(3)	562.31(2)	570.60(1)	584.50(2)
Z	4	4	4	4
profile range	$10° \leq 2\theta \leq 120°$	$5° \leq 2\theta \leq 120°$	$5° \leq 2\theta \leq 120°$	$4° \leq 2\theta \leq 70°$
no. data points	11000	11500	11500	3300
observed reflections	389	443	452	1340
positional parameters	17	19	19	19
profile parameters	7	7	7	7
background parameters	5	3	3	4
R_p	0.0772	0.0508	0.0350	0.0910
wR_p	0.1077	0.0667	0.0462	0.1197
R_F	0.0718	0.0749	0.0589	0.0867

K$_3$P$_6$N$_{11}$[3] and the hitherto unknown isotypic compound Cs$_3$P$_6$N$_{11}$, respectively, as by-products. The lattice constant of Cs$_3$P$_6$N$_{11}$ was refined to a value of a = 1064.70(7) pm. Very small amounts of hexagonal boron nitride resulting from the hBN capsules were detected in the diffraction patterns of NaP$_4$N$_7$ and RbP$_4$N$_7$.

During the crystal structure refinement of NaP$_4$N$_7$ the distance P1−N4 had to be restrained with a starting value of 170 pm corresponding to the distance P−N[3] found in HP$_4$N$_7$.[7] For all refinements the thermal displacement factors of N were constrained to be equal. Detailed crystallographic data are summarized in Table 1, the refined parameters are listed in Table 2 and 3. Table 4 and 5 give selected interatomic distances and angles.[16]

Table 2. Atomic coordinates and isotropic displacement factors [pm^2] of NaP$_4$N$_7$.

Atom	Wyckoff position	x	y	z	U_{iso}[a]
Na	4e	0	0.2112(7)	$\frac{1}{4}$	435(23)
P1	8f	0.3301(2)	0.4261(4)	0.1972(6)	83(10)
P2	8f	0.3759(2)	0.0781(4)	0.2048(6)	59(9)
N1	4e	0	0.5218(2)	$\frac{1}{4}$	64(13)
N2	8f	0.1351(5)	0.0503(8)	0.073(2)	64(13)
N3	8f	0.3600(5)	0.247(1)	0.329(2)	64(13)
N4	8f	0.1852(4)	0.4485(8)	0.116(2)	64(13)

[a] U_{iso} is defined as $\exp(-8\pi^2 U_{iso}\sin^2\theta/\lambda)$, the displacement factors of N were constrained to be equal.

Table 3. Atomic coordinates and isotropic displacement factors [pm^2] of KP$_4$N$_7$, RbP$_4$N$_7$, and CsP$_4$N$_7$ (first, second, and third line, respectively).

Atom	Wyckoff position	x	y	z	U_{iso}[a]
M	4c	0.3507(3)	$\frac{1}{4}$	0.7590(8)	156(7)
		0.3598(2)	$\frac{1}{4}$	0.7707(4)	88(3)
		0.3562(3)	$\frac{1}{4}$	0.7735(10)	110(9)
P1	8d	0.0890(3)	0.1315(2)	0.2877(6)	122(6)
		0.0887(2)	0.1300(2)	0.2858(5)	56(5)
		0.0897(10)	0.1286(5)	0.2870(27)	63(23)
P2	8d	0.3467(3)	0.0010(2)	0.2755(6)	120(6)
		0.3442(2)	0.0005(2)	0.2769(6)	110(5)
		0.3449(10)	−0.0008(7)	0.2819(26)	56(22)
N1	4c	0.1300(8)	$\frac{1}{4}$	0.2322(26)	162(10)
		0.1289(2)	$\frac{1}{4}$	0.2111(2)	70(8)
		0.1208(37)	$\frac{1}{4}$	0.213(9)	100(40)
N2	8d	0.1122(7)	0.1081(4)	0.6268(11)	162(10)
		0.1120(5)	0.1096(5)	0.6203(2)	70(8)
		0.1102(27)	0.1098(17)	0.617(4)	100(40)
N3	8d	0.4382(6)	0.1057(4)	0.3218(14)	162(10)
		0.4361(5)	0.1048(5)	0.3124(2)	70(8)
		0.4393(24)	0.0976(17)	0.311(6)	100(40)
N4	8d	0.2000(6)	0.0489(4)	0.1228(13)	162(10)
		0.2021(5)	0.0465(5)	0.1223(9)	70(8)
		0.2062(24)	0.0488(22)	0.105(5)	100(40)

[a] U_{iso} is defined as $\exp(-8\pi^2 U_{iso}\sin^2\theta/\lambda)$, the displacement factors of N were constrained to be equal.

