Solid-State Structures

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An Unprecedented AB_2 Tetrahedra Network Structure Type in a High-Pressure Phase of Phosphorus Oxonitride (PON)

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Compounds exhibiting AB_2-type tetrahedral network structures are versatile materials and of great technical importance. First of all microporous zeolites are known for their outstanding absorption properties and catalytic behavior and are therefore extensively used in industrial, agricultural, and laboratory environments.[1] However, the importance of dense AB_2 networks should not be underestimated. SiO_2 and to a minor extent $GaPO_4$ are applied in piezoelectric devices, such as pressure sensors and microbalances,[2] while quartz-like compounds in general, including phosphates such as $AlPO_4$ and BPO_4, can also be used for second-harmonic generation (SHG) purposes.[3,4] Owing to the variety of applications, widespread research into novel AB_2-type structures was conducted, including the prediction of more than two million unique prospective crystal structures for zeolites.[5] However, only a minute subset of possible structures has been realized to date. In this search for new structure types, we have directed our attention to the system P-O-N, which is isoelectronic to silica. The inclusion of nitrogen provides additional structural flexibility, which theoretically opens up an even wider range of possible structure types. The few known compounds in this system include the first nitridic zeolites NPO[6] and $Ba_{19}P_{36}O_{6+x}N_{66-x}Cl_{8+x}$ ($x \approx 4.54$)[7] as well as the nitridic clathrate $P_4N_4(NH)_4(NH_3)$[8] and the polymorphs of PON exhibiting cristobalite-,[9] quartz-,[10] and moganite-type[11] structures. Glassy compounds in the system Li-Ca-P-N also exhibit desirable properties, such as a high hardness and refractive index.[12] The great potential for novel structure types in this system is offset by difficulties in preparation, such as thermal decomposition, low reactivity, and a low degree of crystallinity. To circumvent the mentioned problems, we developed a novel synthetic approach, utilizing an amorphous single-source precursor. Herein, we report on a new high-pressure phase of phosphorus oxonitride PON. Since this is the fourth known polymorph of PON, we propose the name δ-PON. Unlike the quartz and moganite polymorphs, it is not directly accessible by treating cristobalite-type PON under high-pressure/high-temperature conditions. This result hints at the possibility of δ-PON being thermodynamically metastable at these conditions. Instead, we prepared δ-PON by carrying out the final thermal condensation step of an amorphous phosphorus oxonitride imide under high pressure by employing the multianvil technique.[13] The starting material was subjected to a temperature of around 1350 °C at 12 GPa for 120 min in a Walker-type module. The product could be obtained as a hard, colorless solid.

The crystal structure of δ-PON was elucidated ab initio with X-ray powder diffraction data in space group $P2_1/c$ (no. 14).[21] Final refinement was carried out by employing the Rietveld method (Figure 1). Energy-dispersive X-ray spectroscopy showed the presence of P, O, and N, while no other elements were detected. The product was further characterized by FTIR and solid-state NMR spectroscopy.

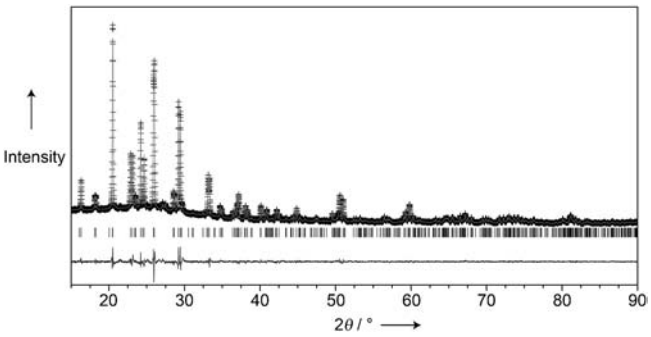

Figure 1. Observed (crosses) and calculated (gray line) powder diffraction pattern of δ-PON as well as position of Bragg reflections (vertical lines) and difference profile (dark gray line).

The crystal structure of δ-PON exhibits a three-dimensional network composed of all-side vertex sharing $P(O,N)_4$-tetrahedra representing an unprecedented topology (Figure 2). The arrangement of the tetrahedra is characterized of condensed 4-, 6-, and 8-rings, which is expressed by the cycle class sequence according to Klee[14] (Table S5). The comparison with the cycle class sequences of the other polymorphs shows that δ-PON is not topologically equivalent to any of the known phases. The arrangement of $P(O,N)_4$-tetrahedra into 4- and 6-rings is reminiscent of that of moganite PON, but owing to the difference in framework topologies no crystallographic group–subgroup relation between the two phases exists. One type of the two crystallographically independent 4-rings forms ladder-like chains along [010] (Figure 3), which are surrounded by 6-rings.

