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LETTER TO THE EDITOR

High pressure behaviour of the β -cristobalite-type phase of phosphorus oxynitride, PON

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Abstract. Phosphorus oxynitride, PON, is isoelectronic with SiO₂ and can be used as a model for silica. The crystalline behaviour of the β -cristobalite-type phase was determined as a function of pressure by angular dispersive x-ray diffraction in a diamond anvil cell to 48 GPa. No evidence for a phase transition or amorphization was observed. The cell parameters were measured as a function of pressure. The macroscopic bulk modulus is 71(3) GPa with a first pressure derivative of 3.2(5). The polyhedral bulk modulus was inferred to be about 800 GPa, assuming that the tetrahedra remain regular.

Phosphorus oxynitride, PON, is isoelectronic with SiO₂ and is its chemical analogue. Under normal conditions, the crystal structures of the two compounds are very similar. At room temperature PON adopts a $P\bar{4}$ structure, which is a very slight distortion of the β -cristobalite structure $I4\bar{2}d$, from which it cannot be distinguished by x-ray diffraction. The oxygen and nitrogen atoms are randomly distributed between the two anionic sites. The atomic positions determined from neutron diffraction [1] deviate from the positions in the $I4\bar{2}d$ structure by only a few standard deviations. Under normal conditions, the cell parameters are $a = 4.6266 \text{ \AA}$ and $c = 7.0037 \text{ \AA}$ with $Z = 4$. The existence of a phase with a hexagonal cell has been reported at 4.5 GPa and 700 °C but the pressure–temperature (P – T) phase diagram of PON is not known.

At room temperature SiO₂ can be found in the metastable α -cristobalite phase of space group $P4_12_12_1$, which transforms to the $I4\bar{2}d$ β -cristobalite structure above 275 °C; the two structures [2] are derived from the parent $Fd\bar{3}m$ structure by different rotations of the SiO₄ tetrahedra. Silicon dioxide displays a complex P – T behaviour [3] with several polymorphs: tridymite, α - and β -cristobalite, α - and β -quartz, coesite and stishovite (rutile structure). The large variety of low-pressure SiO₂ polymorphs is a result of the many ways that tetrahedra can be linked. Structures based on networks of corner-sharing tetrahedra of anions coordinating a central cation are among the most important in crystal chemistry. The phase transition behaviour of framework silicates has been the subject of major interest in recent years. With the concomitant development of mean-field theories of phase transition behaviour, computer modelling has facilitated a profound reevaluation of

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structural behaviour. In order to investigate in more detail the complex relationship between polymorphs in framework silicates, the lattice behaviour of the β -cristobalite phase of PON, a structure which cannot at present be studied in SiO_2 as it is a high-temperature phase, was examined by x-ray diffraction as a function of pressure.

X-ray amorphous, PON phosphorus oxynitride, was prepared from ammonium dihydrogen phosphate and urea $(\text{NH}_2)_2\text{CO}$ or melamine $(\text{NCNH}_2)_3$, following Sommer [4]. Crystallization was obtained after heating the powder in an evacuated quartz ampoule at 700–800 °C for several days. The purity of the sample was verified by direct chemical analysis of the nitrogen content as NH_3 , according to a previously described procedure [5].

The sample was then mixed with silicone grease as the pressure transmitting medium and was placed in a 120 μm diameter hole of a steel gasket preindented to a thickness of 150 μm , along with a small amount of ruby and TiC powders between the anvils (culet of 500 μm) of a diamond anvil cell. Pressures were obtained from the shift of the R_1 and R_2 fluorescence lines of ruby [6] emitted from a definite narrow region of the sample about 15 μm in diameter. The titanium carbide allows the radiation from a 50 W Nd^{3+} :YAG laser to be absorbed for heating. The focal spot (10 μm diameter) was swept across the whole sample. This provided a relaxation of the anisotropic stresses as shown by the changes in the ruby emission: the two lines of the ruby doublet were then well separated as at normal pressure, except for the highest pressure, where they were easily deconvoluted by fitting two Lorentzians of the same width to the data. Pressure differences indicated from the shifts of the two lines were less than 1 GPa at the highest pressures and the whole pressure uncertainty is estimated to be equal to this value.

X-ray diffraction patterns were obtained on an imaging plate placed at distances of 85.09 and 144.98 mm from the sample [7]. The incident x-ray beam from a fine-focus Mo tube operated at 13 mA and 50 kV was filtered using Zr foil and collimated to 130 μm . Exposure times were 24 or 48 h. Intensities were integrated as a function of the diffraction angle 2θ to yield standard diffraction patterns. The Debye–Scherrer pattern of the starting sample was in good agreement with the reported diffraction pattern.

