Collapsing Cristobalitelike Structures in Silica Analogues at High Pressure

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The cristobalitelike forms of the ternary silica analogues BPO_4 and $BAsO_4$ were investigated at high pressure by x-ray diffraction and theoretical methods. The behavior of these compounds represents an extreme case in which the tilt angle of the constituent tetrahedra increases in a spectacular way at high pressure resulting in a major change in topology from a cristobalitelike framework towards a "collapsed cristobalite" structure. These compounds provide the first examples of the collapse of a framework structure to a close-packed form in a continuous manner without an intervening phase transition.

Framework silicates represent an important class of compounds, which are of great interest for solid state physics, crystal chemistry, and Earth and materials science. These compounds include many rock-forming minerals (quartz, feldspars, etc.) and technologically important materials (zeolites, etc.). Some of these materials exhibit interesting physical properties such as negative thermal expansion. The structures of these solids can be considered to be built up of relatively rigid polyhedra, tetrahedra in the case of silicates and analogue materials. These polyhedra are linked by their corners to form relatively flexible frameworks, in which polyhedral tilting is allowed. The physical and thermodynamic properties of these materials have been linked to polyhedral tilting and to rigid unit modes of vibration of the constituent polyhedra [1]. The ideal-high-cristobalite structure type (space group $Fd\bar{3}m$, $Z = 8$) is the prototype for the cristobalite group. This group includes the high-temperature, disordered β-cristobalite structure (space group $Fd\bar{3}m$, $Z = 8$), the low-temperature ordered, α-cristobalite type, and, in the case of systems with very small cations such as boron or phosphorus, partially collapsed cristobalitelike structures [2,3]. The latter (space group $I\bar{4}2d$ or $I\bar{4}$ for AX_2 or ABX_4 compounds, respectively, $Z = 4$) are obtained from the parent ideal-high-cristobalite structure type by tilting the tetrahedra about their twofold axes parallel to **c**. In the present Letter, x-ray diffraction and theoretical results are used to show, for the first time, that pressure can drive this process towards its extreme limit leading to a collapsed structure based on a cubic close-packed (ccp) anion sublattice. This tilting process represents a novel way to reduce volume at high pressure in order to obtain close-

packed structures, in contrast to the first-order transformations observed in other materials.

BPO_4 (Alfa products) was dried for 4 d at $110\,°C$ before use. $BAsO_4$ was prepared by rapid evaporation of a solution of boric and arsenic acids. The crystal structures of both compounds [4] were refined using time-of-flight neutron powder diffraction data obtained on the Polaris diffractometer at the ISIS Spallation Source (Rutherford Appleton Laboratory, Chilton, U.K.). Rietveld refinements were performed using the program GSAS [5].

The high-pressure, angle-dispersive, x-ray powder diffraction experiments were performed in a diamond anvil cell. The materials were placed along with ruby powder in the 150 μm diameter holes, which had been drilled in stainless steel gaskets preindented to a thickness of 100 μm. Pressures were measured based on the shifts of the ruby R_1 and R_2 fluorescence lines [6]. The 16:3:1 methanol:ethanol:H_2O mixture was used as a hydrostatic pressure-transmitting medium. Heating was performed at the highest pressures reached using a 50 W Nd:YAG laser in order to minimize deviatoric stress. Platinum was added in the BPO_4 experiment in order to absorb the laser radiation.

X-ray diffraction patterns were obtained with zirconium-filtered molybdenum radiation from an 800 W microfocus tube. X-ray capillary optics were used giving a 100 μm diameter beam. Detection was performed with an imaging plate placed at 143.61 mm from the sample. Exposure times were typically between 48 and 60 h. The observed intensities on the imaging plates were integrated as a function of 2θ. The individual peaks were fitted to pseudo-Voigt functions and unit cell refinements

were performed using the program U-FIT [7]. Rietveld refinements were performed using the program FULLPROF [8]. All figures in parentheses refer to estimated standard deviations.

