Synthesis and Crystal Structure of Lithium Phosphorus Nitride Li₇PN₄: The First Compound Containing Isolated PN₄-Tetrahedra

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Single phase Li_7PN_4 was synthesized under nitrogen atmosphere at 620°C by solid state reaction of Li_3N and P_3N_5 with molar ratio 7:1. Li_7PN_4 has cubic symmetry, $P\bar{4}3n$, $a = 936.48(3)$ pm, $Z = 8$. (Rietveld profile refinement method; X-ray powder diffraction data; $R(wp) = 0.099$ and $R(I, hkl) = 0.0744$; 77 nonzero reflections observed, 9 positional parameters refined.) Li_7PN_4 is an ionic solid containing both lithium cations and isolated PN_4 anions. Atomic arrangement in the solid derives from an anti-fluorite type of structure. The P–N bond lengths (average: 171 pm) correspond to a bond order of approximately $1\frac{1}{4}$ in the PN_4-tetrahedra. In the cubic unit cell the phosphorus atoms resemble β-tungsten analogous arrangement. © 1990 Academic Press, Inc.

Introduction

The knowledge about syntheses, properties, and structures of binary phosphorus nitride (P_3N_5) and its ternary compounds in combination with electropositive elements is still very unsatisfactory and poor. Detailed structural data have not been evaluated for any of these compounds. Investigation of this class of compounds especially has been made impossible by the unavailability of pure, crystalline, and stoichiometric P_3N_5. Recently, we have developed a new synthetic route for this compound (*1*). We started to investigate systematically the quasi-binary system Li_3N–P_3N_5. Solid state reaction of the binary nitrides with molar ratio 1:1 yields $LiPN_2$ (*2–4*). Using the Rietveld method applied on X-ray powder diffraction data we were able to refine the crystal structure of this compound. As already studied by other authors (*3, 4*) a three-dimensional polymeric net of vertex-sharing PN_4-tetrahedra (similar to β-cristobalite) was found in $LiPN_2$ (*2*).

In contrast to that the stoichiometry of Li_7PN_4 supposes the existence of isolated PN_4-tetrahedra framed by lithium cations. The aim of this study was to decide on the existence of complex PN_4^{7-} anions within the ionic compound Li_7PN_4.

Experimental

1. Materials Used

Li_3N was synthesized by reaction of metallic lithium and pure nitrogen in the procedure described by Rabenau (*5*). The purity of the compound was checked by means of chemical analyses and powder

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diffraction techniques. Phosphorus nitride P_3N_5 was synthesized by a method described elsewhere by reaction of $(PNCl_2)_3$ and NH_3 (*1*).

2. Synthesis of Li₇PN₄

Single phased Li_7PN_4 (10–20 mmol per batch) was synthesized by solid state reaction of the binary nitrides. An intimate mixture of both educts was kept at 620°C in a tungsten crucible which was sealed in a quartz tube under pure nitrogen atmosphere. After a reaction period of 24 hr the reaction mixture was cooled to room temperature and small portions of lithium nitride (1–2 mol%) were added in order to achieve compensation for the loss of Li_3N due to thermal decomposition. This mixture was finely ground before reheating and this process was repeated until pure Li_7PN_4 was obtained (two to three times). Both Li_3N and the product Li_7PN_4 are rather sensitive against moisture. Accordingly all operations were carried out under careful inert conditions (pure nitrogen atmosphere).

3. Analyses

For determination of the chemical composition of the product the substances were dissolved in water. In order to prevent loss of ammonia formed during hydrolysis of the ternary nitride a closed autoclave system was used to dissolve the product (*6*). Lithium content was determined by atomic emission analysis. Phosphorus was determined photometrically as phosphomolybdate vanadate, and nitrogen, as indophenol.

