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# High-Pressure Synthesis of $\gamma$-$P_3N_5$ at 11 GPa and 1500 °C in a Multianvil Assembly: A Binary Phosphorus(V) Nitride with a Three-Dimensional Network Structure from $PN_4$ Tetrahedra and Tetragonal $PN_5$ Pyramids**

Kai Landskron, Hubert Huppertz, Jürgen Senker, and Wolfgang Schnick*

Phosphorus(V) nitride, $P_3N_5$, has structural similarities to the polymeric nonmetal nitrides $\alpha$- and $\beta$-$Si_3N_4$ as well as to cubic boron nitride (*c*-BN). These compounds are built up from three-dimensional networks of linked $TN_4$ tetrahedra (T = B, Si, P). In cubic boron nitride as well as in $\alpha$- and $\beta$-silicon nitride corner-sharing tetrahedra exclusively occur, whereas in $\alpha$-$P_3N_5$ corner- and edge-sharing $PN_4$ units exist.[1, 2] Recently the synthesis of cubic $\gamma$-$Si_3N_4$ was reported. This high-pressure modification, which crystallizes in the spinel structure type, consists of $SiN_4$ tetrahedra and $SiN_6$ octahedra.[3]

With respect to its material properties phosphorus(V) nitride differs significantly from BN and $Si_3N_4$: $P_3N_5$ is thermally stable only up to 850 °C, whereas boron nitride and silicon nitride decompose at much higher temperatures.[1] The thermal lability of phosphorus(V) nitrides is an important reason why the synthesis of highly condensed crystalline nitridophosphates (molar ratio $P:N > 1:2$) is difficult. The irreversible elimination of $N_2$, which is the main process during the thermal decomposition of phosphorus(V) nitrides, can be suppressed by using high-pressure conditions. Recently, the synthesis of highly condensed nitridophosphates by reaction of the respective metal azides with $P_3N_5$ was successfully carried out at about 4 GPa and 1300 °C. We obtained the alkali and alkaline earth nitridophosphates (e.g. $M^IPN_2$, $M^IP_4N_7$, $M^I_3P_6N_{11}$, $M^{II}P_2N_4$)[4] without thermal decomposition of $P_3N_5$ or the reaction products.

By increasing the pressure further we have now been able to synthesize the high-pressure phase $\gamma$-$P_3N_5$. The reaction was carried out at 1500 °C and 11 GPa with partially crystalline $P_3N_5$ as starting material. The reaction was performed by using a boron nitride capsule in a multianvil assembly, which allowed the synthesis of about 50 mg $\gamma$-$P_3N_5$ (see Experimental Section).

The crystal structure of $\gamma$-$P_3N_5$ (Table 1) was determined by direct methods from powder X-ray diffraction data and refined using the Rietveld method (Figure 1).[5] The novel high-pressure modification consists of a polymeric three-dimensional network structure of linked $PN_4$ tetrahedra and tetragonal-pyramidal $PN_5$ units. In accord with the nomen-

Table 1. Atomic parameters and isotropic thermal displacement factors [pm²] of $\gamma$-$P_3N_5$.[a]

| Atom | Wyckoff position | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| P1 | 2*a* | 0 | 0 | 0.3114(10) | 274(14) |
| P2 | 4*c* | 0.8191(2) | 1/2 | −0.0420(9) | 360(10) |
| N1 | 2*b* | 0 | 1/2 | 0.5159(15) | 62(29) |
| N2 | 4*c* | 0.8953(4) | 0 | 0.0768(9) | 214(19) |
| N3 | 4*c* | 0.7265(6) | 1/2 | 0.2196(12) | 263(25) |

[a] The temperature factor is defined by $\exp(-8\pi^2 U_{iso} \sin^2\theta/\lambda^2)$, space group *Imm*2, $a = 1287.20(5)$, $b = 261.312(6)$, $c = 440.04(2)$ pm, $Z = 2$.

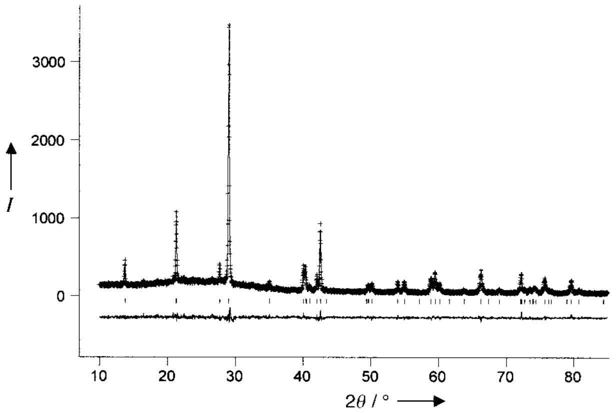

Figure 1. Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as difference profile (bottom line) of the Rietveld refinement of $\gamma$-$P_3N_5$. Positions of Bragg reflections are marked by vertical lines. The diffraction pattern was obtained with a conventional STOE-Stadi-P powder diffractometer ($Cu_{K\alpha 1}$, $\lambda = 154.05$ pm).

