Characterization of a high-pressure phase of silica from the Martian meteorite Shergotty

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ABSTRACT

Recently, there has been substantial interest in post-stishovite high-pressure polymorphs of SiO₂, discovered as extraterrestrial minerals, or synthesized in the laboratory. Previous investigators reported the presence of " α -PbO₂-like" and "baddeleyite-like" SiO₂ in the Martian meteorite Shergotty, and also the synthesis of an α -PbO₂-like phase at pressures of 60–80 GPa in a laser-heated diamond anvil cell. To provide definitive information about the nature of the natural " α -PbO₂ phase," we recovered a small sample from the Shergotty meteorite, obtained powder X-ray diffraction patterns, and performed a Rietveld refinement of the structure. The resulting cell parameters and space group are *a* = 4.097(1) Å, *b* = 5.0462(9) Å, *c* = 4.4946(8) Å, and *Pbcn*. The structure refinement confirms that this sample does have the α -PbO₂ structure.

INTRODUCTION

The study of high-pressure phase transitions in silica has recently gained significant attention. The discovery of coesite in eclogites from ultra-high pressure metamorphic terranes and of coesite and stishovite from impact craters led to several experimental investigations of the pressure and temperature stability relations of these phases. It has been suggested that free silica could be present in the lower mantle, perhaps in the D" region. An octahedrally coordinated form of SiO₂, stishovite, undergoes further distortions and transformations at pressures and temperatures characteristic of the lower mantle [see Hemley et al. (1994) for a review]. The nature and mechanisms of these transformations and the structures of post-stishovite phases are crucial for understanding the physical and seismological properties of the lower mantle. The lack of full understanding of the higher-pressure behavior of SiO₂ motivated several theoretical and experimental studies aimed at determining post-stishovite phase transitions, and characterization of the crystal structures of high-pressure phases. Molecular dynamics and ab initio calculations by Belonoshko et al. (1996) indicated the possibility of a new SiO₂ phase with Pb2n symmetry¹, which is more stable than stishovite and its CaCl2-like modification at pressures >120 GPa. Karki et al. (1997), however, reported on the basis of firstprinciples calculations a pressure of 98 GPa for the transition of the CaCl₂ structure to Pnc2 and a pressure of 226 GPa for the transition of this polymorph to the pyrite structure (this was previously predicted by Park et al. 1988). Teter et al. (1998) noted that when the Pnc2-type structure of SiO₂ is examined using first-principles methods, it adopts the higher symmetry *Pbcn* space group. At any given pressure, the optimized *Pnc*2 and α -PbO₂ structures have the same total energies and simulated diffraction patterns.

Following the discovery of coesite and stishovite, several syntheses of other high-pressure forms were reported. Roomtemperature static compression studies by Kingma et al. (1995) showed transformation of stishovite to an orthorhombic CaCl₂like form near 50 GPa, in excellent agreement with the theoretical predictions of Cohen (1992). Several attempts have been made to synthesize quenchable high-pressure phases; these include German et al. (1973) and Tsuchida and Yagi (1989, 1990). More recently, Dubrovinsky et al. (1997) synthesized a phase at 2000 K and between 68–85 GPa, which they reported had the *Pnc2* space group when quenched to ambient conditions; they noted that the structure of this phase was intermediate between the α -PbO₂ and β -ZrO₂ structures. Dubrovinsky et al. (2001) and Dubrovinskaia et al. (2001) later identified this material as having the α -PbO₂-type structure².

Other reported high-pressure SiO₂ forms include an Fe₂Ntype structure (Liu et al. 1978), α -ZrO₂/baddeleyite (El Goresy et al. 1998), a 3 × 2 zigzag chain form (Haines et al. 2001), and an undetermined stishovite-like structure (Yamakata and Yagi 1997). Sharp et al. (1999) and El Goresy et al. (2000) reported the presence of " α -PbO₂-like" and "baddeleyite-like" SiO₂, respectively, in the Martian meteorite Shergotty. Although the electron diffraction results (Sharp et al. 1999) did not produce lattice parameters or systematic absences close enough to the synthesis values to confirm the presence of α -PbO₂-like SiO₂ in Shergotty, these results did indicate that a new orthorhombic SiO₂ phase was present. They stated that their "SiO₂ structure is distinctly different from the α -PbO₂ and *Pnc*2 structures but similar to a *Pbcn* structure produced in shock experiments at

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¹Previous authors often used *Pnc2* as the space group for this structure. However to have an orientation consistent with the centrosymmetric space group *Pbcn*, we use *Pb2n* throughout this paper.

