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Phosphorus Nitrides

A High-Pressure Polymorph of Phosphorus Oxonitride with the Coesite Structure[**]

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Dedicated to Professor Rüdiger Kniep on the occasion of his 70th birthday

Abstract: *The chemical and physical properties of phosphorus oxonitride (PON) closely resemble those of silica, to which it is isosteric. A new high-pressure phase of PON is reported herein. This polymorph, synthesized by using the multianvil technique, crystallizes in the coesite structure. This represents the first occurrence of this very dense network structure outside of* SiO_2*. Phase-pure coesite PON (coe-PON) can be synthesized in bulk at pressures above 15 GPa. This compound was thoroughly characterized by means of powder X-ray diffraction, DFT calculations, and FTIR and MAS NMR spectroscopy, as well as temperature-dependent diffraction. These results represent a major step towards the exploration of the phase diagram of PON at very high pressures and the possibly synthesis of a stishovite-type PON containing hexacoordinate phosphorus.*

Owing to its unique properties, silica (SiO_2) has been of great interest for physicists, chemists, and geoscientists for many decades. This is partly due to its properties and the resultant applications, such as nonlinear optical properties[1] or piezoelectricity,[2] but it is also to a large extent due to the wide variety of crystal structures found for this material.[3] With SiO_2 being the parent compound of the major components of the crust and mantle of the Earth,[4–6] precise knowledge of the phase diagram of silica leads to a detailed understanding of many geological processes. The high-pressure polymorph coesite was artificially synthesized[7] and studied in detail[8,9] before it was first discovered in nature as a product of meteorite impacts.[10] Subsequent investigations showed that the presence of coesite in rocks can serve as an indicator of the material having undergone ultrahigh-pressure metamorphism.[11–13] This enables a detailed understanding of the geological history of these rocks. Similarly, the polymorphs stable at even higher pressures, namely stishovite[14,15] and seifertite,[16,17] can be used as indicators of previous impact events. Stishovite has additionally drawn particular interest because of remarkable mechanical properties. It held the record for the hardest oxide[18] until it was surpassed by cotunnite-type TiO_2 in 2001.[19]

In order to gain a more detailed understanding of the high-pressure behavior of silica-related phases, we have investigated the phase diagram of phosphorus oxonitride PON, which is isosteric to SiO_2[20] and its analogues PN(NH)[21] and $AlPO_4$.[22] Owing to the similar ionic radii (Si^{4+}: 26 pm, P^{5+}: 17 pm; O^{2-}: 135 pm, N^{3-}: 146 pm)[23] some of the polymorphs exhibited by silica can also be found in PON. At ambient pressure, PON adopts a β-cristobalite-type structure and has no known high-temperature polymorphs.[24] The high-pressure phases include quartz-[25] and moganite-type polymorphs.[26] In the case of silica, moganite has only been found in microscopic quantities in nature, whereas it is synthetically accessible in bulk quantities for PON. Recently, we were able to synthesize another polymorph of phosphorus oxonitride that crystallizes in a unique structure type that had not been observed in any other compound before.[27] This indicates that the diversity of possible structure types for PON could possibly even exceed that for SiO_2. A particular factor that could extend the range of possible AB_2 structures in PON is the fact that the nitride ion is able to connect more than two neighboring $P(O,N)_4$ tetrahedra.[28] Notable examples that contain triply bridging nitrogen atoms are α- and β-HP_4N_7,[29,30] P_4N_6O,[31] and the layered oxonitridophosphate $Sr_3P_6O_6N_8$.[32]

Herein, we report the discovery of a new polymorph of PON that crystallizes in the coesite structure type, for which we propose the name coesite PON or *coe*-PON. This high-pressure phase was synthesized in a modified Walker-type multianvil assembly. The starting material cristobalite-type PON was treated at 15.5 GPa and approximately 1300 °C for 60 min. The product could then be isolated as a colorless crystalline solid. Energy-dispersive X-ray (EDX) spectroscopy was used to establish the absence of any elements other than P, O, and N. The crystal structure was elucidated from powder X-ray diffraction data.[33] Structure solution was performed by using the charge-flipping algorithm.[34–36] Both structure solution and Rietveld refinement were carried out by using TOPAS-Academic 4.1.[37] Rietveld refinement showed no signs of any amorphous or crystalline side phases (Figure 1). The unit cell of *coe*-PON ($a = 6.95903(8)$, $b = 12.0610(2)$, $c = 6.96821(8)$ Å, $\beta = 120.0348(7)°$) displays remarkable lattice pseudosymmetry, appearing hexagonal at first glance. The symmetry of the structure itself, however, is

