Stishovite's Relative: A Post-Coesite Form of Phosphorus Oxonitride

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Abstract: Phosphorus oxonitride PON is isoelectronic with SiO₂ and may exhibit a similar broad spectrum of intriguing properties as silica. However, PON has only been sparsely investigated at high-pressure conditions and there has been no evidence on a PON polymorph with an increased coordination number of P (CN > 4). Herein, we report on a post-coesite (pc) PON polymorph exhibiting a stishovite-related structure with P in a (5+1) coordination. The pc-PON was synthesized using the multianvil technique and characterized by powder X-ray diffraction, solid-state NMR, TEM measurements and in situ synchrotron X-ray diffraction in diamond anvil cells. The structure model was verified by single-crystal X-ray diffraction at 1.8 GPa and the isothermal bulk modulus of pc-PON was determined to $K_0 = 163(2)$ GPa. Moreover, an orthorhombic PON polymorph (o-PON) was observed at high-pressure conditions and corroborated as the stable modification at pressures above 17 GPa by DFT calculations.

The pressure-coordination rule, stating that the coordination number increases with an increase of pressure,^[1] has already been verified for fundamental inorganic nitrides and oxides such as BN,^[2] Si₃N₄,^[3] P₃N₅,^[4] CO₂,^[5–8] and SiO₂.^[9–15] Respective high-pressure polymorphs show intriguing properties, such as increased incompressibility, high density or changes in types of chemical bonding. For instance, rutile-type SiO₂ (stishovite), with Si situated in an octahedral six-fold coordination by O, is one of the hardest oxides known.^[9,16,17] Extensive in situ investigations in diamond anvil cells revealed post-stishovite SiO₂ polymorphs with CaCl₂-, α -PbO₂- and high-pressure PdF₂-type structures, which all have the motif of SiO₆ octahedra in common.^[10–15] Phosphorus oxonitride PON is isoelectronic with silica and adopts cristobalite-, moganite- and quartz-type structures, which are isotopic with the eponymous SiO₂ forms.^[18–20] Furthermore, an additional δ -PON modification with a unique structure related to a theoretically predicted SiO₂ polymorph has been synthesized at 12 GPa while at 15.5 GPa a coesite-type (coe) PON form has been prepared, which hitherto represents the top end of the PON phase diagram.^[21,22] PON polymorphs with an increased coordination number of P, however, seem to be

feasible, considering findings from fundamental structural research on solid-state P–N and P–O compounds. Square pyramidal and trigonal bipyramidal PN₅ units have been reported in the high-pressure phases γ -P₃N₅ and γ -HP₄N₇ and six-fold coordinated P has been predicted for the high-pressure phases δ -P₃N₅ and spinel-type BeP₂N₄.^[4,23–26] Recently, five- and six-fold O-coordinated P has been reported for TiPO₄-V and a distorted CaCl₂-related form of AlPO₄, respectively.^[27,28] In contrast, high-pressure polymorphs of PON with an increased coordination number of P (CN > 4), are still unknown. Considering the kinship of PON and SiO₂, a stishovite-type PON polymorph with a six-fold coordination of P may be plausible and is considered the missing link in fundamental structural research on phosphorus (oxo)nitrides.

Herein, we report on a stishovite-related post-coesite (pc) form of PON with a (5+1) coordination of P, which was prepared from cristobalite-type (cri) PON at 20 GPa using a 1000 t hydraulic press and the multianvil technique based on a modified Walker-type setup.^[29,30] Energy dispersive X-ray (EDX) spectroscopy showed no other elements than P, O and N in the sample and any presence of N–H or O–H functionality was ruled out by FTIR spectroscopy. The pc-PON structure was solved and refined from powder X-ray diffraction (PXRD) pattern ($P4_2/mnm$ (no. 136), $a = 4.6184(2)$, $c = 2.45536(9)$ Å, $Z = 2$, $R_{\text{Bragg}} = 0.021$) and cell metrics were confirmed by selected area electron diffraction (SAED) tilting series.^[31] pc-PON adopts a stishovite-related structure with one P site located in an octahedral coordination sphere of O and N (Figure 1a). The refined coordinates of P are close to Wyckoff position $2a$ ($m.m.m$), but refinement indicated a significant displacement. Thus, P was refined at Wyckoff position $4f$ ($m.2m$), which results in a split position of P (site occupation factor (*s.o.f.*) = 0.5) with a 0.874(1) Å distance between the two electron density maxima (Figure 1b). There is, however, no evidence for any superstructure caused by a systematically ordering of P in pc-PON, as there were no additional reflections observed during PXRD, TEM measurements or single-crystal XRD presented below. Considering the split position, P is in a (5+1) coordination by O and N with distorted square pyramidal geometry for the first coordination sphere (Figure 1c). The P(N,O)₅ pyramids share common edges along c and common vertices along $\langle 110 \rangle$. The interatomic distances between P and (N,O) are 1.696(1) Å for equatorial and 1.752(1) Å for axial position, which is in good agreement with the five-fold coordinated P positions in γ -HP₄N₇ and γ -P₃N₅.^[4,23] The P–(N,O) distance of the second axial (N,O) position in pc-PON is 2.626(1) Å corresponding to minor interactions only and thus, this (N,O) position is assigned to the second coordination sphere. The ³¹P solid-state MAS NMR spectrum of pc-PON shows one broadened signal at $\delta = -86.9$ ppm (FWHM = 20 ppm), in line with one crystallographic position of P in the pc-PON structure. Peak broadening may be caused by varying local N/O coordination of P and has been observed in other PON modifications