²Previous authors reporting on post-stishovite phases of SiO₂ refer to most of them using the name of a mineral having the same structure, e.g., "the baddeleyite-like form of SiO₂." However, none of them use the accepted mineral name for α -PbO₂ scrutinyite (Taggart et al. 1988). For this paper we decided to maintain continuity with previous publications while noting the inconsistency in nomenclature in this footnote.

70 to 90 GPa by German et al. (1973)." In this investigation, we confirm that the post-stishovite phase in Shergotty is, in fact, the α -PbO₂ phase and report the results of a crystal structure refinement.

SAMPLE CHARACTERIZATION

Shergotty is a member of the SNC group of meteorites. It is a basaltic shergottite, composed mainly of felspathic glass and pigeonite, with minor amounts of Fe-Ti oxide minerals. In Shergotty, silica is an accessory phase, and occurs mostly in association with feldspathic glass. On the basis of shock wave experiments, the pressure at which the feldspathic glass formed is estimated at 35-40 GPa (Malavergne et al. 2001). The silica grains show two different morphologies: (1) tabular grains, exhibiting small lamellae oriented in the same direction as the interstitial silica glass, and (2) equant grains, containing two or more sets of lamellae (Fig. 1b). The silica glass is formed by partial amorphization of the high-pressure silica phase on decompression. Electron microprobe analyses of several silica grains show that they contain ~98 wt% silica, the main impurities being Al_2O_3 (0.8 to 1.6 wt%) and Na_2O (0.2 to 0.5 wt%), in agreement with Sharp et al. (1999). Boctor et al. (2001) measured the water abundance and hydrogen isotope composition of the silica grains. They concluded that the silica phase is hydrous $(30 \pm 3 \text{ to } 81 \pm 15 \text{ ppm water})$ and that its hydrogen isotope signature is extraterrestrial. They were unable, however, to determine whether the water resides in the post-stishovite phase or in the glass that formed by partial vitrification on decompression. Recent investigations of hydroxyl solubility in coesite and stishovite show that both minerals are capable of accommodating structurally bound hydrogen. For coesite, hydroxyl solubility increases with pressure (Köch-Muller et al. 2001; Mosenfelder 2000), and for stishovite, it increases with increasing Al content (Pawley et al. 1993). If post-stishovite phases contain structurally bound H, they may be candidates for storage of minor amounts of water in the lower mantle. It has been shown, e.g., for olivine \leftrightarrow wadsleyite, that the presence of even a very small amount of hydrogen in the structure can have significant consequences for the phase relations (Wood 1995).

In their paper on the synthesis of the α -PbO₂-type SiO₂ phase, Dubrovinsky et al. (2001) postulated on the basis of piezoelectric measurements (indentation technique) that their sample was acentric, with space group Pnc2. Alternatively, in the recent study of post-stishovite SiO₂ synthesized using cristobalite as a starting material, Dubrovinskaia et al. (2001) proposed a centrosymmetric space group. To verify whether the structure of the silica phase we studied is centrosymmetric or not, we performed a series of second harmonic generation (SHG) experiments. We used quartz and urea single crystals as reference standards. For the Shergotty silica sample we did not detect an SHG signal at a detectable level; however, the sample could have been amorphized in the laser beam during the experiment. In the absence of any compelling evidence for a noncentrosymmetric structure, we conclude that the structure of the α -PbO₂ silica phase from Shergotty is centrosymmetric and the correct space group is Pbcn. This conclusion is consistent with those of Teter et al. (1998), who calculated that the noncentrosymmetric structure spontaneously converged to the centrosymmetric phase.

X-ray diffraction was performed on the grain in Figure 1a before any other tests. X-ray powder patterns were collected using a Rigaku R/AXIS-RAPID diffractometer equipped with a three-circle goniometer and a curved imaging plate detector. X-rays were produced from a rotating-anode X-ray generator with an Mo anode. Data were collected using the Rapid-auto program. A 12 hour exposure was made, during which the sample was rotated about the vertical goniometer φ axis at a rate of 1°/s. The resulting diffraction image, presented in Figure 1d, was processed using the CylInt program.