Results and Discussion

NaP$_4$N$_7$, KP$_4$N$_7$, RbP$_4$N$_7$, and CsP$_4$N$_7$ are the first highly condensed nitridophosphates that have been synthesized under high-temperature high-pressure conditions. Since all nitridophosphates obtained so far have been prepared below 1000 °C these results demonstrate the high synthetic potential that might be achieved through an extraordinary increase of the reaction temperature by more than 1000 °C. This thermal activation seems to be crucial for a convenient crystallization of the highly condensed products. Simultaneously the high-pressure conditions in the belt apparatus suppress the formation of gaseous products and they support crystallization by favoring close-packed crystalline phases versus less

dense amorphous ones. Moreover the azides act as the nitriding agent and by their thermal dissociation a high N$_2$ partial pressure is maintained above the reaction partners. Presumably this nitrogen atmosphere shows oxidizing properties under these high-temperature conditions and therefore phosphorus in the oxidation state +v is stabilized. Accordingly the formation of elemental phosphorus or alkali metal phosphides, which normally occurs by thermal dissociation of nitridophosphates,[2] has not been observed in these high-temperature high-pressure reactions.

In the solid state NaP$_4$N$_7$, KP$_4$N$_7$, RbP$_4$N$_7$, and CsP$_4$N$_7$ contain three-dimensional P−N network structures with channels containing the alkali metal ions. NaP$_4$N$_7$ is isotypic

Table 4. Interatomic distances [pm] and angles [°] in NaP_4N_7.

P1–N2[2]	157.4(6)	N2[2]-P1-N2[2]	120.0(3)
P1–N2[2]	155.3(7)	N2[2]-P1-N3[2]	107.9(3)
P1–N3[2]	167.8(8)	N2[2]-P1-N4[3]	101.7(4)
P1–N4[3]	175.6(4)	N2[2]-P1-N3[2]	113.7(3)
		N2[2]-P1-N4[3]	103.8(4)
		N3[2]-P1-N4[3]	108.5(3)
P2–N1[2]	157.3(4)	N1[2]-P2-N3[2]	114.5(4)
P2–N3[2]	160.6(9)	N1[2]-P2-N4[3]	104.5(4)
P2–N4[3]	171.4(6)	N1[2]-P2-N4[3]	108.6(3)
P2–N4[3]	167.3(7)	N3[2]-P2-N4[3]	104.9(4)
		N3[2]-P2-N4[3]	116.6(4)
		N4[3]-P2-N4[3]	106.6(3)
Na–N1[2]	264.7(13)	P2-N1[2]-P2	144.4(7)
Na–N2[2]	247.9(8) 2 ×	P1-N2[2]-P1	132.4(5)
Na–N2[2]	304.9(7) 2 ×	P1-N3[2]-P2	133.5(4)
Na–N3[2]	248.1(6) 2 ×	P1-N4[3]-P2	119.1(4)
		P1-N4[3]-P2	115.8(4)
		P2-N4[3]-P2	117.4(3)

Table 5. Interatomic distances [pm] and angles [°] in MP_4N_7 (M = K, Rb, Cs).

