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A High-Pressure Polymorph of Phosphorus Nitride Imide

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Abstract: *Phosphorus nitride imide, PN(NH), is of great scientific importance because it is isosteric with silica (SiO_2). Accordingly, a varied structural diversity could be expected. However, only one polymorph of PN(NH) has been reported thus far. Herein, we report on the synthesis and structural investigation of the first high-pressure polymorph of phosphorus nitride imide, β-PN(NH); the compound has been synthesized using the multianvil technique. By adding catalytic amounts of NH_4Cl as a mineralizer, it became possible to grow single crystals of β-PN(NH), which allowed the first complete structural elucidation of a highly condensed phosphorus nitride from single-crystal X-ray diffraction data. The structure was confirmed by FTIR and ^{31}P and ^{1}H solid-state NMR spectroscopy. We are confident that high-pressure/high-temperature reactions could lead to new polymorphs of PN(NH) containing five-fold- or even six-fold-coordinated phosphorus atoms and thus rivalling or even surpassing the structural variety of SiO_2.*

With more than 1000 minerals, silicates are the largest, the most important, and the most varied class of minerals.[1,2] More than 90% of the earth's crust is composed of silicate materials. SiO_2 is the binary parent compound of silicates, and simultaneously one of the most fundamental oxides in terms of crystal structure, structural phase transitions, and physical and chemical properties.[2–4] It shows a remarkably rich polymorphism, including more than 30 stable and metastable polymorphs, with some of them being abundant in nature.[5,6] The wide range of applications in ceramic and glass industries, as well as great potential in microelectronics, optical fibers, and catalysis makes SiO_2 an irreplaceable material in modern industry.[1,7–9] Accordingly, the great structural variety of silica, and the resulting diversity of properties, makes structures that are analogous to silica an important research target. The replacement of Si and O by P and N may lead to nitridophosphates in which the PN_2^- substructure is isoelectronic to SiO_2. From a structural point of view, nitridophosphates could exhibit a higher structural diversity than silica. In comparison to vertex-sharing SiO_4 tetrahedra in SiO_2, the PN_4 tetrahedra in nitridophosphates can be edge-sharing as well. For silica, edge-sharing has only been postulated for fibrous SiO_2. However, the existence and true nature of this material has not been unequivocally proven to date.[10] Substitution of O by N provides significantly increased structural possibilities. Whereas the structures of oxosilicates are limited to terminal ($O^{[1]}$) or singly bridging oxygen ($O^{[2]}$) positions, N in nitridophosphates may occur as $N^{[1]}$, $N^{[2]}$, $N^{[3]}$, or even ammonium-like $N^{[4]}$ atoms, which can connect up to four neighboring tetrahedral centers.[11] An even greater structural variety can be obtained by substituting Si with P, which may be coordinated by up to five nitrogen atoms. This situation has been found in the high-pressure polymorph γ-P_3N_5, the network of which is built up of vertex-sharing PN_4 tetrahedra and distorted PN_5 pyramids.[12] The nitridic clathrate $P_4N_4(NH)_4(NH_3)$ is also an excellent example for the increased structural possibilities of nitridophosphates in comparison to oxosilicates.[13] The framework structure of this compound has been predicted for silicates, however it has thus far only been observed in this nitridophosphate. The $P_4N_4(NH)_4(NH_3)$ clathrate contains encapsulated molecules of ammonia, which are trapped inside a phosphorus nitride framework. Consequently, it has been discussed as a possible gas storage material.[14] Phosphorus(V) nitride, P_3N_5, is the binary parent compound of nitridophosphates. It is used industrially as flame retardant, as a gate insulator material in metal-insulator semiconductor field-effect transistors (MISFETs) and as a getter material for the elimination of oxygen during the production of incandescent and tungsten halogen lamps.[15–17] Within the class of nitridophosphates and phosphorus nitrides, two cationless compounds that are isosteric to silica (valence electron concentration VEC = 16/3), namely PON and PN(NH), have been described. Four modifications of PON are known: β-cristobalite-type,[18,19] quartz-type,[20] and moganite-type PON,[21] as well as δ-PON.[22] The imide group in PN(NH) is isolobal with O in PON. However, only one polymorph of PN(NH), which crystallizes in the β-cristobalite-type of structure, has been described in the literature.[23,24] Accordingly, it may be possible that further modifications of PN(NH) do exist. Actually, the existence of a high-pressure phase of PN(NH) was discussed in earlier experiments, however, no complete crystal structure or specific properties have been investigated thus far.[13,25,26]