Analysis of the diffraction image revealed that the sample shows high preferred orientation and contains a significant amount of amorphous material, as indicated by a complicated background and the presence of a very broad maximum in the vicinity of $2\theta = 10^{\circ}$ (Fig. 1c). Intensities were integrated over the whole range of $\phi = 360^\circ$. For further analysis, the range of 2θ between 12 and 50° was chosen. Ten strong peaks from the range 12-35° were chosen for peak indexing. This was performed using the Jade program, which gave among other possible choices an orthorhombic unit cell very similar to that of the α -PbO₂-like silica phase described by Dubrovinsky et al. (2001) and predicted by Teter et al. (1998). Rietveld refinement was performed using GSAS (Larson and Von Dreele (2000) via the EXPGUI interface (Toby 2001; the refinement results are presented in Table 1. A comparison of observed and calculated peak intensities is presented in Table 2. All structure models proposed by Teter et al. (1998) were checked for agreement with the recorded pattern. Only the α -PbO₂ structure (Pbcn) and the lower symmetry orthorhombic structure (Pb2n) gave satisfactory reproduction of peak positions and intensities. Both of the above models were used for Rietveld refinement and both produced very similar results with final Rfactors $R(F^2) = 3.4\%$ and 2.9\%, respectively. The refinement using the Pb2n model was less stable and simultaneous optimization of all the parameters was not possible. Alternatively, the refinement using the Pbcn model was very stable and in the final stages we optimized the atomic positions, isotropic temperature displacement parameters, peak profiles (Voight function), background (20th order shifted Chebyshev function), preferred orientation (10th order spherical harmonics model), and scale factor all at once. The powder pattern calculated on the basis of the refined model gave a very good reproduction of the recorded experimental pattern. Both observed and calculated patterns are presented in Figure 1c. The Pbcn model was more stable during refinement, and although we do not have an unambiguous argument for the centrosymmetry, as it is based solely on the XRD data and the SHG experiments, we conclude that the structure is most likely centrosymmetric.

TABLE 1. Refined atom coordinates, cell, and space group for the Shergotty SiO₂ sample with the α -PbO₂ structure

Atom	Site	x	У	Ζ	B (Ų)
Si	4c	0	0.1522(9)	-	0.8(1)
0	8d	0.7336(19)	0.6245(12)	0.9186(29)	0.1(2)
Note: Pbcn (a = 4.0 no. 60)	97(1) Å, <i>b</i> = 5.	0462(9) Å, <i>c</i> = 4	4.4946(8) Å, sj	pace group



FIGURE 1. (a) The silica-rich sample recovered from the Shergotty meteorite, the linear size of the grain is about 0.3 mm; (b) BES photomicrograph of the grain of silica; (c) the results of the Rietveld refinement of the crystal structure. The crosses represent experimental points, the gray solid line the calculated pattern, the dashed gray line calculated background, and the black solid line below the diffraction pattern is the difference curve lo-lc. The details of the refinement are given in Table 1. (d) Diffraction pattern of the slica-rich fragment of meteorite recorded with the use of imaging plate detector.

DISCUSSION

The existence of a stable phase of silica with the α -PbO₂ structure at ambient pressure has importance for the whole family of compounds, including dioxides (SiO₂, GeO₂, TiO₂, SnO₂, PbO₂), and berlinites (ABO₄, A = Al,Ga, B = P,As), which under certain conditions can assume the rutile structure. The phase relations, existence of post-rutile phases, and the possibility of transformation to higher-pressure phases in these systems have been the subject of numerous extensive studies [see, e.g., Haines and Leger (1997) for a review]. In most of these examples, the phase transformation sequence leads from the low-pressure, four-coordinated phases, through the octahedrally coordinated phases, to fluorite structures.