Compound	KP_4N_7	RbP_4N_7	CsP_4N_7
M–N1[2]	309.9(2)	302.9(8)	313(4)
M–N3[2]	327.7(7) 2 ×	291.6(6) 2 ×	300(3) 2 ×
M–N3[2]	283.1(7) 2 ×	321.1(2) 2 ×	327(3) 2 ×
M–N2[3]	298.7(7) 2 ×	302.8(5) 2 ×	310(3) 2 ×
M–N2[3]	314.8(7) 2 ×	313.3(5) 2 ×	312(3) 2 ×
M–N4[3]	335.5(6) 2 ×	334.9(5) 2 ×	331(3) 2 ×
M–N1[2]	329(1)	343.3(5)	347(4)
M–N1[2]	359(1)	354.2(5)	351(4)
M–N1[2]	365(1)	365.3(5)	355(4)
M–N4[3]	376.8(6) 2 ×	375.5(5) 2 ×	380(3) 2 ×
P1–N1[2]	153.2(4)	156.9(1)	157(2)
P1–N2[2]	162.2(5)	160.3(4)	159(3)
P1–N3[2]	160.0(6)	160.8(5)	162(3)
P1–N4[3]	167.2(6)	170.4(5)	175(3)
P2–N2[2]	155.9(5)	160.1(4)	162(3)
P2–N3[2]	158.1(5)	158.2(5)	155(2)
P2–N4[3]	179.5(6)	177.9(6)	173(3)
P2–N4[3]	171.5(6)	168.0(5)	171(3)
N1[2]-P1-N2[2]	106.9(6)	109.2(4)	109(2)
N1[2]-P1-N3[2]	112.0(4)	110.8(4)	110(2)
N1[2]-P1-N4[3]	108.6(5)	107.5(3)	107(2)
N2[2]-P1-N4[2]	104.7(4)	104.5(3)	108(2)
N2[2]-P1-N3[2]	114.0(4)	112.6(3)	111(2)
N3[2]-P1-N4[3]	110.2(4)	111.9(3)	110(2)
N3[2]-P2-N2[2]	127.5(4)	125.4(3)	122(2)
N4[3]-P2-N2[2]	109.2(3)	108.4(3)	106(2)
N4[3]-P2-N2[2]	100.1(3)	102.2(3)	102(6)
N4[3]-P2-N3[2]	107.5(4)	108.5(4)	112(2)
N4[3]-P2-N3[2]	104.9(3)	104.6(3)	104(2)
N4[3]-P2-N4[3]	105.9(3)	106.6(2)	108(9)
P1-N1[2]-P1	143.5(8)	140.5(6)	145(3)
P1-N2[2]-P2	128.1(3)	128.3(3)	129(2)
P1-N3[2]-P2	129.8(4)	131.8(4)	137(2)
P1-N4[3]-P2	116.8(4)	115.8(3)	116(2)
P1-N4[3]-P2	124.6(4)	124.1(4)	120(2)
P2-N4[3]-P2	118.3(4)	119.9(4)	123(2)

with the oxides $M(M')_4O_7$ (M = Ca, Sr; M' = Al, Ga),[17–20] while KP_4N_7, RbP_4N_7, and CsP_4N_7 are isotypic with the mineral barylite, $BaBe_2Si_2O_7$.[21–23]

As a consequence of the molar ratio P:N = 4:7 two sorts of nitrido bridges (denoted as N[2] and N[3]) occur in the molar ratio 5:2. According to $^3_\infty[(P_4^{[4]}N_5^{[2]}N_2^{[3]})^-]$ these nitrogen atoms

are connected to two and three neighboring phosphorus atoms, respectively. Nitrido bridges N[3] have rarely been identified in phosphorus nitrides and the only representatives known are P_3N_5,[5] HP_4N_7,[7] P_4N_6O,[24] $Na_3P_6N_{11}$,[25] and $K_3P_6N_{11}$.[3] In contrast analogous N[3] connections between three Si tetrahedral centers have frequently been found in nitridosilicates and in dimorphic Si_3N_4 they occur exclusively.[2, 6]

In the four title compounds MP_4N_7 (M = Na, K, Rb, Cs) the PN_4 tetrahedra are linked exclusively through common vertices. Within the group of highly condensed nitridophosphates (molar ratio P:N > 1:2) this situation has only been found in the compounds $M_3P_6N_{11}$ (M = Na, K, Cs). In contrast, in HP_4N_7,[7] which formally represents the corresponding acid to the salts MP_4N_7 and in formally isosteric P_4N_6O[24] as well as in P_3N_5[5] the PN_4 tetrahedra are connected by both corners and edges.