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before.^[21,22] Moreover, statistic occupation of the split position of P can enhance peak broadening in this case.

A simplified description of the pc-PON structure may be revealed by reducing the split position of P to its center of gravity, resulting in an octahedral coordination of P by N and O atoms. This simplified structure model would be isotypic with stishovite (rutile-type SiO_2) as the $\text{P}(4f, m.2m)$ site ($s.o.f. = 0.5$) would be transformed into a $\text{P}(2a, m.mm)$ site ($s.o.f. = 1$). Thus, pc-PON may be understood as the analog of stishovite in the phase diagram of PON and represents the first phosphorus oxonitride with exclusively five-fold coordination of P. More detailed information on the synthesis of pc-PON and its characterization by PXRD, TEM, EDX, NMR and FTIR is provided in the Supporting Information.

Figure 1. The crystal structure of pc-PON (a) shows a split position for P located in octahedral coordination by O and N (b). An occupation of 0.5 of the P position leads to a (5+1) coordination with distorted square pyramidal geometry (c). P: black, N/O: gray.

In order to investigate pc-PON on its elastic properties, in situ XRD measurements with synchrotron radiation in diamond anvil cells (DAC) were performed. At an initial pressure of 1.8 GPa a single-crystal data set was collected, which verifies the structure model presented above.^[32] Owing to the measuring geometry of DACs the single-crystal (SC) XRD data set is incomplete (77 %). A comparison of the electron density maps and respective standard deviations, however, indicate that PXRD and SC-XRD refinements are tantamount in quality and accuracy, as presented in the Supporting Information. Subsequently, 16 PXRD patterns up to a maximum pressure of almost 40 GPa were collected in which the PXRD pattern of pc-PON is

preserved up to a pressure of ca. 20 GPa. At pressures exceeding 20 GPa, however, a new phase is observed, as reflections in the region $10.0^\circ < 2\theta < 11.5^\circ$ change significantly (Figure 2). The coexistence of both phases at 19.6 GPa is a strong indication for a second order phase transition, which was described by a *translationengleiche* symmetry reduction ($t2$) to the orthorhombic crystal system ($P4_2/mnm$ (no. 136) $\rightarrow Pnnm$ (no. 58)). In order to gain further information on the nature of the tetragonal $\rightarrow$ orthorhombic phase transition, the recovered sample was re-measured at ambient conditions, showing tetragonal symmetry again. Thus, the orthorhombic (o) PON phase is solely stabilized at high pressures and may be the initial product of the multianvil synthesis at 20 GPa, while the tetragonal pc-PON phase might form upon pressure quenching. In turn, pc-PON is unstable at ambient conditions as well, but kinetically inert towards transformation to cri-PON, as indicated by temperature-dependent PXRD.

This reversible tetragonal $\rightarrow$ orthorhombic phase transition of PON is of remarkable similarity to the stishovite ($P4_2/mnm$) $\rightarrow$ CaCl_2 -type SiO_2 ($Pnnm$) phase transition of silica, which is characterized by an alternating tilting of the SiO_6 octahedra in the a - b plane with increasing pressure.^[10,33] Considering a spontaneous strain analysis of pc- and o-PON, the phase transition in PON appears to proceed in a similar way, suggesting an alternating tilting of the P coordination polyhedra and a CaCl_2 -related structure for o-PON (Figure 2).^[33] More detailed information on the experimental setup and the synchrotron measurements as well as on the spontaneous strain formalism is provided in the Supporting Information.