4. X-ray Diffraction Measurements

X-ray powder diffraction measurements were performed on a STOE STADI/P transmission powder diffractometer in Debye-Scherrer mode using 0.5-mm capillaries sealed under inert atmosphere. A small linear position-sensitive proportional counter (mini PSD, STOE (*7*)) covering a 2Θ range

of 6.7° was used. The distance from X-ray tube to monochromator and from monochromator to detector was chosen to be 260 mm in order to obtain maximum reflection intensity while providing sufficient angular resolution of the diffractometer. A curved germanium monochromator was used to obtain a focused monochromatized CuKα1 primary beam (λ = 154.056 pm). Thus during an exposure time of 12 hr in a 2Θ range 5–101° sufficiently high counting rates were achieved.

Results

1. Composition of the Product

Pure Li_7PN_4 was obtained after a total reaction period of 3 days as a pale yellow and fine crystalline powder. The compound is rather sensitive against moisture. Above 650°C Li_7PN_4 decomposes without melting. Chemical analyses confirmed the composition Li_7PN_4 of the product. Lithium found: 35.3%, theor.: 35.84%; phosphorus found: 22.3%, theor.: 22.85%; nitrogen found: 41.9%, theor.: 41.31%. The absence of hydrogen bonded to nitrogen in the compound was proved experimentally by IR spectroscopy.

2. Determination of the Structure

All of the observed X-ray reflections (Table I) could be indexed assuming cubic symmetry and a primitive Bravais lattice. Analysis of the observed powder pattern of Li_7PN_4 revealed some similarity to the powder diagram reported for Li_7VN_4. For the latter compound Juza *et al.* supposed an ordered superstructure of anti-flourite type. However, up to now for Li_7VN_4 no structure refinement has ever been reported (*8*). Indexing of the observed X-ray reflections of Li_7PN_4 followed the general extinction rule $l = 2n$ for all *hhl* reflections corresponding to the possible spacegroups $P\bar{4}3n$ and $Pm3n$. Only the lower symmetric space-