Upon increasing pressure, five intense lines (101, 112, 213, 204 and 312) were observed up to 9 GPa (the 211 line was mixed with a line from the iron gasket and could not be observed). From 9 to 25 GPa, only the 101 and 112 lines were observed as lines from α and ϵ iron from the gasket overlapped the other sample lines. Above 25 GPa, the 101, 112 and 213 lines were observed. After decompression, a Debye pattern obtained from the sample still in the gasket yielded the same pattern as from the starting sample although measured intensities were much weaker. No evidence for amorphization was noticed under pressure, but the amplitudes of the diffraction lines decreased regularly with a small increase of their widths.

The β -cristobalite-type phase of PON is stable at least up to 48 GPa. The pressure variations of the cell parameters, the c/a ratio and the volume are displayed in figures 1 and 2. The a parameter decreases much more rapidly with pressure than the c parameter and the c/a ratio increases linearly with pressure. The experimental data for the volume of the cristobalite phase of PON has been fitted using a Birch–Murnaghan equation of state [8]:

$$P = 1.5B_0 \left[(V/V_0)^{-7/3} - (V/V_0)^{-5/3} \right] \left[1 + 0.75(B'_0 - 4) \left((V/V_0)^{-2/3} - 1 \right) \right]$$

where B_0 is the bulk modulus, B'_0 its first pressure derivative and V_0 the volume at ambient, respectively. The bulk modulus is 71(3) GPa and the first pressure derivative is 3.2(5).

The α - and β -cristobalite structures of space groups $P4_12_12$ and $I4\bar{2}d$, respectively, are derived from a common parent structure of space group $Fd\bar{3}m$ by rotations of the SiO_4

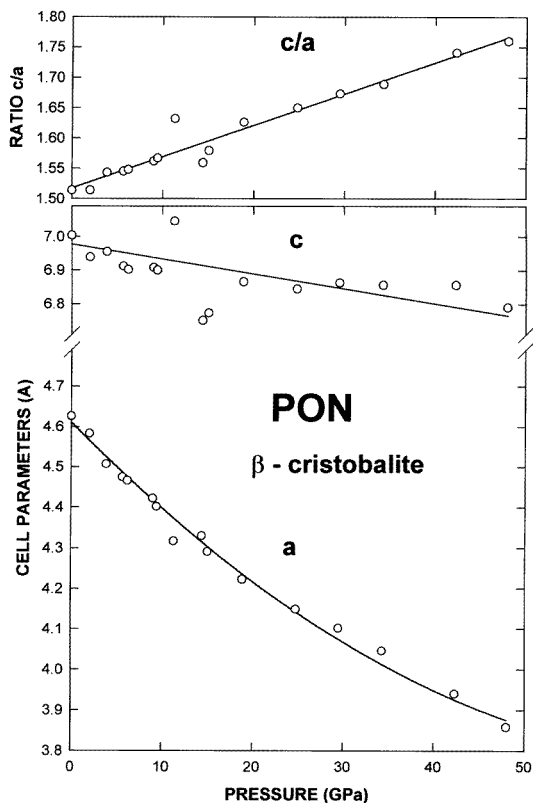


Figure 1. Cell parameters (Å) and c/a ratio of the tetragonal β -cristobalite-type PON as a function of pressure (solid lines, least squares fits to the data).

tetrahedra. In the β -cristobalite structure, the rotation angle ϕ and the oxygen positional parameter x are simply related [2] by $\phi = -\tan^{-1}(4x)$. Assuming the tetrahedra are regular, the oxygen position is directly related to the c/a ratio: $c/a = (2 + 32x^2)^{1/2}$ and the Si–O–Si angle is given by $\cos^{-1}(16x^2 - 3)/(48x^2 + 3)$; the shortest O–O distance, the tetrahedron edge [2], is thus $c/(8)^{1/2}$.

The structure of phosphorus oxynitride PON is of $P\bar{4}$ symmetry, but as the atomic positions are very close to those of the $I4\bar{2}d$ group [1] we assume this last structure in order to evaluate the effect of pressure. The $-x$ parameter is 0.138 at normal pressure as determined from neutron scattering [1]; it is larger than the 0.095 indicated by the c/a ratio assuming regular tetrahedra. The same situation is observed for SiO_2 . All the (O, N)–(O, N) distances are actually not equal ($2.56 \text{ \AA} \times 4$ and $2.64 \text{ \AA} \times 2$). Under high pressure, these distances would decrease to $2.39 \text{ \AA} \times 4$ and $2.35 \text{ \AA} \times 2$ at 30 GPa assuming that x keeps its normal pressure value (notice the change in the bond distribution). However, the c/a ratio increases (figure 1) with pressure which indicates an increase of the $-x$ value to 0.16; taking account of the larger measured (0.138) $-x$ value at zero pressure, the increase of the c/a ratio corresponds to a higher value, $-x = 0.20$ at 30 GPa. The (O, N)–(O, N) distances are then $2.53 \text{ \AA} \times 4$ and $2.62 \text{ \AA} \times 2$. The increase in the $-x$ position with pressure considerably slows down the decrease in the (O, N)–(O, N) distances.