Some trends, common for most of these systems, seem to be very important for understanding the sequence of phases observed at high pressure: (1) Hydrostaticity has a very significant effect on the transformations to rutile and post-rutile phases (Haines and Leger 1997). (2) Rutile-to- α -PbO₂ transformations are very sluggish or do not occur at all at ambient temperature (Arlt et al. 2000). (3) The existence of the α -PbO₂ phase (in most cases quenchable) can be followed by a transformation to a nonquenchable baddeleyite phase at higher pressure (Haines and Leger 1993; Lagarec and Desgreniers 1995). (4) Transformation to α -PbO₂ from lower pressure phases (with fourfold coordination) usually occurs more easily and at lower pressure than the rutile-to- α -PbO₂ transformation. Rutile is usually not an intermediate step in the transformation of these fourcoordinated phases to α -PbO₂. (5) For rutile-to- α -PbO₂ transformations there is an intermediate stage, through the CaCl₂ structure (Haines and Leger 1997; Kingma et al. 1995). This transformation involves a minor distortion to the tetragonal rutile structure (through octahedral rotation) and it is secondorder. (6) For most of the systems assuming rutile structures, the α -PbO₂ phases are only slightly denser (2%) than the rutile phase, whereas the baddeleyite phase is significantly denser (11%). (7) The starting material in the high-pressure experiments is important.

According to the assumed α -PbO₂ model, the space group of the high-pressure silica phase from Shergotty is orthorhombic *Pbcn*, with Laue symmetry *mmm*. Lattice constants determined from Rietveld refinement are a = 4.097(1) Å, b =5.0462(9) Å, and c = 4.4946(8) Å, compared to the values a =4.099(3), b = 5.018(4), and c = 4.547(2) Å obtained for a synthetic high-pressure silica phase by Dubrovinsky et al. (2001), and a = 4.049 Å, b = 5.001 Å, and c = 4.468 Å predicted by Teter et al. (1998). The final reduced $\chi^2 = 4.34$ for 59 variables, and the final *R*-factors for 178 observed reflections were $R(F^2)$ = 3.41%, $wR_p = 1.4\%$, and $R_p = 1.0\%$. The calculated unit-cell

TABLE 2. Measured and calculated intensities and positions of diffraction peaks for the α -PbO₂-type SiO₂ phase

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h	k	1	d _{calc}	I _{obs}	I _{calc}
1	1	0	3.181	72.0	71.8
1	1	1	2.596	100.0	100.0
0	2	0	2.523	4.3	5.0
0	2	2	2.247	1.0 5.4	0.3
1	0	2	1.970	25.3	24.9
1	2	1	1.938	63.9	64.0
1	1	2	1.835	13.9	14.9
2	1	1	1.749	0.6	0.3
0	2	2	1.678	0.5	0.3
2	2	0	1.590	2.7	3.2
2	0	2	1.514	31.4	31.7
2	2	1	1.499	43.5	44.0
1	3	1	1.470	1.1	0.9
2	1	2	1.450	0.4	0.3
1	1	3	1.355	12.3	12.8
3 2	2	2	1.318	1.0	1.7
0	2	3	1.288	19.3	19.2
1	3	2	1.279	11.9	11.8
3	1	1	1.265	15.4	15.6
0	4	0	1.262	10.9	11.2
2	3	1	1.249	0.3	0.4
3	4	2	1.215	2.3	1.8
3	2	1	1 160	4.9	5.0
3	1	2	1.137	6.1	6.3
2	3	2	1.125	0.1	0.1
0	0	4	1.124	0.6	0.6
0	4	2	1.100	0.2	0.2
1	3	4	1.064	0.7	1.5
1	4	2	1.062	3.3	3.3
3	3	0	1.060	2.8	2.9
1	1	4	1.059	1.8	1.9
2	4	1	1.045	3.8	3.7
3 0	3	1	1.032	0.9	1.0
4	0	ō	1.024	6.2	6.4
3	1	3	0.990	2.3	2.1
2	0	4	0.985	4.5	4.5
4	1	1	0.980	0.3	0.3
2	4	2	0.969	8.0	8.0
3	3	2	0.905	4.6	0.2 4.8
1	5	1	0.957	3.1	3.3
4	2	0	0.949	0.3	0.4
4	0	2	0.932	0.6	0.6
4	2	1	0.929	1.0	0.7
2	2	4	0.918	0.2	0.1
4	3	2	0.917	29	3.4
4	2	2	0.874	0.4	0.4
2	4	3	0.873	1.3	1.2
3	0	4	0.868	0.7	0.7
1	1	5	0.865	1.3	1.3
3	4	2	0.857	1.4	1.4
0	2	5	0.847	0.2	0.2
õ	6	õ	0.841	0.4	0.4

formula weight was 240.34, which corresponds to a density ρ = 4.295 g/cm³. This density is 0.23% greater than that of stishovite, where ρ = 4.285 g/cm³ at ambient pressure (Finger and Hazen 1991). Such relationships between the ambient pressure densities of rutile and α -PbO₂ phases are consistent with the findings regarding other rutile-type dioxide systems.