TABLE I
X-Ray Powder Diffraction Data for Li₇PN₄

h	k	l	2Θ$_{obsd}$	FWHM	I$_{obsd}$	I$_{calcd}$	h	k	l	2Θ$_{obsd}$	FWHM	I$_{obsd}$	I$_{calcd}$
1	1	0	13.36	0.15	0.0	0.3	7	2	0	73.57	0.20	25.0	22.5
2	0	0	18.94	0.16	506.2	517.6	5	5	2	74.38	0.20	19.4	18.9
2	1	0	21.20	0.16	1310.3	1291.2	6	3	3	74.38	0.20	8.8	8.6
2	1	1	23.25	0.16	1123.7	1107.4	7	2	1	74.38	0.20	54.0	52.7
2	2	0	26.91	0.16	14.1	0.1	6	4	2	75.98	0.21	10.4	6.1
3	1	0	30.15	0.16	6.8	0.3	7	3	0	77.57	0.21	3.8	0.2
2	2	2	33.11	0.16	1200.6	1061.9	7	3	1	78.37	0.21	3.6	0.1
3	2	0	34.50	0.16	137.4	158.2	6	5	0	79.94	0.21	48.6	42.2
3	2	1	35.85	0.16	160.2	208.9	6	4	3	79.94	0.21	26.2	22.8
4	0	0	38.42	0.16	19.4	61.9	6	5	1	80.73	0.21	90.2	79.1
4	1	0	39.65	0.16	0.0	0.9	7	3	2	80.73	0.21	30.1	26.4
3	3	0	40.85	0.17	0.0	3.0	8	0	0	82.30	0.22	104.7	99.6
4	1	1	40.85	0.17	0.0	2.5	7	4	0	83.08	0.22	0.1	0.1
4	2	0	43.17	0.17	74.0	60.7	6	5	2	83.08	0.22	0.5	0.2
4	2	1	44.29	0.17	124.1	110.8	8	1	0	83.08	0.22	1.0	0.4
3	3	2	45.39	0.17	126.0	121.2	8	1	1	83.86	0.22	18.2	18.1
4	2	2	47.53	0.17	39.2	28.6	7	4	1	83.86	0.22	0.8	0.8
4	3	0	48.57	0.17	1.3	0.2	5	5	4	83.86	0.22	0.1	0.1
4	3	1	49.60	0.17	158.7	137.6	6	4	4	85.42	0.22	6.0	5.9
5	1	0	49.60	0.17	0.2	0.2	8	2	0	85.42	0.22	30.2	30.0
5	2	0	52.58	0.18	14.4	12.5	7	4	2	86.20	0.22	42.5	38.9
4	3	2	52.58	0.18	196.9	170.7	8	2	1	86.20	0.22	37.0	33.9
5	2	1	53.55	0.18	19.4	20.4	6	5	3	86.97	0.22	3.6	7.1
4	4	0	55.46	0.18	1084.6	1086.2	6	6	0	88.52	0.23	0.0	0.1
4	3	3	57.32	0.18	4.7	3.7	8	2	2	88.52	0.23	2.0	9.6
5	3	0	57.32	0.18	1.7	1.3	8	3	0	89.30	0.23	0.0	0.6
5	3	1	58.24	0.18	0.0	0.2	8	3	1	90.07	0.23	0.7	1.0
4	4	2	59.14	0.18	69.6	77.5	7	4	3	90.07	0.23	12.9	18.6
6	0	0	59.14	0.18	0.2	0.2	7	5	0	90.07	0.23	0.1	0.1
6	1	0	60.04	0.18	0.0	3.1	7	5	1	90.85	0.23	0.0	0.4
5	3	2	60.93	0.18	95.1	104.2	6	6	2	91.63	0.23	26.0	33.5
6	1	1	60.93	0.18	0.5	0.6	6	5	4	92.40	0.23	2.3	2.1
6	2	0	62.69	0.19	0.3	0.1	8	3	2	92.40	0.23	36.5	32.7
5	4	0	63.56	0.19	0.0	0.1	7	5	2	93.18	0.23	33.9	29.3
6	2	1	63.56	0.19	0.0	0.8	8	4	0	94.73	0.24	81.7	68.3
5	4	1	64.43	0.19	7.2	16.8	8	4	1	95.51	0.24	0.2	0.4
6	2	2	66.13	0.19	105.1	125.8	8	3	3	96.29	0.24	25.9	22.3
5	4	2	66.98	0.19	66.0	65.1	9	1	0	96.29	0.24	0.2	0.1
6	3	0	66.98	0.19	44.4	43.8	7	5	3	97.07	0.24	0.5	0.2
6	3	1	67.82	0.19	113.8	114.4	8	4	2	97.85	0.25	40.0	35.2
4	4	4	69.48	0.20	42.7	40.2	7	6	0	98.64	0.25	15.3	12.8
6	3	2	70.31	0.20	0.0	0.4	9	2	0	98.64	0.25	14.8	12.4
5	5	0	71.13	0.20	0.0	0.6	7	6	1	99.42	0.25	20.7	19.2
5	4	3	71.13	0.20	0.0	0.2	9	2	1	99.42	0.25	22.8	21.2
7	1	0	71.13	0.20	0.0	0.1	6	5	5	99.42	0.25	1.3	1.2
6	4	0	72.76	0.20	66.6	60.5	6	6	4	101.00	0.25	0.0	0.2
6	4	1	73.57	0.20	92.8	83.7							

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TABLE II

CRYSTAL DATA FOR Li_7PN_4

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Crystal system, space group, Z	cubic, $P\bar{4}3n$, 8
a (pm)	936.48(3) (77 reflections used)
Cell volume (10^6 pm^3)	821.29
Radiation	$CuK\alpha1$, λ = 154.056 pm
Monochromator	Germanium monochromator
2Θ range	$5° < 2\Theta < 101°$
Measuring instrument/detector	STOE STADI/P
	Transmission powder diffractometer
	Position sensitive detector (STOE-PSD 2)
Measuring time (hr)	12
X-ray density (g/cm^3)	2.193
X-ray absorption coefficient (cm^{-1})	42.9
No. of reflections observed	77 (nonzero)
No. of profile parameters refined	16
No. of positional parameters refined	9
No. of thermal parameters refined	3
R(wp), R(I, hkl)	0.099, 0.0744

group $P\bar{4}3n$, however, was compatible with the structural model assumed for this compound. Furthermore, this is the same space-group suggested by Juza for the vanadium compound (8).