Figure 2. Exemplary PXRD patterns from synchrotron measurements at high-pressure conditions ($\lambda = 0.28874 \text{ \AA}$) with enlarged regions of interest and a schematic illustration of the tetragonal $\rightarrow$ orthorhombic phase transition assumed for PON.

Lattice parameters of pc- and o-PON were refined from PXRD data with the method of Le Bail using tetragonal ($P4_2/mnm$,

$p < 20$ GPa) and orthorhombic ($Pn\bar{n}m$, $p > 20$ GPa) metrics, respectively (Figure 3). Subsequently, the isothermal bulk modulus K_0 of pc-PON was determined to 163(2) GPa from equation of state and with that, pc-PON exhibits a twice as high bulk modulus than cri-PON ($K_0 \approx 80$ GPa).^[34] However, pc-PON seems to be significantly more compressible than stishovite ($K_0 \approx 310$ GPa), which may be due to the (5+1) coordination polyhedra of P being less rigid than the SiO_6 octahedra.^[33] Furthermore, the lattice parameter a was found to be notably more compressible than c ($K_0(a^3) = 109(2)$ GPa, $K_0(c^3) = 927(35)$ GPa), which may be an effect of the $\text{P}(\text{N},\text{O})_5$ pyramids sharing common vertices along $\langle 110 \rangle$, but common edges along c . Thus, a decrease in volume upon compression in pc-PON is mostly effected by a contraction of the cell along a , which in turn corresponds to an axial compression of the $\text{P}(\text{N},\text{O})_{5+1}$ polyhedra and a decrease of the axial P–(O,N) interatomic distances. Consequently, a hitherto unreported regular six-fold coordination of P in phosphorus (oxo)nitrides might be plausible for PON at sufficiently high pressure and may lead to a significant increase of its incompressibility and bulk modulus. More detailed information on the elastic properties of pc-PON is provided in the Supporting Information.

Figure 3. Refined lattice parameters of pc- and o-PON as a function of pressure.

In order to prove experimental findings and to corroborate o-PON as the high-pressure polymorph, DFT calculations within the generalized gradient approximation (GGA) were performed. Accounting for the split position of P a $2 \times 2 \times 2$ supercell was constructed with P at the center of the N/O octahedra and different charge neutral N/O-ordering models were constructed to approximate statistical N/O-disorder. Disregarding unreasonable or computationally collapsing structures, relaxation of the supercell resulted in an alternating displacement of P atoms from the center of the $\text{P}(\text{N},\text{O})_6$ octahedra, in line with the experimental findings of the split position of P (Figure 4a). This systematic ordering of P appears as a coupled feature of the introduced N/O-ordering, as the displacement of each P site is systematically directed towards an axial N position. As a result N and O are found exclusively in three- and two-fold coordination, respectively, as expressed by the Niggli formula $\text{[P}^{[5]}\text{O}^{[2]}\text{N}^{[3]}]$.^[35] Thus, the axial P–N interaction seems to be more favorable than the axial P–O

interaction. Concerning the experimental data presented above, there are, however, no indications of a superstructure caused by a systematic ordering of P. Considering the favored axial P–N interaction this random distribution of P may be correlated with a N/O-disorder in pc-PON.

The tetragonal structure model was used for construction of an orthorhombic model and subsequent energy-volume calculations of both cells. The respective total energies of both phases corroborate o-PON the stable modification above 17 GPa. The transition pressure was determined from the relative enthalpy plot (Figure 4b) and is in accordance with the experimental findings, considering the approximated structure model used for the DFT calculations. More detailed information on the theoretical study of both PON polymorphs is provided in the Supporting Information.

Figure 4. Approximated structure model of pc-PON from structure relaxation with N/O-order used for DFT calculations (a). P: black, O: gray, N: white. Relative enthalpy plot with transition pressure of 17 GPa derived from calculated E - V data of pc- and o-PON (b).

Recapitulating, the phase diagram of PON is extended by two high-pressure polymorphs. pc-PON adopts a stishovite-related structure with a split position of P in a (5+1) coordination and has been considered the missing link in fundamental structural research on phosphorus (oxo)nitrides, previously. In addition, o-PON is found to be the stable polymorph at pressures > 20 GPa, which has been proven by ab initio calculations, as well. In turn, P is just on the brink of a regular six-fold coordination in PON polymorphs and its experimental evidence will be the great goal of future high-pressure investigations.

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