

## 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” (SiO<sub>2</sub>). 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 AX<sub>2</sub> 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 SiO<sub>4</sub> 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  $\alpha$ - $\beta$  transitions. Whether  $\beta$ -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 SiO<sub>2</sub> 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. GeO<sub>4</sub> tetrahedra are larger than the SiO<sub>4</sub> tetrahedra, and the pressure-induced transitions in GeO<sub>2</sub> 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 ABO<sub>4</sub> (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, BPO<sub>4</sub> and BAsO<sub>4</sub> 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 AO<sub>4</sub> and BO<sub>4</sub> 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  $\beta$ -cristobalite, the high-temperature polymorph of silica. The structure belongs to the space group  $P\bar{4}$ ,  $Z = 4$ , 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  $I\bar{4}2d$  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 [ $P3_21$ ,  $Z = 3$ ;  $a = 4.757(4)$  Å,  $c = 5.2460(2)$  Å]. The oxygen and nitrogen atoms are disordered over the available anion sites. The structure

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