Plane-wave total electronic energy calculations were performed with the VASP code [9,10]. Projected augmented wave potentials for B, P, As, and O atoms [11] using the Perdew-Wang exchange correlation functional [12] taken from the standard pseudopotential library were used. All calculations were done with the generalized gradient approximation (GGA). The atomic configurations are $s^2 p^1$, $s^2 p^3$, $s^2 p^3$, and $s^2 p^4$ for the B, P, As, and O atoms, respectively. A plane-wave energy cutoff of 400 eV was used in all calculations. An $8 \times 8 \times 8$ Monkhorst-Pack [13] mesh for k-point sampling was employed for Brillouin zone integrations.

The crystal structures of BPO_4 and $BAsO_4$ are partially collapsed with respect to the ideal-high-cristobalite aristotype with $c/a = 1.531\,51(3)$, $x = 0.1402(1)$ for BPO_4 and $c/a = 1.5258(1)$, $x = 0.1578(1)$ for $BAsO_4$, respectively (ideal-high-cristobalite: $c/a = 2^{1/2}$). The compression of both BPO_4 and $BAsO_4$ was found to be extremely anisotropic, Fig. 1, with c decreasing very slightly as a function of pressure and then

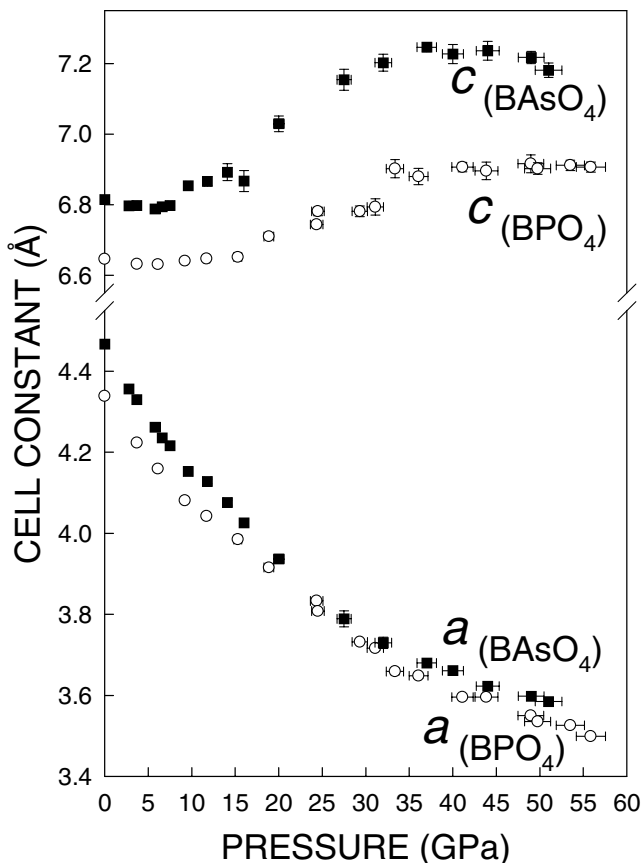*increasing.* Both experiment and theory indicate that the c/a cell constant ratios increase in a spectacular way, Fig. 2, and that the c/a ratio tends towards a value of close to 2 corresponding to a ccp oxygen sublattice. Structure refinements as a function of pressure, Fig. 3, indicate that in the case of BPO_4, the oxygen x coordinate increases from 0.140 24(7) to 0.2346(7) over the pressure range from 0.1 MPa to 50 GPa. The pressure-volume data show no discontinuities and can be described using a single Birch-Murnaghan equation of state [14] in each case with bulk moduli B_0 and first pressure derivatives of B_0' along with their standard deviations as follows: $B_0 = 56(3)$ GPa, $B_0' = 4.7(3)$ (BPO_4); $B_0 = 49(2)$ GPa, $B_0' = 5.0(2)$ ($BAsO_4$). The corresponding theoretical values are $B_0 = 44(1)$ GPa, $B_0' = 4.9(1)$ (BPO_4); $B_0 = 38(2)$ GPa, $B_0' = 5.1(2)$ ($BAsO_4$). Very good agreement is obtained for the B_0' values. The lower bulk moduli obtained from theory are related to the ambient-pressure cell volumes, which as is commonly the case using GGA are 5%–9% higher than those observed experimentally.

