

A moganite-type phase in the silica analog phosphorus oxynitride

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ABSTRACT

A new polymorph of phosphorus oxynitride (PON) a silica analog has been recovered at ambient pressure by quenching after a treatment at 850 °C under a pressure of 2.5 GPa using cristobalite- or quartz-type phases as starting materials. This PON polymorph is a thermodynamically stable phase with its own stability field in a *P-T* diagram. The structure of this PON phase was refined by the Rietveld method from an X-ray powder diffractogram. It is isostructural with “moganite” (SiO₂). The discovery of this PON polymorph should stimulate a renewed interest in the occurrence of this phase in the silica system, because “moganite” may have a small but defined *P-T* stability field. These results confirm the structure of “moganite” as a new structure-type in AX₂ compounds.

INTRODUCTION

The natural abundance, geological and geophysical importance, and technological properties of silica make it one of the most thoroughly studied compounds. Its polymorphism is very complex (Heaney et al. 1994), as the numerous crystalline and amorphous phases are built of corner-sharing SiO₄ tetrahedra (below about 10 GPa). These tetrahedra can be linked in many different ways and, in addition, are able to tilt easily under the influence of temperature and/or pressure. Although silica polymorphism has been studied extensively, the stability of the phases at atmospheric or low pressures (below 1 GPa) is not yet established clearly. At atmospheric pressure, cristobalite is the stable high-temperature phase; quartz is a lower-temperature higher-pressure phase, which is stable at room temperature. Both quartz and cristobalite undergo displacive α - β transitions. Whether β -quartz transforms directly to cristobalite, or whether there is a stable phase field for tridymite, an intermediate phase between quartz and cristobalite has been disputed (Navrotsky 1994). The calculated cristobalite-tridymite phase boundary does not agree well with reversal experiments of Swamy et al. (1994). It is not yet clear whether tridymite has a stability field in the pure SiO₂ system; furthermore, several modifications of tridymite exist. A new silica polymorph was found in some of the ignimbrite flows of the Mogan formation of Gran Canaria and was described by Flörke et al. (1976). This polymorph of silica has not yet been recognized by the I.M.A. as a mineral species and will be referred to herein as “moganite.” This polymorph occurs as microcrystalline fillings of cavities, fissures, and cooling cracks in natural formations. The presence of 2–3 wt% water was detected in natural samples but this water is not essential to the structure. Moganite persists at temperatures at which the samples have already lost their entire content of water. This novel silica polymorph was later shown by Heaney and Post (1992) to be widespread in microcrystalline quartz varieties, and its presence may explain differences

in phase boundary determinations using natural samples of quartz. Moganite may be a stable phase of silica; however, it has not yet been synthesized experimentally nor has its *P-T* field of thermodynamic stability been determined.

Many compounds have structures built of corner-sharing tetrahedra and display several phases isostructural with those observed among the silica polymorphs. GeO₄ tetrahedra are larger than the SiO₄ tetrahedra, and the pressure-induced transitions in GeO₂ are lowered with respect to those in silica and thus the stability fields of the lower pressure phases are reduced. The stable phases at atmospheric pressure are the quartz-type at high temperature and the rutile-type at low temperature; the latter phase is built of octahedra like those found in stishovite, which is found above 9 GPa. Several ABO₄ (A = B, Al, Ga, and B = As, P) silica analogs crystallize in the cristobalite- or quartz-type structures as described by O'Keefe and Hyde (1976). For example, BPO₄ and BAsO₄ crystallize in cristobalite-type structures at atmospheric pressure and transform under higher pressure to the quartz-type structures (Fukunaga and Yamaoka 1979). However, the different sizes of the AO₄ and BO₄ tetrahedra make comparisons with silica difficult.

Other silica analogs exist, in which there are only one cation and two anions of approximately the same size. Phosphorus oxynitride, PON, is one such example. At atmospheric pressure, Boubkir et al. (1989) showed by neutron diffraction that PON adopts a slightly distorted variant of the structure of β -cristobalite, the high-temperature polymorph of silica. The structure belongs to the space group *P*4, *Z* = 4, with *a* = 4.6266(1) Å and *c* = 7.0037(3) Å. The atomic positions are displaced by only a few standard deviations with respect to the positions in the *I*4*2d* structure type found in silica. The oxygen and nitrogen atoms are completely disordered over 4h sites. At 4.5 GPa and 750 °C, Miller et al. (1981) observed that cristobalite-type PON transforms to a quartz-type phase with a trigonal unit cell. The structure of this phase was refined by Léger et al. (1998) by neutron diffraction at atmospheric conditions [P3₂21, *Z* = 3; *a* = 4.757(4) Å, *c* = 5.2460(2) Å]. The oxygen and nitrogen atoms are disordered over the available anion sites. The structure

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is very close to that of α -quartz ($P3_221$, $Z = 3$; $a = 4.913 \text{ \AA}$ and $c = 5.405 \text{ \AA}$) and the fractional atomic coordinates differ by less than 0.008.