The structural data for the α -PbO₂ phase of silica presented in this paper are relevant for understanding the physical properties of this phase and the other post-rutile phases. Therefore, it seems worthwhile to present here some details regarding the geometry of the coordination polyhedra and comparisons with the stishovite structure. In rutile structures the octahedral chain direction [001] is always less compressible than directions perpendicular to the chains (Angel et al. 2001). The main reason for this anisotropy is a strong electrostatic repulsion between the neighboring Si⁴⁺ ions along the chain. The ambient pressure value of the Si-Si distance in stishovite is 2.668 Å. In the α -PbO₂ structure, because the straight octahedral chains have been replaced by rippled ones, the Si-Si distance along the chain increases to 2.722(4) Å, allowing for significant relaxation of Si-Si repulsion. Conversely, the distance between the centers of the neighboring unoccupied octahedral voids becomes much shorter (2.578 Å). As a result, the translation period along the stishovite [001] direction in the α -PbO₂ structure becomes 7.601(3) Å, which is shorter than analogous period of 8.003 Å in stishovite. The 5% shrinkage of the unit cell along this direction is the main reason for the increased density of the α -PbO₂ structure compared to stishovite.

It has been noted for stishovite that the O-O distance corresponding to the octahedral edge (2.290 Å) shared between two neighboring octahedra is much shorter than the other edges. The O-O distance between the O atoms not involved in octahedral edge-sharing has an average length of 2.523 Å. This effect has been attributed to the shielding effect that involves bringing the two oxygen atoms together to compensate the electrostatic repulsion between neighboring Si⁴⁺ ions. In the α -PbO₂ structure the shared edge is also the shortest [2.404 (11) Å] of the O-O distances, but it is significantly longer than in stishovite. For the rippled octahedral chains of the α -PbO₂ structure there is one octahedral edge for which none of the O atoms is involved in edge sharing. The O-O distance for this edge is 2.657(14) Å, i.e., longer than the average O-O distance of 2.52 Å. The geometry of coordination polyhedra in stishovite and the α -PbO₂ phase are shown in Figures 2c and 2d.

This and other studies provide unequivocal evidence for the occurrence of the α -PbO₂ phase of SiO₂ at ambient conditions, whether recovered from a meteorite or synthesized in the laboratory. The good quality of this Rietveld refinement provides the opportunity to examine and analyze in detail the crystal structure and geometry of the coordination polyhedra of this post-stishovite phase. The analysis of the structure of the α -PbO₂ phase reveals that the change in the arrangement of the Si⁴⁺ ions during the stishovite to α -PbO₂ transition allows for more efficient packing, leading to an increase in density, accompanied by an increase in the nearest-neighbor Si-Si distances and a lowering of the electrostatic repulsion. The pressure estimates reported in the literature for the transition of cristobalite and tridymite to the α -PbO₂ structure based on diamond anvil cell experiments show a strong dependence of the transition pressure upon which low-pressure polymorph (cristobalite or tridymite) was used as a starting material (Dubrovinsky et al. 2001). This is in contrast to the work of Andrault et al. (1998) who saw only a transition to the CaCl₂ structure when starting with stishovite and extending the pressure to 120 GPa (in agreement to the trends found for other rutile-type structures). Perhaps the structural disruption caused by a change from four-to-six-coordinated Si is an important



FIGURE 2. (**a-b**) The comparison of the arrangement of octahedral chains in stishovite (**a**) and α -PbO₂ structure (**b**). The balls-and-sticks in **b** show octahedral voids that are occupied in stishovite and vacant in α -PbO₂. The dashed lines show the path the Si⁴⁺ would need to follow to transform the stishovite structure to α -PbO₂. (**c-d**) The comparison of the geometry of coordination polyhedra in stishovite and α -PbO₂. The large dark spheres represent sites occupied by Si⁴⁺ ions; the light spheres represent the centers of unoccupied octahedral voids.

factor. Also, if the starting material contains H or other minor elements, their presence may have a significant effect on the pressure of the phase transition. Therefore, it seems presumptuous to base estimates of the pressure-history of naturally occurring high-pressure phases of SiO_2 from shocked meteorites directly on the results of currently available laboratory experiments.

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