The topology of this framework (Figure 3) indicated by the vertex symbol $(4_16_28_3)(4_16_48_1)(4_26_38)_2$ (determined by the TOPOS Software)[15] is different from those of all other PON polymorphs and has not been found in any other known

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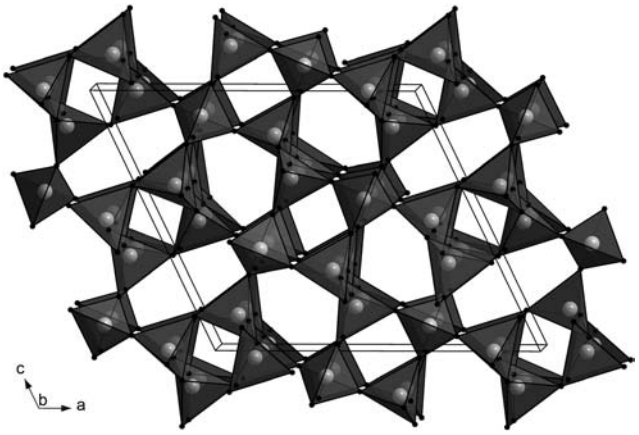

Figure 2. Crystal structure of δ-PON. View along [010] (P: light gray; O/N: black).

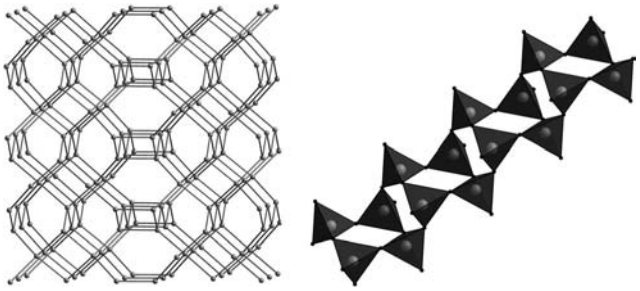

Figure 3. Left: Topological representation of the crystal structure of δ-PON. Right: Section from the crystal structure showing the ladder-like arrangement of 4-rings.

compound as yet. Therefore, δ-PON can be considered a truly novel structure type and correspondingly supplements the few known AB_2 structure types. However, a SiO_2 modification with the same topology in space group *Aea*2 has been predicted and can be found in the Predicted Crystallography Open Database (PCOD; entry 3102887).[16]

P-(O,N) bond lengths vary between 152 and 165 pm, and their variance and the mean bond length are slightly larger than in the other known polymorphs of PON. The bonding angles at the bridging atoms range from 128 to 147°, which is comparable to other PON phases. Deviations from the regular tetrahedral angle vary slightly with values between 104 and 118°. Detailed information on bond lengths and angles can be found in the Supporting Information (Tables S3 and S4). The electrostatic plausibility of the crystal structure was assessed by using the MAPLE (Madelung part of lattice energy) concept.[17] The partial MAPLE values of the atomic sites (O/N = 4460–4778, P = 13941–14878 kJ mol^{-1}) as well as the overall MAPLE value (23809 kJ mol^{-1}) are in good agreement with those calculated for the other PON polymorphs. Notably, the partial MAPLE values of the anion sites are between the literature values for nitrogen (4600–6000 kJ mol^{-1}) and oxygen (2400–2800 kJ mol^{-1}),[18] giving a strong indication for anion disorder.

Since neutron diffraction studies on the known polymorphs of PON by Marchand et al.[9,11] did not show any evidence for O/N-order, we assume similar disorder in δ-PON. To corroborate this hypothesis, δ-PON was characterized further by recording a ^{31}P solid-state NMR spectrum. The chemical shift of $\delta_{iso} = -32.1$ ppm is close to those found for cristobalite-PON ($\delta_{iso} = -26.3$ ppm, see spectrum in the Supporting Information) and $H_3P_8O_8N_9$ ($\delta_{iso} = -31.9$ ppm).[19] As expected for a phase with statistical O/N distribution, the full width at half maximum (FWHM) of the signal is so high that the four individual signals expected for the four crystallographically distinct P atoms cannot be resolved. To rule out the possibility of δ-PON being in fact a phosphorus oxonitride imide, the absence of stoichiometric amounts of hydrogen was confirmed by ^{1}H solid-state NMR spectroscopy as well as FTIR spectroscopy.

With δ-PON, we have found the first polymorph of PON that does not crystallize in a structure type known from SiO_2. This novel AB_2 structure type had only been predicted theoretically so far. With the high-pressure high-temperature condensation of a newly developed amorphous phosphorus oxonitride imide precursor, a powerful synthetic approach towards new high-pressure phases of PON has been established. This method could lead to further high-pressure polymorphs of PON, allowing a structural diversity approaching that of SiO_2. This promising synthesis approach could also be applied to many other systems, possibly facilitating the discovery of a range of novel networks with interesting properties. The high-pressure approach in combination with the inclusion of nitrogen in the framework allows an even wider range of possible frameworks, even including triply coordinated nitrogen atoms or edge-sharing tetrahedra.[20] Even the synthesis of stishovite-like polymorphs with interesting materials properties showing higher coordination numbers of P may be possible.

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[21] Crystal data for δ-PON: formula: PON, $M = 60.98\ \mathrm{g\,mol^{-1}}$, space group $P2_1/c$ (no. 14), $a = 12.2472(2)$, $b = 4.83618(6)$, $c = 10.8604(2)$ Å, $\beta = 115.8026(8)°$, $V = 579.12(2)$ Å^3, $Z = 16$, Cu-Kα_1 radiation ($\lambda = 1.5406$ Å), $T = 298(2)$ K, step size: 0.01°, 474 reflections, 90 parameters, $R_p = 0.03806$, $wR_p = 0.04910$, $\chi^2 = 1.447$, $R_{Bragg} = 0.012128$, background: shifted Chebychev, 32 background parameters. Further details on the 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-423589.