The P–N network structure of NaP_4N_7 can be separated into layers perpendicular to [100] of condensed P_6N_6 sechser rings built up by chains of PN_4 tetrahedra running along [001]. The tips of the PN_4 tetrahedra of alternating chains point along [100] and [$\bar{1}$00], respectively (Figure 3). Two of these
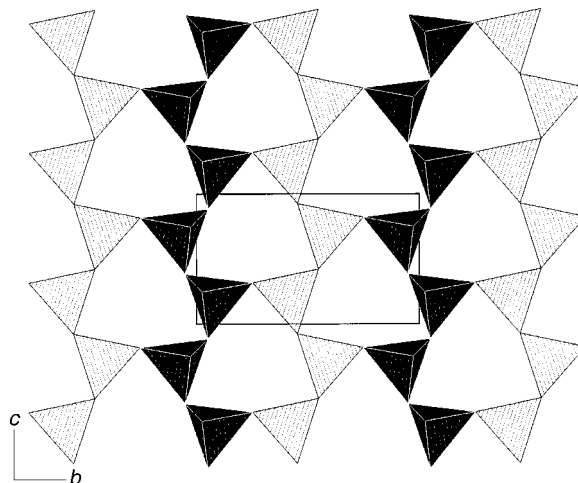

Figure 3. Layer of P_6N_6 sechser rings in NaP_4N_7. View along [100]. $P(1)N_4$ tetrahedra (light) and $P(2)N_4$ tetrahedra (dark) are linked to form chains along [001] by N(2) and N(4), respectively. The chains are bridged through N(3)[2]. Linkage of the layers is accomplished by N(4)[3] and N(1)[2].

layers are connected to each other through N(4)[3] bridges thus forming double layers perpendicular to [100] with characteristic P_4N_4 vierer rings (Figure 4). Furthermore, these double layers are connected by N(1)[2] forming the P–N network structure which exhibits large achter ring channels running along [001]. The Na+ ions are positioned in these large channels (Figure 4).

The crystal structure of isotypic KP_4N_7, RbP_4N_7, and CsP_4N_7 can be described as the aristotype of the structure of barylite, $BaBe_2Si_2O_7$. The P–N network structure may be separated into layers vertical to [010] consisting of condensed P_3N_3 dreier and P_4N_4 vierer rings (Figure 5). Crosslinking of these layers is accomplished by $P(1)N_4$ tetrahedra. Thus pairs of $P(1)N_4$ tetrahedra result, that correspond to the Si_2O_7 units in barylite. The alkali ions (K+, Rb+, and Cs+) are positioned in
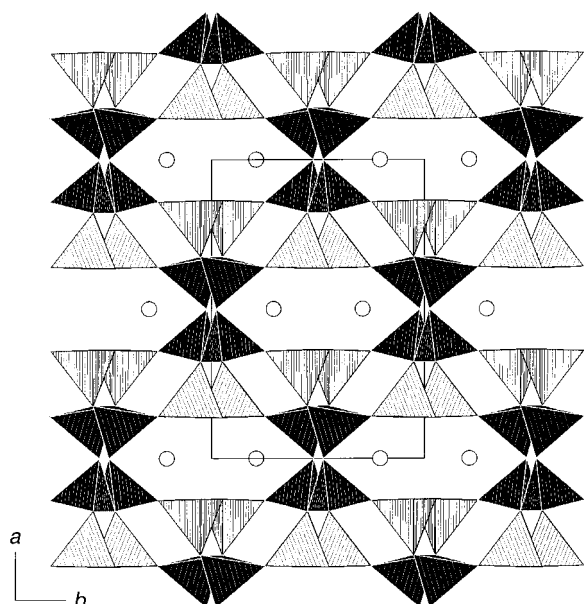
Figure 4. Crystal structure of NaP_4N_7. View along [001]. Characteristic vierer and achter ring channels run along [001]. All Na^+ ions are positioned in the achter ring channels.
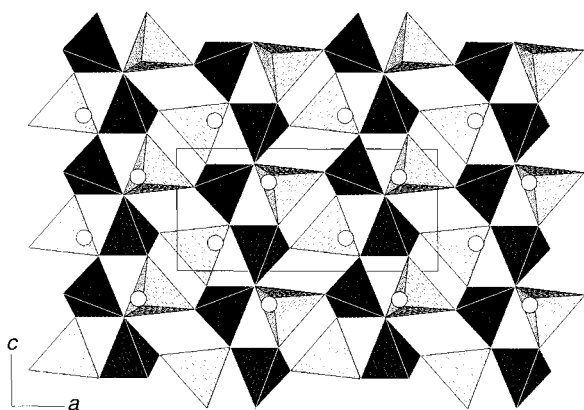

Figure 5. Crystal structure of (K, Rb, Cs)P_4N_7. View along [010]. Chains of $P(2)N_4$ tetrahedra (dark) are linked by $P(1)N_4$ tetrahedra (light) to form sheets of highly condensed dreier and vierer rings. These sheets alternate with layers of alkali metal ions (white circles) and are linked by $N(1)^{[2]}$ bridges.