The structures of these PON phases and those of the silica polymorphs are built of AX_4 tetrahedra. Because P^{5+} is smaller than Si^{4+} , the $P(O,N)_4$ tetrahedra are smaller than the SiO_4 tetrahedra in SiO_2 , and higher pressures are required than for SiO_2 to induce phase changes in PON. The quartz-type phase of PON is effectively prepared only at high pressure and not at atmospheric pressure. In PON, the phase transformations are displaced toward higher pressures relative to those in SiO_2 leading to extended fields of stability facilitating the study of the lower pressure phases.

In this Letter, we report the occurrence of a new phase in PON obtained by high-pressure, high-temperature treatment. This is a stable phase because it can be obtained either from the cristobalite- or the quartz-type phases; it has a structure that is very similar to moganite. The pressure-induced polymorphism in PON is thus very similar to that of SiO_2 and could shed light on the polymorphism of SiO_2 and help in identifying potential thermodynamically stable phases at lower pressures.

EXPERIMENTAL PROCEDURE AND RESULTS

Cristobalite-type PON was prepared as described previously by Boubkir et al. (1989). No trace of any other crystalline phase was detected. Transformation of PON from the cristobalite- to the quartz-type phase occurred at 4.5 GPa and 750 °C, as reported previously by Miller et al. (1981) using the same techniques as described below. Cristobalite- and quartz-type PON samples were used as the starting materials for the high-pressure synthesis of moganite-type PON.

Samples of 10–50 mg were placed in crucibles made of platinum or in gold tubes closed by end disks; these crucibles were placed in boron nitride tubes surrounded by a graphite heater and pyrophyllite jackets. They were subjected to high-pressure, high-temperature treatments in a belt type apparatus as described by Boire et al. (1991). The pressure was first increased at room temperature and was determined from a previous calibration curve. The temperature was then increased at constant load pressure, and the temperature at the center of the cell was monitored with a chromel-alumel thermocouple. The vertical temperature gradients in the high-pressure cell of about 60 °C/mm were measured with a second off-center thermocouple. In a single run, several samples placed at different heights along the vertical axis thus could be subjected to the same pressure but different temperatures. After temperature quenching followed by slow decompression, the samples were recovered and analyzed using an X-ray diffractometer ($CuK\alpha$ radiation) equipped with a curved graphite diffracted-beam monochromator.

Treatment of the cristobalite phase of PON at 2.5 GPa and 850 °C for one hour yielded a new phase that was isostructural with moganite. This recovered sample consisted almost entirely of the pure moganite-type phase, with only 1.6% of the quartz-type phase and 1.1% of the cristobalite-type phase (Fig. 1). The temperature gradient in the high-pressure cell proved to be sufficient to obtain different transformation yields according to the exact temperature, which can explain the presence of quartz- and cristobalite-type phases in the recovered samples. At 800 °C, the conversion of cristobalite- to moganite-type PON was not complete, and about

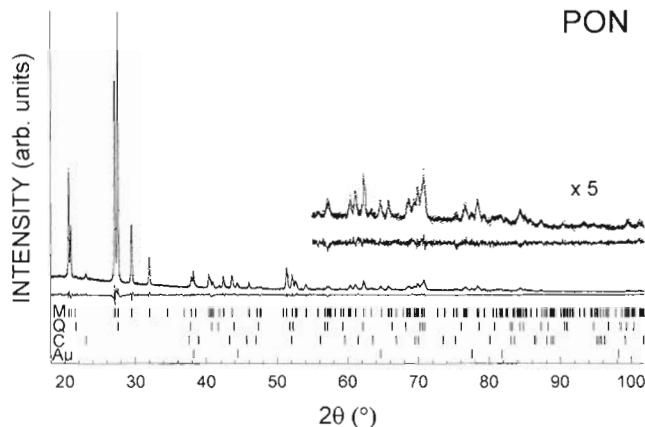


FIGURE 1. Experimental (·) and calculated (solid line) X-ray ($CuK\alpha$ radiation) powder diffraction profile from the Rietveld refinement of moganite-type (M) PON. Intensity is in arbitrary units and the difference profile is shown on the same scale; vertical bars indicate all possible Bragg reflections. Some quartz- and cristobalite-type (Q and C, respectively) PON was detected (1.6 and 1.1%, respectively); trace gold from the crucible was also detected on the surface sample.