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[*] Prof. Dr. W. Schnick, Dipl.-Chem. K. Landskron, Dr. H. Huppertz, Dr. J. Senker
Department Chemie der Ludwig-Maximilians-Universität
81377 München (Germany)
Fax: (+49) 89-2180-7440
E-mail: wsc@cup.uni-muenchen.de

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clature for silicates introduced by Liebau, $\gamma$-phosphorus(v) nitride can be described as a phosphorus nitridophosphate nitride $P^{[5]}_2[P^{[4]}N_3]N_2$ (the superscripted number in square brackets after the element symbol denotes the coordination number).[6] Rods from *trans*-edge-sharing $PN_5$ units running along [010] are linked by vertices, leading to the formation of layers perpendicular to [100] (Figure 2). These layers are reminiscent of fragments of the rutile structure type, in which the octahedra have been cut off at one vertex to give tetragonal pyramids (Figure 3). Rods of corner-sharing $PN_4$ tetrahedra running along [010] link the layers built up from $PN_5$ units (Figure 2). In accordance with the pressure–coordination rule[7] a partial increase of the coordination number of the phosphorus atoms from four in $\alpha$-$P_3N_5$ to five in $\gamma$-$P_3N_5$ is observed. The bond lengths P–N in the $PN_5$ pyramids (166(1), 171(1), and 177(1) pm) are significantly longer than in the $PN_4$ tetrahedra (159(1) and 170(1) pm) (Figures 4 and 5), which corresponds to the pressure–distance paradox.[8] A quite similar observation is made in the spinel structure of cubic $\gamma$-$Si_3N_4$, in which the coordination numbers of silicon are partially increased from four to six compared to those in $\alpha$- and $\beta$-$Si_3N_4$, which are the stable phases at normal pressure.[3]

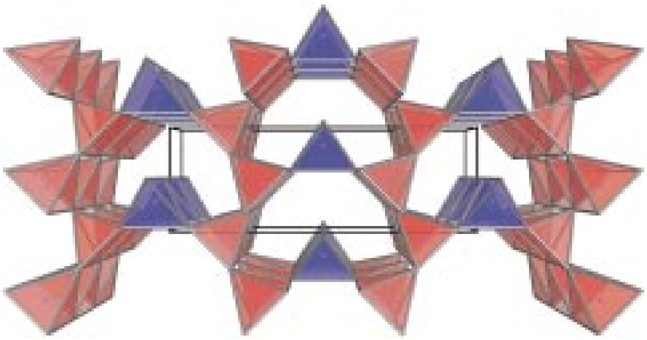

Figure 2. Crystal structure of $\gamma$-$P_3N_5$, view along [010]. Layers of edge-sharing and corner-sharing $PN_5$ pyramids (red) are linked by rods of corner-sharing $PN_4$ tetrahedra (blue) to give a three-dimensional network structure.

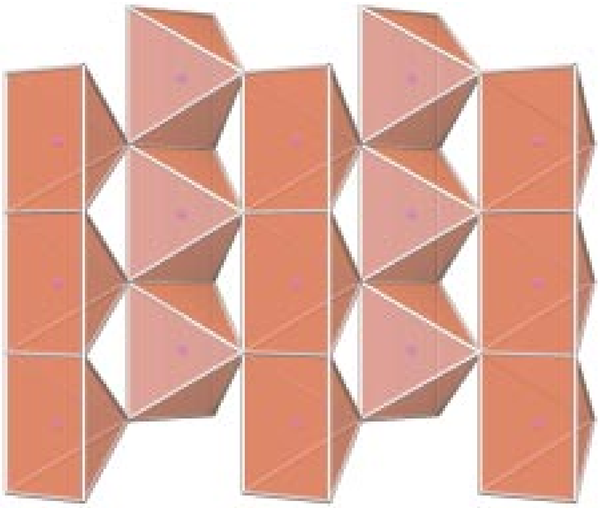

Figure 3. Layers of rods of *trans*-edge-sharing tetragonal $PN_5$ pyramids linked through vertices are reminiscent of fragments of the crystal strucure of rutile; view along [100].