Herein, we report on the synthesis and structural investigation of the first high-pressure polymorph of PN(NH). Because this is the second known modification of this compound, we propose the name β-PN(NH). We succeeded in growing single crystals of β-PN(NH), which enabled the structural determination of an uncharged highly condensed phosphorus nitride on the basis of single-crystal X-ray diffraction data.

β-PN(NH) was synthesized by a high-pressure/high-temperature reaction using a Walker-type multianvil assembly at 6 GPa and 1000 °C.[27] Amorphous PN(NH) was used as the starting material. By adding catalytic amounts of NH_4Cl to the starting material, colorless platelet single crystals of β-

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PN(NH) were obtained and isolated. This is the first known synthesis of microscopic single crystals of a highly condensed phosphorus nitride (atomic ratio $P/N \geq 1{:}2$), which had, until now, been considered unattainable. HCl, which is intermediately formed by the dissociation of NH_4Cl, presumably enables reversible and reconstructive bond cleavage and reformation, and thus facilitates conditions for the growth of single crystals.[11] In order to remove NH_4Cl from the product, it was washed with water and ethanol.

The crystal structure of β-PN(NH) was solved and refined from single-crystal X-ray diffraction data in monoclinic space group $P2/c$ (no. 13).[28] The hydrogen atom positions were unequivocally determined from difference Fourier syntheses and were refined isotropically using restraints for the N–H distances. All non-hydrogen atoms were refined anisotropically. The structure elucidation was additionally confirmed by Rietveld refinement (Figure 1). Furthermore, the product was characterized by EDX, FTIR, and solid-state NMR spectroscopy.

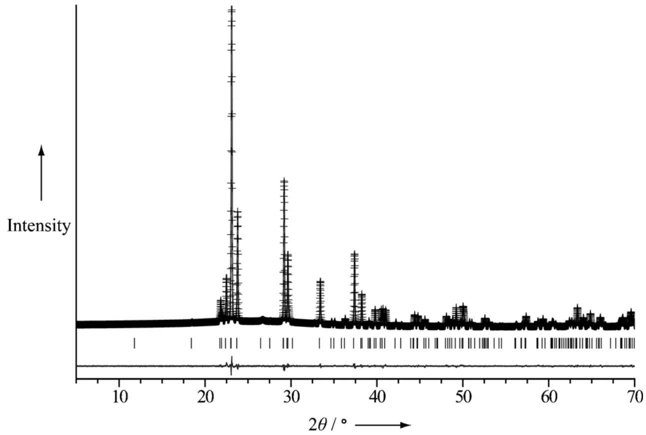

Figure 1. Observed (crosses) and calculated (light gray line) X-ray powder diffraction pattern. Positions of Bragg reflections (vertical lines), difference profile for the Rietveld refinement of β-PN(NH) (dark gray line).

The crystal structure of β-PN(NH) is built up of a three-dimensional network of PN_4 tetrahedra that share vertices on all sides, and in which the hydrogen atoms are covalently bound to half of the N atoms (Figure 2). Owing to a pseudo-twofold screw axis along [010], the structure can almost be described in space group $P2_1/c$ (Figure S1). The framework of β-PN(NH) may be compared to that of α-PN(NH), high and low cristobalite.[23,24,29,30] To characterize the ring sizes in the structure topologically, the cycle class sequence for β-PN(NH) was calculated using the program TOPOLAN.[31] It specifies the relative abundance of P_nN_n ring sizes per unit cell. The results, which are identical with the results for the isotopological frameworks of α-PN(NH), high and low cristobalite, are summarized in Table S9 in the Supporting Information. The secondary building units of β-PN(NH) are six-membered rings, P_6N_6, which are also those with the smallest ring size in this compound.