6% of the former remained after one hour. In comparison, 30% of the cristobalite-type PON remained after one hour at 775 °C. At 700 °C, no conversion was observed. Complete conversion of the cristobalite- to the moganite-type phase was obtained at 1.8 GPa and 900 °C. Starting from the quartz-type phase, the resultant moganite-type phase was mixed with 2% cristobalite-type phase at 2.5 GPa and 835 °C. At 750 °C, little transformation was obtained, and the recovered sample consisted of 80% untransformed quartz-type and 20% moganite-type phases.

These experiments reveal that moganite-type PON was obtained at 2.5 GPa and 850 °C starting from either the cristobalite- or the quartz-type phases. Moganite-type PON is thus a thermodynamically stable phase with its own field stability in the P - T diagram.

The X-ray powder diffractogram of this new PON phase is shown in Figure 1. It is very similar to the diffraction pattern of moganite obtained by Mieke and Graetsch (1992). However, the diffraction lines from PON are much sharper than those reported for moganite and a crystallite size on the order of 70 nm was deduced from their widths. This was in agreement with the visual examination of the sample. After the high-pressure synthesis, the sample was a sintered powder that appeared grayish; after grinding, translucent grains (1–10 μm in size with no particular shapes)

TABLE 1. Cell parameters for the moganite-type phases of PON and SiO_2

Cell parameters	PON	SiO_2^*
a (Å)	8.5173 (5)	8.758 (2)
b (Å)	4.7453 (3)	4.876 (1)
c (Å)	10.3990 (6)	10.715 (2)
β (°)	90.00 (1)	90.08 (3)
V (Å ³)	420.30	457.57

* Cell parameters of Mieke and Graetsch (1992).

TABLE 2. Atomic positions in the moganite-type phases of PON* and SiO₂

Position	PON			SiO ₂ [†]		
	x	y	z	x	y	z
A1	0.25	-0.0131(20)	0	0.25	-0.0092(17)	0
A2	0.0031(7)	0.2429(5)	0.1653(3)	0.0115(4)	0.2533(6)	0.1678(2)
X1	-0.0050(16)	0.0602(11)	0.2904(5)	-0.0314(12)	0.0680(13)	0.2860(5)
X2	0.1648(9)	0.1842(19)	0.0987(7)	0.1711	0.1770	0.1050
X3	-0.1330(8)	0.2022(19)	0.0715(8)	-0.1343(5)	0.2148(12)	0.0739(8)

Notes: $I2/a$, $Z = 12$; A = P or Si, X = (O, N) or O.

* B_{ov} (Å²) = 3.86(3).

[†]Positions of Miehé and Graetsch (1992).

composed of aggregated smaller particles were observed.

Structure refinements were performed using a moganite structural model (see Tables 1 and 2) with the Fullprof program (Rodríguez-Carvajal, unpublished). Four phases were included in the refinement: the cristobalite-, quartz-, and moganite-type PON phases and gold metal (trace from the crucible); 97% of the investigated sample was in the moganite-type phase. For the latter, the scale factor, the line shape parameters, the lattice constants, the atomic positions and the overall atomic displacement parameter were refined. For the cristobalite- and quartz-type phases, only the scale factors were refined; for gold, the scale factor, the line-shape parameters, the lattice constant, and the overall atomic displacement parameter were refined. The refinement converged rapidly and it was not necessary to impose any constraints in contrast to the study of Miehé and Graetsch (1992) in which it was necessary to fix the position of 1 O atom (O2) based on the results of distance least-squares calculations. The Bragg agreement factor was 4.8%; the unweighted profile and weighted profile agreement factors were 14.9 and 13.3%, respectively.