The optimized structural parameters from the theoretical calculations at selected external pressures are in excellent agreement with experiment. The predicted c/a ratios are compared with the corresponding experimental
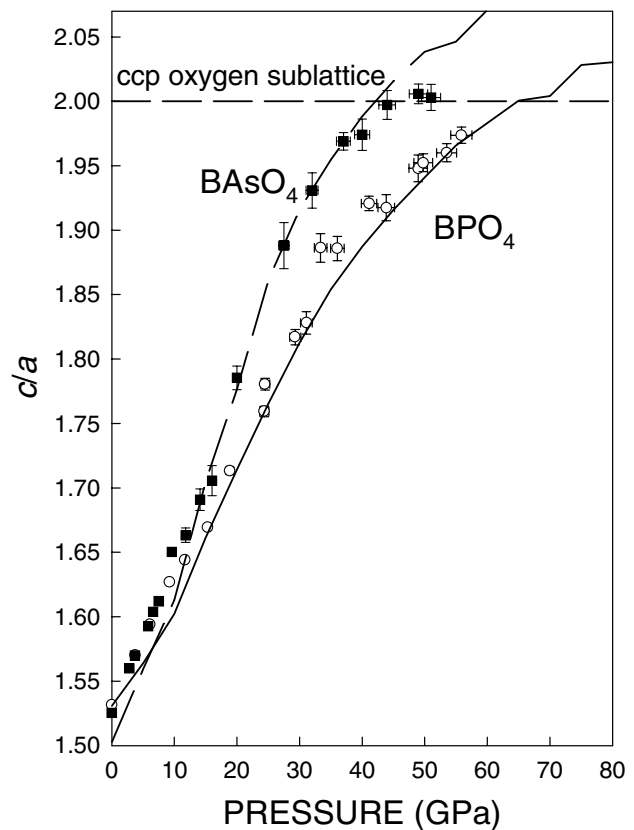

FIG. 1. Unit cell constants of BPO_4 and $BAsO_4$ as a function of pressure.

FIG. 2. Experimental (symbols) and theoretical (lines) c/a cell constant ratios for BPO_4 and $BAsO_4$ as a function of pressure.

FIG. 4. Polyhedral representations of the crystal structure of BPO_4 at 0.1 MPa and 50 GPa. Inset: experimental (symbols) and theoretical (solid line) average tilt angle in BPO_4 as a function of pressure.
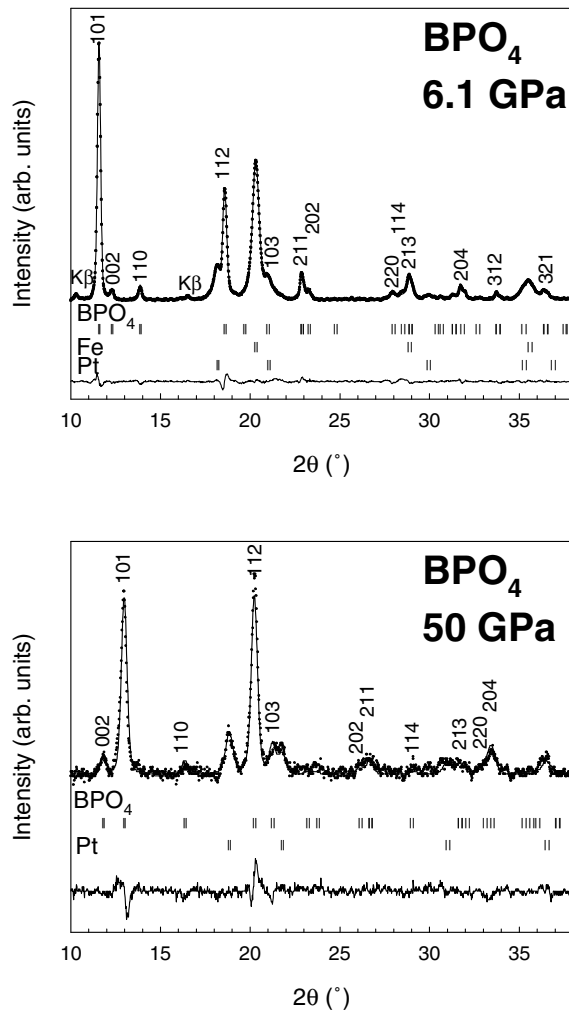