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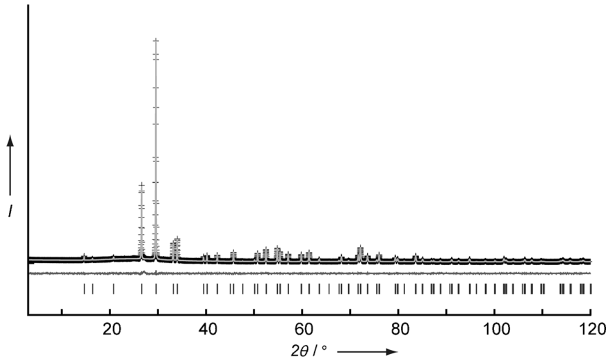

Figure 1. Observed (crosses) and calculated (light gray line) powder diffraction pattern of *coe*-PON, as well as the difference profile (dark gray line). Black vertical bars represent the positions of Bragg reflections.

monoclinic, a fact that has similarly been observed for coesite SiO_2.[9]

The crystal structure (Figure 2) closely resembles that of coesite. The compound is composed of a three-dimensional network of all-side vertex-sharing $P(O,N)_4$ tetrahedra. As with the other known polymorphs of PON, there was no indication of any ordering of the anion positions. We thus assume a statistical disorder of the anions. In the case of cristobalite PON, this was confirmed by neutron diffraction experiments.[38] The topological identity of the networks of coesite SiO_2 and PON is also illustrated by topological analysis with TOPOS.[39,40] Both compounds are described by the point symbol $(4^2.6.8^2.9)(4^2.6^3.8)$.

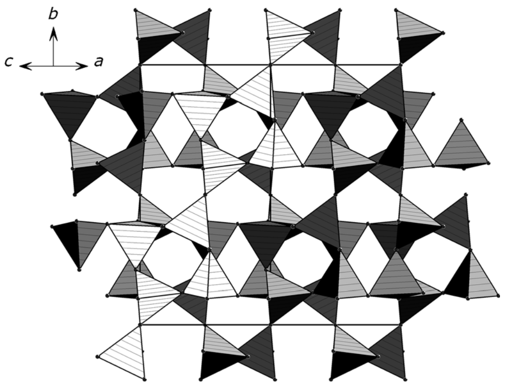

Figure 2. Polyhedral representation of the crystal structure of *coe*-PON in. View along [101]. One fundamental chain is highlighted in white.

According to the nomenclature established by Liebau, the crystal structure of *coe*-PON can be described as loop-branched dreier single chains that are interconnected to form a three-dimensional network. This leads to a loop-branched dreier framework $\{\mathbf{lB}, {}^{3}_{\infty}\}[{}^{3}P_4(O,N)_8]$ similar to that found in feldspars.[41]

The P−(O,N) bond lengths are in the range of 154 to 164 pm (Figure 3). A similarly large variance in the interatomic distances has been observed in δ-PON.[27] The $P(O,N)_4$ tetrahedra are slightly distorted, but to a lesser degree than those in δ-PON. The P-(O,N)-P angles around most of the anion sites range from 137 to 147° and are therefore very similar to those found in coesite SiO_2. The angle P1-(O,N)1-P1, however, exhibits an intriguing value of 180°. Since this same angle occurs in coesite SiO_2 as well and differs greatly from the value of 140° for a strain-free Si-O-Si bond, it has been discussed in detail by Liebau.[41] He came to the conclusion that this angle is not an artifact caused by the fact that the bridging atom resides on an inversion center but is intrinsic to the crystal structure. In order to show the same for *coe*-PON, we also performed the structure solution in the noncentrosymmetric space group *Cc*. This did not lead to a significant deviation of this angle from 180°, thus indicating that the structural model in space group *C*2/*c* is correct. Another possible cause of an apparent angle of 180° could be static or dynamic disorder of the bridging atom around the crystallographic site. Such an effect, which can also be described as a coupled rotation of the involved tetrahedra, has been discussed for β-cristobalite.[42] This would, however, lead to a significantly increased displacement parameter for the anion site. Since the B_{eq} value for (O,N)1 is similar to those of the other anion sites, this phenomenon is unlikely for *coe*-PON.

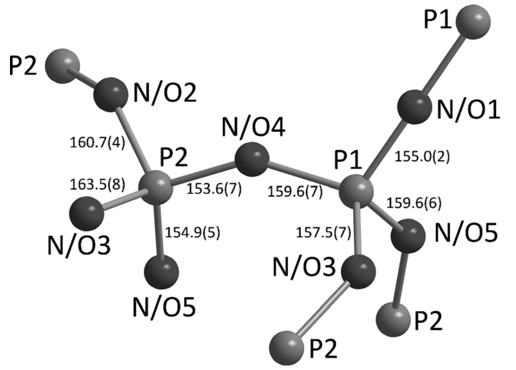

Figure 3. Atomic arrangement and bond lengths in *coe*-PON. Bond lengths are given in pm.

In order to quantify the similarity between the crystal structures of coesite SiO_2 and coesite PON, the two were compared by using the COMPSTRU program of the Bilbao Crystallographic Server.[43] The calculated arithmetic mean of the distance between equivalent atomic sites amounts to just 4.4 pm. This leads to a measure of similarity[44] (Δ) of 0.014, thus indicating that the two crystal structures are in fact very closely related.