The structure of moganite-type PON is monoclinic, $I2/a$, $Z = 12$, $a = 8.5173(5)$ Å, $b = 4.7453(3)$ Å, $c = 10.3990(6)$ Å, and $\beta = 90.00(1)^\circ$. The oxygen and nitrogen atoms were assumed to be disordered over the available anion sites as in the quartz-type phase of PON, and their occupation factor was set to 0.5. Atoms are on the general 8f positions except for P(1) which is on 4e positions ($1/4, y, 0$). The atomic positions in moganite-type PON are in-

deed very close to those in moganite (Table 2). The refined fractional atomic coordinates of phosphorus and (O,N) differ from the respective values of silicon and oxygen in silica by less than 0.020 and in most cases by less than 0.008. The A-X distances in the AX₄ tetrahedra are given in Table 3; they are typically 0.06 Å less in PON than in SiO₂ and range from 1.527(9) to 1.575(6) Å in PON and 1.596 to 1.636 Å in SiO₂ (average 1.554 and 1.615 Å, respectively).

The structure of moganite was described by Miehé and Graetsch (1992). It is based on alternating slabs of left- and right-handed quartz. In addition to the six- and eight-membered rings, the structure contains four-membered rings of SiO₄ tetrahedra, which form chains in the direction of the x axis. Chains of this type are not known in other silica polymorphs, but they do occur in aluminosilicates.

DISCUSSION

The occurrence of the moganite-type phase in PON confirms the close structural similarities between PON and SiO₂. The atomic positions observed in the PON and SiO₂ polymorphs are always very close in each structure-type adopted. The three phases known in PON under atmospheric conditions or at high pressure have the same structures as three phases of silica obtained at atmospheric pressure, although there is a slight distortion in the case of the cristobalite-type PON phase.

Two of these PON polymorphs cannot be prepared at atmospheric pressure but only under high pressure, which shows that the stability fields of the lower pressure phases are extended toward higher pressures in PON compared to SiO₂. The moganite-type phase of PON is found between the cristobalite- and quartz-type phases upon increasing pressure at high temperature: it is a high-pressure, high-temperature phase with respect to the cristobalite-type phase.

Under atmospheric conditions, the molar volumes for the cristobalite-, moganite- and quartz-type phases of PON are 22.58, 21.05, and 20.64 cm³, respectively. In silica, the molar volumes of the corresponding phases (25.93, 22.97, and 22.69 cm³) follow the same trend, and the stability field of moganite should lie in the same relative place, between cristobalite and quartz. This is precisely where tridymite is found, the thermodynamic stability of which has not been confirmed. However, the relative volume difference between the moganite- and quartz-type phases is larger in PON (2.0%) than in silica (1.2%). This difference could explain why the moganite-type phase can be readily isolated in PON whereas in silica, it is always found mixed with microcrystalline

TABLE 3. Selected bond distances (Å) in moganite-type PON and SiO₂ at ambient

	PON	SiO ₂ [*]
A1 - X2	1.568(10)	1.603
A1 - X2 [†]	1.568(10)	1.603
A1 - X3 [‡]	1.533(10)	1.630
A1 - X3 [§]	1.533(10)	1.630
Mean	1.550	1.616
A2 - X1	1.564(6)	1.602
A2 - X1	1.575(6)	1.621
A2 - X2	1.567(9)	1.596
A2 - X3	1.527(9)	1.636
Mean	1.558	1.614

*Values of Miehé and Graetsch (1992) with O2 fixed based on results of distance least-squares calculations.

[†] $1/2 - x, y, -z$.

[‡] $-x, -y, -z$.

[§] $1/2 + x, -y, z$.

^{||} $-x, 1/2 + y, 1/2 - z$.

quartz. Moganite could be the thermodynamically stable silica phase under temperature and pressure conditions close to the quartz-tridymite boundary. However, the question of the stability of moganite has not been answered, as stated by Navrotsky (1994). Upon heating a moganite sample at 900 °C, the beginning of a reconstructive transformation to disordered cristobalite was detected by Mieke and Graetsch (1992). No tridymite phase was observed, although this transformation occurs in the temperature range where tridymite is generally encountered. This confirms that the stability field of moganite could occupy part of that currently attributed to tridymite. Moganite has not been obtained via direct synthesis.

The smaller size of the $P(O,N)_4$ tetrahedron relative to that of SiO_4 widens the pressure fields of stability for the lower pressure phases, which allowed for the discovery of the P - T stability field of the moganite-type phase of PON. The stability field of moganite itself may be small and partially occupy that attributed to tridymite. In addition, the present results confirm the moganite-type structure as a new structure-type in AX_2 compounds.

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