FIG. 3. Experimental and calculated diffraction profiles for BPO_4 at 6.1 and 50 GPa after laser heating. The difference profiles are on the same scale. Vertical bars indicate the calculated positions ($K\alpha_1$ and $K\alpha_2$) of the diffraction lines of BPO_4, platinum (Pt), and iron from the gasket (Fe). $K\beta$ indicates the strongest line arising from $K\beta$ radiation. The principal diffraction lines are indexed. Results of the Rietveld refinements: 6.1 GPa $- a = 4.1595(2)$ Å, $c = 6.6310(4)$ Å, B $(0, 1/2, 1/4)$, P $(0, 0, 0)$, O $(0.1642, 0.2528, 0.1271)$; 50 GPa $- a = 3.5316(5)$ Å, $c = 6.9020(9)$ Å, B $(0, 1/2, 1/4)$, P $(0, 0, 0)$, O $(0.2346, 0.2470, 0.1322)$.

values in Fig. 2. More significantly, the calculations reproduce the fine details of the observed structural trends described above. For example, it was observed, in both BPO_4 and $BAsO_4$, that the change of c/a with pressure is highly anisotropic. The length of the a axis decreases monotonously with pressure. In contrast, the c axis decreases slightly and then increases with pressure. For $BAsO_4$, the c axis reaches a maximum at 45 GPa and then decreases again with pressure. In the case of BPO_4, the c axis reaches an almost constant value when the pressure exceeds 45 GPa. These observations are correctly duplicated by the theoretical calculations. Similarly, in
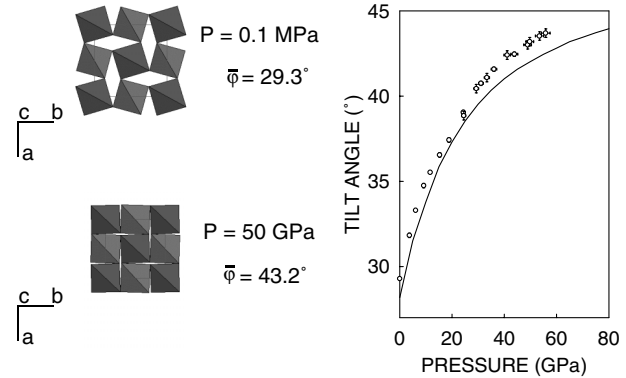
the case of the oxygen x coordinate of BPO_4, the theoretical values of 0.1340 at 0.1 MPa and 0.2254 at 50 GPa are in very good agreement with experiment.

The increase in the x coordinate corresponds to a tilt of the various tetrahedra in the structure about their twofold axes parallel to $\mathbf{c}$, which can be described by the average tilt angle [2] $\overline{\varphi} = \tan^{-1}(4x)$. This tilt angle was found to increase from $29.29(1)°$ at 0.1 MPa to $43.2(1)°$ at 50 GPa, Fig. 4, from the experimental structure refinements. The theoretical calculations yield values of $28°$ at 0.1 MPa and $42°$ at 50 GPa for BPO_4. The highest values obtained for BPO_4 are $43.7(1)°$ at the highest pressure attained experimentally of 56 GPa and $44°$ at a pressure of 80 GPa in theoretical calculations. The experimental results for $BAsO_4$ indicate that the tilt angle increases from $32.27(1)°$ at 0.1 MPa to $44.8(3)°$ at 51 GPa. The calculated values are $32°$ at 0.1 MPa and $45°$ at 55 GPa. The latter value corresponds to a collapse of the cristobalitelike structure. Because of the different sizes of the constituent tetrahedra, some distortion inevitably remains (different bond lengths and angles, different individual tetrahedral tilting angles, etc.). It can be noted that the predicted pressures at which the c/a ratio approaches 2 of 42 GPa and 65 GPa, for $BAsO_4$ and BPO_4, respectively, are almost in quantitative agreement with experiment.