DFT calculations were employed to validate our experimental findings. Owing to the statistical O/N disorder, energy–volume curves were calculated for all six chemically reasonable arrangements of O and N. For comparison, the energy–volume curves for cristobalite PON with the lowest energy O/N arrangements were also determined. Details of the calculations and ordered structural models can be found in the Supporting Information. The corresponding enthalpy–pressure diagram (Figure S7 in the Supporting Information) shows that coesite PON is expected to be more stable than the ambient pressure polymorph above 7.5–10.5 GPa, which is in good agreement with the pressure of 15.5 GPa used in the

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synthesis. The predicted bulk modulus for *coe*-PON is in the range of 151 to 170 GPa.

The high-pressure high-temperature conditions used for the synthesis, combined knowledge of the phase diagram of closely related SiO_2, strongly suggest that *coe*-PON is a high-pressure phase of phosphorus oxonitride and therefore metastable at ambient pressure. In order to corroborate this hypothesis, we performed temperature-dependent powder X-ray diffraction up to 1000 °C. The results (Figure 4) show that at ambient pressures, *coe*-PON transforms back into the cristobalite polymorph above 750 °C. This result indicates that temperatures above 700 °C are needed to initiate reconstructive transformations in phosphorus oxonitride, which is consistent with our laboratory experience. At 975 °C, the first signs of thermal decomposition can be observed.

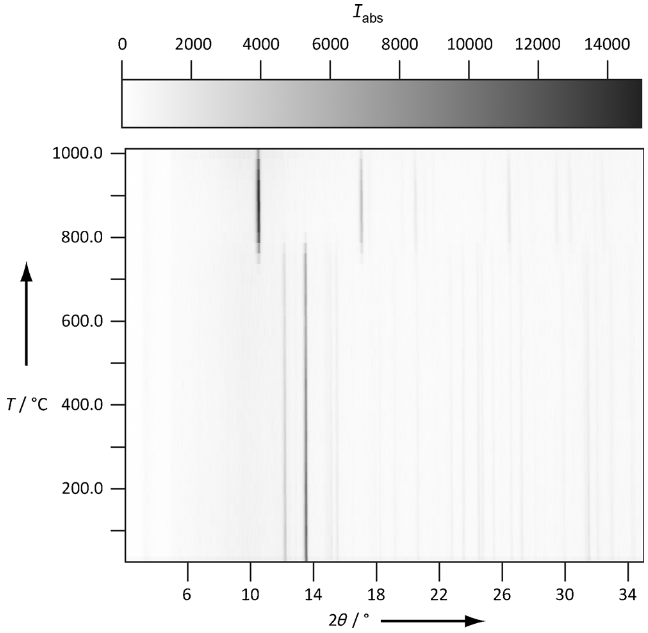

Figure 4. Temperature-dependent powder X-ray diffraction data for *coe*-PON in air. The transformation to cristobalite PON starts at 750 °C.

In order to corroborate the results of the structure solution, a ^{31}P MAS NMR spectrum was acquired (Figure S1). The spectrum shows two rather broad peaks at −48 and −66 ppm that can be attributed to the two crystallographic P sites. The broad signals can be explained by statistical O/N disorder. This leads to a range of distinct local environments around the P nuclei. Since the NMR signal is an average over all of the P sites in the sample, this leads to a broadening of the NMR signals. A similar effect has been observed in the case of δ-PON.[27] In order to rule out the presence of NH groups in the sample, which could in theory replace the isoelectronic O^{2-}, an FTIR spectrum of the sample was collected (Figure S2). It showed no signs of the characteristic N−H vibrations around 3000 cm^{-1}, which is a strong indication of the absence of hydrogen in the sample.

The discovery of *coe*-PON provides new insight into the high-pressure chemistry of phosphorus oxonitride. Previous investigations up to a pressure of 70 GPa with diamond anvil cells at room temperature showed no reconstructive transformations to new high-pressure phases,[45] while experiments in laser-heated diamond anvil cells at 20 GPa led to the formation of the already known moganite PON. The new results presented herein show that it is indeed possible to obtain further high-pressure phases of PON through a combined high-temperature high-pressure approach by using the multianvil technique. The formation of a coesite-type phase shows that the similarity between SiO_2 and PON extends to higher pressures. However, the pressure needed for the transformation of PON (15.5 GPa) is significantly higher than that for SiO_2 (3.5 GPa).[7] It is plausible that this similarity could extend to the extreme pressure phases known for silica. Stishovite-type PON containing hexacoordinate phosphorus might thus be accessible, albeit at even higher pressures than for stishovite SiO_2. The possibility of synthesizing and recovering compounds containing pentacoordinate phosphorus has already been shown for the closely related systems P_3N_5[46] and $P_4N_6(NH)$.[47]

Keywords: high-pressure chemistry · nitrides · phosphorus · solid-state reactions · solid-state structures

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