Figure 6. Crystal structure of (K,Rb,Cs)P_4N_7. View along [001]. Vierer and sechser ring channels run along [100]. The alkali metal ions (white circles) are positioned in the large sechser ring channels.

Figure 7. Crystal structure of (K,Rb,Cs)P_4N_7. View along [100]. Pairs of $P(1)N_4$ tetrahedra (light) link the chains of $P(2)N_4$ tetrahedra to give a three-dimensional P–N network. Channels of sechser rings run along [100].

the resulting sechser ring channels running along [100] and [001]. Perpendicular to [100] the sechser rings are connected by dreier rings, while the sechser rings perpendicular to [001] are bridged by vierer rings (Figures 6 and 7).

The space group of the barylite type of structure has not unequivocally been confirmed in the literature.[21–23] Non-linear optical behavior proven by the second harmonic generation (SHG) test on barylite single crystals supports the noncentrosymmetric space group $Pn2_1a$. However the single-crystal structure refinement in both space groups $Pnma$ and $Pn2_1a$ yielded no significant difference of the crystallographic parameters within standard deviations.[23] Analogously for MP_4N_7 (K, Rb, Cs) no clear distinction between $Pn2_1a$ and $Pnma$ was possible. A final decision will be anticipated by the SHG test.

The topological differences between the network structures in the formally isosteric nitridophosphates HP_4N_7,[7] NaP_4N_7,
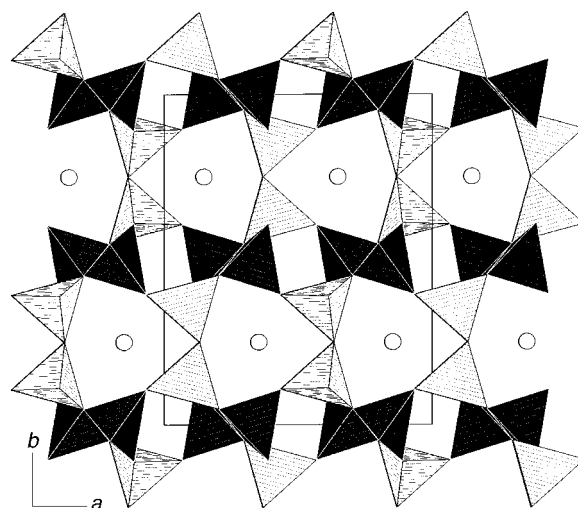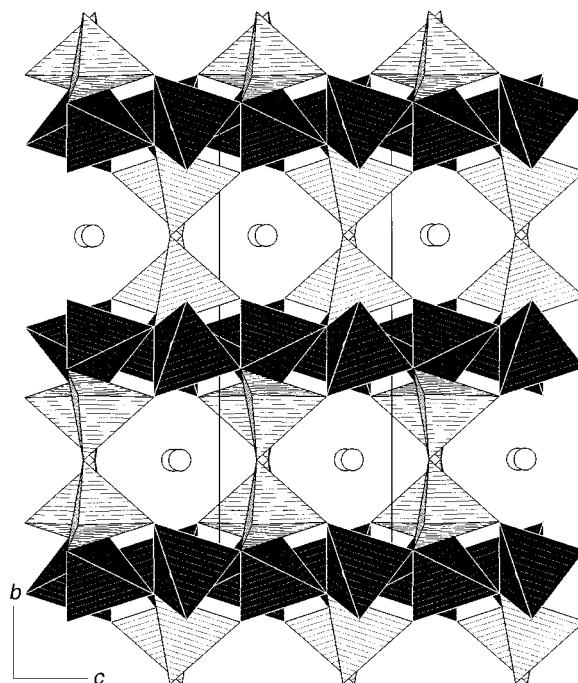
KP_4N_7, RbP_4N_7, CsP_4N_7, and P_4N_6O[24] can be quantitatively represented by the cycle class sequences.[26, 27] These give the relative frequencies of the T_nX_n rings per unit cell (T = P; X = N, O; $n = 1, 2, 3,..$): HP_4N_7: {-, 4, 0, 4, 16, 60, 72, 252,..}, NaP_4N_7: {-, 0, 4, 4, 8, 28, 48, 148,..}, (K,Rb,Cs)P_4N_7: {-, 0, 8, 8, 16, 44, 72, 272,..}, P_4N_6O: {-, 2, 0, 2, 8, 16, 40, 132,..}. It is remarkable that in contrast to HP_4N_7, dreier rings ($n = 3$) exist in NaP_4N_7 and (K,Rb,Cs)P_4N_7, while edge-sharing tetrahedra ($n = 2$, zweier rings) do not occur. As a consequence topologically very different network structures occur in these nitridophosphates. In contrast NaP_4N_7 and (K,Rb,Cs)P_4N_7 show structural