For the structure refinement, which was performed by the use of the Rietfeld full-profile method (7), step intensities in the range $5° < 2\Theta < 101°$ were used with an angular resolution of about 0.08°. Due to the use of a position sensitive proportional counter the reflection profiles exhibited a rather symmetric shape. Thus a modified Lorentzian function (Model 2 Lorentzian) proved to be suitable for representation of the individual reflection profiles. The angular dependence of the peak full-width at half-maximum (FWHM) was described by a proper Tchebychev polynomial. The background intensity line was also refined during the calculation using a Tchebychev polynomial of up to the 9th degree. The integration range used was 3.0 FWHM on both sides of the diffraction line positions. Refinement of the half-width parameters, the zero point, and the scale factor was performed before

the refinement of the positional parameters was started. Refinement of the crystal structure of Li_7PN_4 (cf. Table II) was started on the basis of the ideal atomic positions corresponding to an ordered superstructure of anti-fluorite type (according to (Li_7PN_4 with P at the origin) as assumed for the vanadium compound Li_7VN_4 by Juza et al. (8).

Combined isotropic thermal parameters for the three atom types Li, P, and N were used in order to get a reasonably good degree of overestimation between number of reflections observed (77 nonzero reflections, 9 positional parameters) and parame-
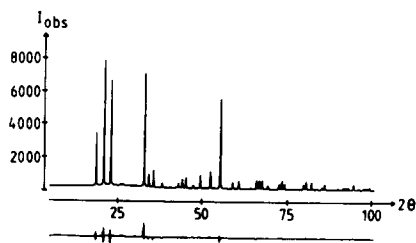

FIG. 1. Observed (top) and difference (bottom) intensity powder diffraction pattern for Li_7PN_4.

TABLE III

REFINED STRUCTURAL AND THERMAL PARAMETERS FOR Li_7PN_4 (WITH ESD'S)

Atom	Position	x/a	y/b	z/c	$U(iso) \cdot 10^4$ (pm^2)
Li (1)	$6b$	0	$\frac{1}{2}$	$\frac{1}{2}$	0.0185(25)
Li (2)	$6d$	$\frac{1}{4}$	0	$\frac{1}{2}$	$U_{(Li1)}$
Li (3)	$8e(xxx)$	0.2245(29)	0.2245(29)	0.2245(29)	$U_{(Li1)}$
Li (4)	$24i$	0.2493(43)	0.2386(44)	−0.0258(34)	$U_{(Li1)}$
Li (5)	$12f$	0.2576(77)	0	0	$U_{(Li1)}$
P (1)	$6c$	$\frac{1}{2}$	0	$\frac{1}{4}$	0.0082(10)
P (2)	$2a$	0	0	0	$U_{(P1)}$
N (1)	$24i$	0.3532(8)	0.3844(8)	0.1012(13)	0.0125(17)
N (2)	$8e(xxx)$	0.1040(14)	0.1040(14)	0.1040(14)	$U_{(N1)}$

ters refined. Refinement of the thermal parameters was performed after refinement of the positional parameters had been finished. The final residual factors obtained for Li_7PN_4 were $R(wp) = 0.099$ for the profile and $R(I, hkl) = 0.0744$ for the structure refinement, respectively. The final parameters are given in Table III. The fit between the observed and the calculated X-ray diffraction pattern of Li_7PN_4 is illustrated in Fig. 1.
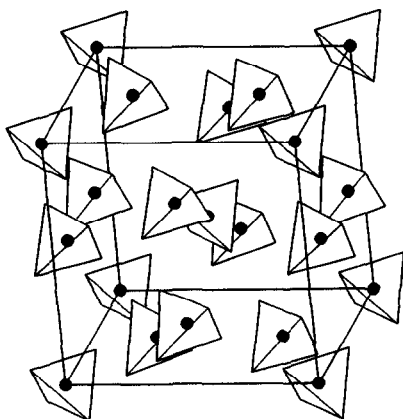

FIG. 2. Unit cell of Li_7PN_4 (lithium cations omitted). The nitrogen atoms of the PN_4-tetrahedra present a distorted cubic close packing. The phosphorus and lithium atoms together occupy all of the tetrahedral sites. The phosphorus atoms resemble an A15-analogous arrangement.