The P–(O, N) distance calculated in the $I4\bar{2}d$ structure is 1.586 \AA at normal pressure

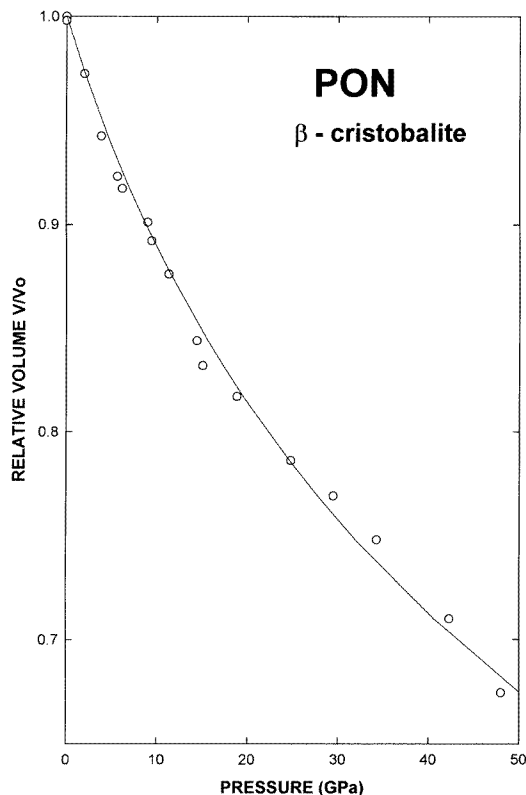


Figure 2. Relative volume of PON as a function of pressure (solid line, Birch–Murnaghan equation of state with parameters as given in the text).

which is the average value of the distances observed by neutron diffraction in the $P\bar{4}$ structure (the values range from 1.582 to 1.592 Å). At 30 GPa, this value is reduced to 1.568 Å ($-x = 0.20$). From these P–(O,N) distances, a mean polyhedral bulk modulus of 870 GPa is obtained.

This value for the polyhedral bulk modulus of β -cristobalite PON can be compared with the value [9] deduced from the polyhedral bulk modulus measured in quartz SiO_2 , 500 GPa. The polyhedral bulk modulus [9] of an ionic compound is proportional to $Z_a Z_c / d^3$ where Z_a and Z_c are the anionic and cationic charges and d the mean cation–anion distance; according to this relationship the polyhedral bulk modulus of PON should be $B_{\text{SiO}_2} (12.5/8) (1.62/1.59)^3 = (1.65) B_{\text{SiO}_2} = 830$ GPa, which is close to the above value deduced for β -cristobalite PON.

The macroscopic bulk modulus is very low compared to this value; this is due to the tilting of the polyhedra and the bending of the P–(O,N)–P angle. The variation of this angle can be estimated from the c/a ratio, assuming regular tetrahedra: the P–(O,N)–P angle decreases by about 40° at 30 GPa. This bending is very large, but it is of the same order as observed in α -cristobalite SiO_2 , where it decreases by 6° GPa^{-1} at low pressures [10]. This shows that the variations of the intertetrahedra angles are alike in β -cristobalite PON and α -cristobalite SiO_2 . The bending and tilting are around axes which are differently oriented with respect to the lattice cells and the c/a ratios vary in opposite directions [10].

The bulk modulus of β -cristobalite PON 71.2 GPa, is considerably larger than that of α -cristobalite SiO₂ (11.5, 16.4 or 18 GPa as obtained using different measurement techniques [3]). The difference is not primarily due to the different lengths of the cation–anion bonds or the electronic charges, but rather arises from the different structures. In the $I4\bar{2}d$ structure, the symmetry reduces the possible tilting and bending of the tetrahedra with respect to the $P4_12_12$ structure, thus yielding a higher bulk modulus. As no lattice change was observed to 48 GPa, we infer that the small distortion from the $I4\bar{2}d$ structure observed at normal pressure does not increase with pressure, but, on the contrary, that it may decrease.

In PON, the high-pressure behaviour of the tetrahedra was inferred from the crystallographic changes, assuming regular tetrahedra. The increase in the $-x$ position allows for a small volume reduction of the tetrahedra and a small decrease of the P–(O,N) distances. The tilting and bending of the tetrahedra are very marked, but do not induce a structure change.

The existence of a β -cristobalite phase at room temperature in phosphorus oxynitride PON, which is isoelectronic with SiO₂ and is its chemical analogue, permitted the experimental investigation of corner-linked tetrahedra at high pressure in a structure, which has not been studied in SiO₂.

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