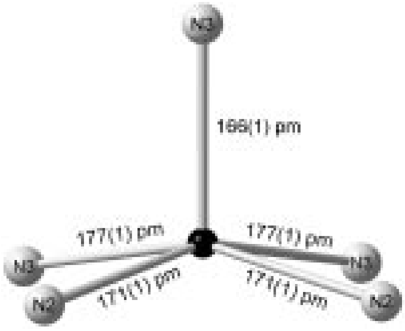

Figure 4. Tetragonal $PN_5$ pyramids in $\gamma$-$P_3N_5$ ($\sphericalangle$(N-P-N) 2 × 100(1)°, 2 × 101(1)°, 2 × 79(1)°, 95(1)°, 99(1)°, 2 × 158(1)°).

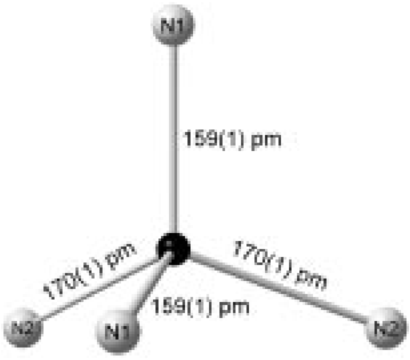

Figure 5. $PN_4$ tetrahedra in $\gamma$-$P_3N_5$, the P atoms show nearly regular tetrahedral coordination by N atoms ($\sphericalangle$(N-P-N) 105(1)°, 4 × 110(1)°, 111(1)°).

All nitridophosphates investigated to date are built up by $PN_4$ tetrahedra.[1, 4] $PN_5$ units are known from molecular spirocyclic compounds, but exact structural data exists for a few cases only.[9] In accordance with the VSEPR concept, which favors the trigonal-bipyramidal conformation over the square-pyramidal one, distorted $PN_5$ bipyramids are observed in all studied compounds. The P–N bond lengths in the trigonal bipyramids of aminodiazadiphosphetospirobis(triazaphosphole) are similar to those in the $PN_5$ pyramids of $\gamma$-$P_3N_5$.[9a] In contrast, P–N compounds with square- or tetragonal-pyramidal $PN_5$ units are unknown yet.

In $\gamma$-$P_3N_5$ the bond lengths of the $PN_4$ and $PN_5$ units vary far less than in $\alpha$-$P_3N_5$ (151–174 pm), which is exclusively built up from $PN_4$ tetrahedra. This and the fact that phosphorus(v) nitride synthesized at normal pressure is often obtained as $\beta$-$P_3N_5$, a stacking variant derived from $\alpha$-$P_3N_5$, or as a stacking fault variant indicates steric stress in $\alpha$-$P_3N_5$.[2, 10]

One fifth of the N atoms in $\gamma$-$P_3N_5$ is neighbored by two P atoms ($N^{[2]}$). All residual N atoms are bound to three P atoms ($N^{[3]}$). The P–$N^{[2]}$ bonds (159 pm) are significantly shorter than the P–$N^{[3]}$ bonds (166–177 pm). Compared to $\alpha$-$P_3N_5$ (two fifth $N^{[3]}$, three-fifths $N^{[2]}$) the average coordination number of the N atoms is increased. The sum of the bond angles at $N^{[3]}$ is nearly 360° for each atom. The angles P-$N^{[2]}$-P (111°) are significantly smaller than in $\alpha$-$P_3N_5$ (142, 143, and 171°, respectively).[2] They are similar to the corresponding angles in the P–N sodalites $M_{(7-x)}H_{2x}[P_{12}N_{24}]Y_y$ (125–126°)

built exclusively from N$^{[2]}$ bridges,[1] $\mathrm{LiPN_2}$ (124°),[1] and $\mathrm{HPN_2}$ (130°).[11]

The density of $\gamma$-$\mathrm{P_3N_5}$ is 32% higher than the density of $\alpha$-$\mathrm{P_3N_5}$ (values from the X-ray structure determination: 2.77 ($\alpha$-$\mathrm{P_3N_5}$),[2] 3.65 $\mathrm{g\,cm^{-3}}$ ($\gamma$-$\mathrm{P_3N_5}$)). Therefore the high-pressure phase could show interesting materials properties (e.g. great hardness or low compressibility) similar to those predicted for cubic $\gamma$-$\mathrm{Si_3N_4}$ obtained under comparable conditions (1700 °C, 15 GPa).[3]

## *Experimental Section*

The high-pressure synthesis of $\gamma$-$\mathrm{P_3N_5}$ was carried out using the multianvil-technique and a hydraulic 1000 t press.[12, 13] $\mathrm{Cr_2O_3}$-doped MgO octahedra (Ceramic Substrates & Components Ltd., Isle of Wight) with an edge length of 18 mm were used. Eight truncated tungsten carbide cubes (Toshiba Grade F, edge length: 32 mm, truncation edge length: 11 mm) separated by pyrophyllite gaskets served as anvils for the compression of the octahedra ("18/11 assembly" in conventional terminology). Partially crystalline $\mathrm{P_3N_5}$, synthesized in accordance with reference [14], was loaded in a cylindrical capsule from hexagonal boron nitride (Henze, Kempten), (volume: ca. 35 $\mathrm{mm^3}$) and sealed with a BN cap. The capsule was centered within two nested graphite tubes of different length, which acted as an electrical resistance heater. The remaining volume at both ends of the sample capsule was filled with two cylindrical pieces from MgO. This arrangement was placed into a $\mathrm{ZrO_2}$ tube and then transferred into a pierced MgO octahedron. The electrical contact of the graphite tubes was arranged by two plates from molybdenum.