3. Crystal Structure of Li_7PN_4

As suggested, atomic arrangement in Li_7PN_4 derives from an anti-fluorite type of structure: The nitrogen atoms present a distorted cubic close-packed arrangement and the lithium and phosphorus atoms together occupy all the tetrahedral sites of the anionic network (9). In the ternary compound an ordered supercell as compared to the "aristo-type" containing 8 formula units is formed. Distribution of the phosphorus atoms in the cubic unit cell of Li_7PN_4 ($a = 936.48(3)$ pm) resembles a β-tungsten analogous arrangement (A15-type) as illustrated in Fig. 2.

TABLE IV

INTERATOMIC DISTANCES (pm) AND BONDING ANGLES (°) IN Li_7PN_4 (WITH ESD'S)

N(1) – P(1) 173.3(9)	N(2) – P(2) 168.7(12)
– Li(4) 196.9(41)	– Li(3) 195.5(25)
– Li(1) 199.0(80)	– Li(5) 199.2(54)
– Li(4) 205.6(39)	(three times)
– Li(2) 209.1(81)	
– Li(4) 213.8(39)	– Li(4) 221.8(40)
– Li(5) 219.3(45)	(three times)
– Li(3) 224.2(25)	
N(1) – P(1) – N(1)	N(2) – P(2) – N(2)
112.2(4) (two times)	109.5(6) (six times)
108.1(5) (four times)	

SCHNICK AND LUECKE

Taking the differences in electronegativity ($\Delta\chi$, see Ref. (10)) between Li, P, and N into account a purely ionic description of the atomic arrangement in Li_7PN_4 is not appropriate. Covalent P–N bonds ($\Delta\chi = 1.0$) have to be assumed while the Li–N contacts ($\Delta\chi = 2.1$) are predominantely ionic. Each phosphorus atom is bonded to four nitrogen atoms forming tetrahedral PN_4 anions. Two independent sites of the phosphorus atoms occur in Li_7PN_4: While the PN_4-tetrahedra with its center at 000 are regular (N–P–N: 109.5°; P–N: 168.7(12) pm) a slight distortion caused by packing effects in the solid is observed for those with phosphorus at $\frac{1}{2}$ 0 $\frac{1}{4}$ (site symmetry: $\bar{4}$; N–P–N: 108.1° (four times) and 112.2° (two times); P–N: 173.3(9) pm). The nitrogen atoms of the complex PN_4 anions each are coordinated by seven lithium cations (Li–N distances: 195–224 pm; cf. Table IV). The lithium and phosphorus atoms together form a distorted cubic coordination around the nitrogen atoms.

In Li_7PN_4 the PN_4 tetrahedra are not connected via common nitrogen atoms as it has been found in other ternary phosphorus nitrides: In $LiPN_2$ a three-dimensional net and in Mg_2PN_3 infinite chains of vertex-sharing PN_4-tetrahedra have been found (2, 11). Thus Li_7PN_4 represents the first compound containing "isolated" complex PN_4-tetrahedra. The PN_4 anions are isoelectronic to the orthophosphate anion (PO_4^{3-}). With an average P–N bond length of 171 pm within the PN_4-tetrahedra a bond order of approximately $1\frac{1}{4}$ is assumed (12–14). Consequently a description of the complex anions in terms of a simple valence-bond model analogously to the orthophosphate anion is appropriate. According to the formula $(Li^+)_7 (PN_4)^{7-}$ a relatively high electronic charge on the nitrogen atoms of the complex PN_4 anions occurs. Therefore a slight enlargement of the P–N bond lengths from 164 pm in $LiPN_2$

(2) to 171 pm in Li_7PN_4 due to electrostatic repulsion of the nitrogen atoms of the complex PN_4-tetrahedra is observed.

The lithium cations in Li_7PN_4 are nearly tetrahedrally coordinated by the nitrogen atoms of the complex PN_4 anions. The Li–N distances vary between 195 and 224 pm (cf. Table IV). They are comparable to those found in binary lithium nitride Li_3N (Li–N: 194 and 213 pm) (5).

Acknowledgments

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