Collapse of the cristobalite-type structure occurs when the tilt angle reaches $45°$, and, in addition in the case of ideal tetrahedra, when the c/a ratio simultaneously reaches 2, a ccp anion sublattice is obtained. An undistorted ccp anion sublattice is not always observed as in related collapsed structures at ambient pressure such as α-$ZnCl_2$ ($\varphi = 45°$, $c/a = 1.917$) [15] and $CuGaI_4$ ($\overline{\varphi} = 44.9°$, $c/a = 1.878$) [16]. Values for c/a, which differ from 2, imply compressed or elongated tetrahedra.

In contrast to the β-cristobalite structure type, which by definition behaves in an isotropic manner, the compression of BPO_4 and $BAsO_4$ is highly anisotropic. This anisotropy arises from the crystal symmetry, which

permits only tilting of the constituent tetrahedra about their axes parallel to **c**. In the absence of this compression mechanism, β-cristobalite (SiO_2) transforms at relatively low pressures (0–0.6 GPa for $T = 255$–$560\,°C$) to α-cristobalite [17], which undergoes a series of phase transitions with further increases in pressure [18–23]. In the case of BPO_4 and $BAsO_4$, this tilting permits the structure to gradually collapse from the open cristobalite-like framework structure to a dense structure with a cubic close-packed oxygen sublattice with a corresponding overall volume decrease down to 2/3 of the initial volume. The dense, high-pressure structure can be considered as based on the zinc blende type, in which one-half of the cations are removed and the remaining cation sites are occupied in an ordered manner.

The difference between the behavior of BPO_4 and $BAsO_4$ and that of SiO_2 can be related to the various degrees of covalent bonding present. The more covalent PO_4 and AsO_4 units are more rigid and tetrahedral distortion is less important and the tilting mechanism prevails. The difficulty in distorting PO_4 tetrahedra and the resulting effect on high-pressure behavior has also been described for $AlPO_4$ [24]. Size considerations are also important. There are no known examples of increases in coordination number of boron or phosphorus beyond four in oxides. Mechanisms involving an increase in coordination number are apparently absent for the boron compounds in the pressure range investigated, in contrast to SiO_2, for which sixfold coordination at high pressure is well documented. Boron due to its very small size thus has an effect of stabilizing arsenic in fourfold coordination. In other arsenates [25–28], such as $AlAsO_4$ and $GaAsO_4$, Al or Ga are much larger than boron and rapidly undergo increases in coordination number at modest pressures of about 9 GPa. This may facilitate the increase in coordination number of arsenic at pressures below 30 GPa.

The high-pressure behavior of BPO_4 and $BAsO_4$ presents the first example of a continuous topological transformation from a framework structure towards a dense form based on a cubic close-packed anion sublattice. This represents an alternative way to reduce volume at high pressure in order to obtain dense close-packed structures in contrast to the commonly observed first-order phase transitions in other systems. Such polyhedral tilting mechanisms are of great importance in determining the physical and thermodynamic properties of these ordered solids and result in continuous rather than abrupt changes in these properties. Such processes also play a role in the densification of glasses and amorphous solids. The silica analogues BPO_4 and $BAsO_4$ may thus serve as models for other compounds with open framework structures at high pressure including many minerals and technologically important classes of materials such as zeolites.

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