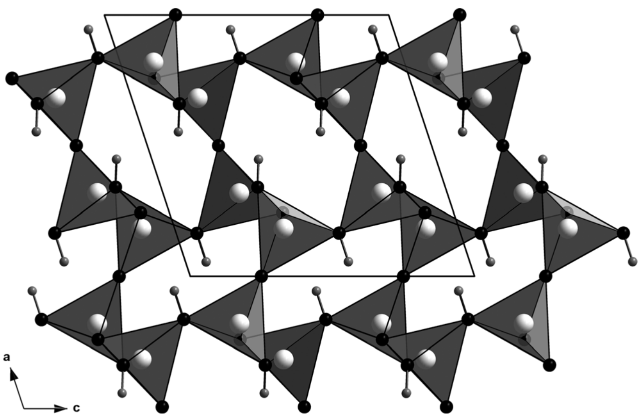

Figure 2. Crystal structure of β-PN(NH), viewed along [010]. H gray, N black, P white.

The differences between the structures of high cristobalite, low cristobalite, α-PN(NH), and β-PN(NH) become readily apparent when regarding the hexagonal layers in these structures (Figure 3). The crystal structures of cubic cristobalite and α-PN(NH) consist of only one type of six-membered rings (Figure 3 a,b). In contrast, they differentiate upon transition from high over low cristobalite (two types of six-membered rings; Figure 3 c) up to β-PN(NH) (three types of six-membered rings; Figure 3 d). Additionally, the six-membered rings adopt a regular chair conformation in high cristobalite, which is significantly distorted in low cristobalite and β-PN(NH). These distortions, which are caused by the tilting of the PN_4 tetrahedra, induce increasing undulations in their respective structures.

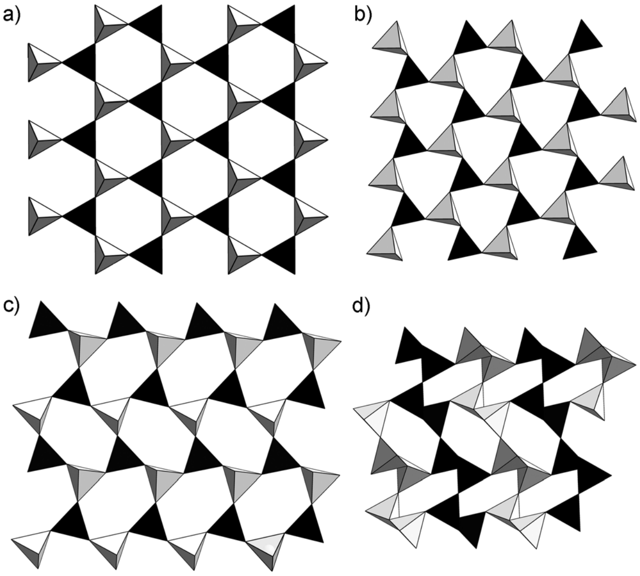

Figure 3. Comparison of hexagonal layers in: a) high cristobalite (view along [-111]), b) α-PN(NH) (view along [-4-12]), c) low cristobalite (view along [0-1-1]), and d) β-PN(NH) (view along [010]). For clarity, tetrahedra with vertices up are depicted in light gray, those with vertices down are depicted in black.

The ranges of the P–N bonds (157–167 pm) and the P-N$^{[2]}$-P angles (126–147°) in the structure of β-PN(NH) are consistent with corresponding values for the low-pressure polymorph α-PN(NH) (160 pm, 130°), and are typical for those in other known phosphorus(V) nitrides. As expected, the P–N$^{[3]}$ bond lengths in the P-NH-P group (167 pm) are significantly longer than the P–N$^{[2]}$ bond lengths in the P-N-P group (157–159 pm), which corroborates the positions of the imide groups. The values for tetrahedral angles vary between 104 and 120°, and thus differ slightly from the regular tetrahedral angle. Detailed information on bond lengths and angles can be found in Tables S1–S4. To verify the electrostatic consistency of the determined crystal structure, the program MAPLE (Madelung part of lattice energy) was used.[32] The partial MAPLE values of the P atom sites (14 320–14 440 kJ mol^{-1}), as well as the overall MAPLE value for β-PN(NH) (23 913 kJ mol^{-1}) are consistent with the corresponding values for α-PN(NH) (MAPLE value of P atom sites: 14 390 kJ mol^{-1}, overall MAPLE value: 23 825 kJ mol^{-1}) with a minor deviation of 0.37 %.