The assembly was compressed up to 11 GPa at room temperature over five hours and then heated up to 1500 °C within 30 min. The sample was held for five minutes at this temperature and then quenched to room temperature. Then the pressure was released over 15 h. The temperature was measured by using a $\mathrm{W_{97}Re_3}$–$\mathrm{W_{75}Re_{25}}$ thermocouple, which was attached coaxially to the resistance heater. Further details about pressure calibration and temperature measurement are described in reference [15].

After the removal of the BN capsule $\gamma$-$\mathrm{P_3N_5}$ was obtained as a crystalline, sinterted, white product. Elemental analysis (%): calcd: P 57.02, N 42.98; found: P 54.8, N 41.6, O 2.3. The absence of hydrogen (N–H) was checked by IR spectroscopy. Owing to the weaker bonds the signals of the vibrations in the P–N network of $\gamma$-$\mathrm{P_3N_5}$ are shifted to significantly lower wavenumbers than in $\alpha$-$\mathrm{P_3N_5}$. Moreover $\gamma$-$\mathrm{P_3N_5}$ was characterized by $^{31}$P-MAS-NMR spectroscopy ($\nu_0 = 202.473$ MHz). The investigation using a rotation frequency $\nu_{\mathrm{rot}}$ of 30 kHz revealed two very sharp signals at $\delta = -12$ and $-101$ (reference: 85% $\mathrm{H_3PO_4}$). The integration of the completely relaxed signals (recycle delay: 5000 s) showed an intensity ratio of 1:1.98, which is in good accordance with the results obtained from the X-ray investigations. This issue and the comparison with the $^{31}$P-MAS-NMR data of $\alpha$-$\mathrm{P_3N_5}$[10] allow the assignment of signals at $\delta = -12$ to the tetrahedral site and the one at $\delta = -101$ to the $\mathrm{PN_5}$ pyramids.

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[5] The X-ray investigations of $\gamma$-$\mathrm{P_3N_5}$ were performed with a conventional powder diffractometer STOE StadiP in Debye–Scherrer geometry using $\mathrm{Cu_{K\alpha1}}$ radiation. The powder diffraction pattern was indexed unambiguously in orthorhombic symmetry by using the program WERNER. From systematic absences the space groups $I222$, $I2_12_12_1$, $Imm2$, and $Immm$ were considered. The integration and extraction of the intensities as well as the structure solution by direct methods was carried out by using the program EXPO. The position of all atoms in chemically plausible locations was only achievable in the space group $Imm2$. The Rietveld refinement of the crystal structure data was performed with the program GSAS. The scaling factor, the lattice constants, the zero point, and the background were refined initially. The profile was fitted by a pseudo-Voigt function corrected for asymmetry. All atom positions and thermal displacement factors were refined. $Imm2$, $a = 1287.20(5)$, $b = 261.312(6)$, $c = 440.04(2)$ pm, $V = 148.0 \times 10^6$ pm$^3$, $Z = 2$, $\rho_{\mathrm{calcd}} = 3.657$ $\mathrm{g\,cm^{-3}}$, $\lambda = 154.05$ pm, measured range $10° < 2\theta < 85°$, 7500 data points, 41 reflections, $R_{\mathrm{p}} = 0.073$, $wR_{\mathrm{p}} = 0.094$, $R_{\mathrm{F}} = 0.048$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411847.

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# Physically Cross-Linked Ultrathin Elastomeric Membranes**

Frank Mallwitz and Werner A. Goedel*

Thin, freely suspended membranes are of great interest for use in micromechanical devices, sensors, and actuators that require repeated elastic deformation, such as accelerometers or membrane valves. The ongoing miniaturization of these devices creates a demand for progressively thin membranes with a broad range of mechanical properties, especially with

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[*] Dr. W. A. Goedel
Universität Ulm
Organische und Makromolekulare Chemie OC3
89069 Ulm (Germany)
Fax: (+49) 731-502-2883
E-mail: werner.goedel@chemie.uni-ulm.de

Dr. F. Mallwitz
Humboldt-Universität zu Berlin
Fachbereich Physik
Berlin (Germany)

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