similarities which is documented by the same frequency of dreier, vierer, and fuenfer rings in the cycle class sequences.

The P−N bond lengths in MP_4N_7 (M = Na, K, Rb, Cs) are in the typical range for P−N[2] (NaP_4N_7: 155 pm < P−N[2] < 168 pm; $(K,Rb,Cs)P_4N_7$: 153 pm < P−N[2] < 162 pm) and P−N[3] (NaP_4N_7: 167 pm < P−N[3] < 175 pm; $(K,Rb,Cs)P_4N_7$: 167 pm < P−N[3] < 179 pm). As expected[5, 7] the average values for P−N[2] are significantly smaller than those for P−N[3]. The bond angles N-P-N vary between 102 and 120° in NaP_4N_7 (100° and 128° for $(K,Rb,Cs)P_4N_7$). The bond angles P-N[2]-P range from 132–144° in NaP_4N_7 (130°–145° in $(K,Rb,Cs)P_4N_7$) being typical for phosphorus(v) nitrides.[2] The sum of angles at the N[3] bridges amounts to nearly 360° for $(K,Rb,Cs)P_4N_7$, therefore these N atoms may be considered as sp²-hybridized. For NaP_4N_7 a considerable deviation from the ideal value is observed (352°).

The alkali metal ions of MP_4N_7 (M = K, Rb, Cs) are each coordinated by 16 N atoms (NaP_4N_7: seven). According to MAPLE calculations[28, 29] in NaP_4N_7 only N[2] atoms significantly contribute towards coordination of the cations. In contrast, in MP_4N_7 (M = K, Rb, Cs) a small coordinative contribution of N[3] atoms has to be included in the coordination sphere of the cations.

Conclusion

In the past several nitridophosphates have been synthesized by the reaction of P_3N_5 with the respective metal nitrides (e.g. Li_7PN_4, $Li_{12}P_3N_9$, $Li_{10}P_4N_{10}$, $LiPN_2$, Mg_2PN_3, Ca_2PN_3).[2] However the binary nitrides M_3N (M = Na – Cs) of the heavier alkali metals are not available.[2] Furthermore highly condensed nitridophosphates with a molar ratio P:N > 1:2 are not easily obtained by this procedure due to kinetic problems during the crystallization of the network structures. The high-temperature high-pressure reaction of alkali metal azides with P_3N_5 performed in a belt apparatus now makes available a broad synthetic approach to novel highly condensed nitridophosphates of all alkali metals and it should easily be extended to other metals. Under normal pressure the nitridophosphates do not congruently melt but decompose above 900 °C. However these reactions have been performed between 1500 and 2000 °C. As a consequence partial melting of the products is likely to occur enhancing crystallization of the products. According to our systematic investigations the molar ratio of P:N (e.g. $NaPN_2$, $Na_3P_6N_{11}$, NaP_4N_7) in the desired product is easily controlled by the stoichiometric amount of the starting compounds in the reaction mixtures.

Furthermore we have also been able to extend this novel synthetic procedure to the synthesis of alkali metal nitridosilicates. Due to the low boiling point of the alkali metals, these nitridosilicates have so far not been accessible by the reaction of the respective metals with silicon diimide using a high-frequency furnace.[6]

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