The analytical composition of β-PN(NH) was analyzed by energy-dispersive X-ray (EDX) spectroscopy. It showed no elements other than P and N. Chemical composition estimated from EDX analysis is in excellent agreement with the predicted composition of the product. The results of the EDX measurements are summarized in Table S10.

The FTIR spectrum of β-PN(NH) (Figure S3) resembles that of the tetragonal polymorph α-PN(NH).[23] It exhibits a significant broad absorption band at 2245–2217 cm^{-1}, which can be assigned to the N–H valence modes of both imide groups of the framework. Furthermore, absorption bands at 808–1261 cm^{-1} are observed and are characteristic for nitridophosphates.[12,23,33] The first group of bands, which occurs at 1070–1261 cm^{-1}, can be assigned to the asymmetric stretching of the PN_4 tetrahedra ν_{as}(PNP). The second group is found at 808–951 cm^{-1}, and is caused by the symmetric valence mode of PN_4 tetrahedra ν_s(PNP).

To confirm the determined structure of β-PN(NH), the product was additionally characterized by solid-state NMR spectroscopy. The ^{31}P solid-state NMR spectrum (Figure S4) shows one sharp signal at a chemical shift of $\delta_{iso} = -18.7$ ppm, with a small shoulder at about $\delta_{iso} = -12$ ppm. These two signals correspond to the two crystallographically distinct P atoms in the unit cell. Additionally, the ^{1}H solid-state NMR spectrum (Figure S5) shows two individual signals with chemical shifts of $\delta_{iso} = 6.2$ and 7.1 ppm, which correspond to the two different crystallographic H atoms.

In summary, we have synthesized β-PN(NH), a high-pressure polymorph of PN(NH). It crystallizes in a distorted cristobalite-type of structure. Moreover, by adding NH_4Cl as a mineralizer, we succeeded in growing single crystals of this compound, which allowed for a complete crystal structure elucidation of β-PN(NH). This novel synthetic approach to growing single crystals of phosphorus nitrides under high-pressure/high-temperature conditions may significantly accelerate investigation of new phosphorus nitrides in the future. Taking into account the fact that four modifications of PON are already known, it is reasonable to suggest that further polymorphs of PN(NH) may exist. Consequently, further high-pressure/high-temperature experiments will probably lead to new modifications of PN(NH) containing five-fold- or even six-fold-coordinated phosphorus atoms, and thus rival or even surpass the structural variety of SiO_2. Accordingly, a wide range of interesting properties can be expected.

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[28] Crystal structure data for β-PN(NH): STOE IPDS, $\text{Mo}_{K\alpha}$ (71.073 pm), $2\theta_{\max} = 63.4°$, crystal size $0.11 \times 0.07 \times 0.02$ mm^3, monoclinic, space group $P2/c$ (no. 13), $a = 788.5(2)$, $b = 482.2(1)$, $c = 814.6(2)$ pm, $\beta = 108.19(3)°$, $V = 0.2946(1)$ nm^3, $Z = 8$, $\rho_{\text{calcd}} = 2.706$ g cm^{-3}, $\mu\text{Mo}_{K\alpha} = 1.222$ mm^{-1}, 2371 measured reflections, 676 of which are independent, $R_{\text{int}} = 0.049$, least-squares refinement on F^2 (G. M. Sheldrick, SHELXL-97, program for the refinement of crystal structures, Universität Göttingen, Göttingen (Deutschland), **1997**); no absorption correction, R-values (all data/$F_o^2 \geq 2\sigma(F_o^2)$) $R_1 = 0.0392/0.0298$, $wR_2 = 0.0785/0.0762$, GooF = 1.018 for 534 observed reflections ($F_o^2 \geq 2\sigma(F_o^2)$) and 64 refined parameters. Further details on crystal structure investigations 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-426003.

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