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HIGH-PRESSURE AND HIGH-TEMPERATURE POLYMORPHISM IN SILICA

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We synthesised a number of new silica modifications in the electrically heated diamond anvil cells at pressures over 100 GPa and temperatures over 1200 K. The structure of these polymorphs is based on hexagonal close packing of oxygen atoms with different degree of ordering of silicon atoms in octahedral and tetrahedral sites.

Keywords: Structure; Silica; High pressure; X-ray diffraction

INTRODUCTION

Despite its simple chemical composition, silica shows rich polymorphism at elevated pressures and temperatures [1, 2]. In low-pressure phases, such as quartz, tridymite, cristobalite, moganite, keatite, and coesite, silicon is tetrahedrally coordinated by oxygen. At pressures above 8 to 12 GPa, depending on temperature, silica crystallises as stishovite, a rutile-type phase in which oxygen atoms form a distorted hexagonal close-packed structure and silicon atoms occupy "straight columns" of octahedral sites. At pressures above 45 to 50 GPa at ambient temperature tetragonal stishovite is known to undergo orthorhombic distortion and to transform to a $CaCl_2$-structured phase [3–5]. In the same pressure range quartz was found [6] to transform in He pressure medium to the monoclinic ($P2_1/c$ space group) phase built up of 3×2 kinked chains of edge-shearing SiO_6 octahedra. Compression of quartz without a pressure medium leads to formation of a mixture of phases or a complex phase which so far have not been identified [1, 6]. If the starting material is α-cristobalite, the compression at ambient temperature in a relatively soft (nitrogen or argon) pressure medium results in formation of α-PbO_2-type silica at pressures between 35 and 40 GPa [7–10] through a series of intermediate phases with still unknown structures. In the α-PbO_2-type structure the edge-shearing SiO_6 octahedra form a "zig-zag" of 2×2 kinked chains.

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In shock wave compression [11] and laser-heated[17] DAC experiments there were reports on formation of fully disordered niccolite (NiAs) structure in which oxygen atoms form the *hcp* sublattice and silicon atoms are statistically distributed over octahedral voids. The structures of these high-pressure silica phases (except α-PbO_2-type) have not been refined and the physical reasons for such variety of modifications as well as their relative stabilities are not known so far.

EXPERIMENTAL

Cristobalite samples were obtained by heating a silica gel (99.99% purity) at 1550 °C for 8 hours and then quenching it or by annealing of silica sol-gel glass. The natural α-quartz (Brazil) and orthorhombic tridymite from San Cristobal (Mexico) used in some runs were provided by Dr. P. Nysten (Uppsala University, Sweden).

The details of the experiments performed with electrically-heated DAC are described in our earlier papers [12, 13]. At ESRF powder diffraction experiments were conducted at the beam lines BM01 and ID30. At the BM01 beam line the data were collected with the MAR345 detector using an X-ray beam of 0.6996 Å wavelengths and size of $50 \times 50\,\mu m$ (beam line BM01), and at ID30 we used MAR345 or Bruker CCD area detectors and a highly focused beam of $10 \times 15\,\mu m$ of 0.3738 Å wavelengths. The detector-to-sample distance varied in different experiments from 170 to 350 mm. Diamonds were mounted on the seats made of B_4C or cBN allowing us to collect the complete Debye rings to 0.95 Å. The collected images were integrated using the Fit2D program in order to obtain a conventional diffraction spectrum. The full-profile refinements of powder X-ray diffraction data were carried out using the GSAS program. As internal pressure standards we used NaCl, Pt or Au powder mixed with a sample in the mass proportion approximately 1:1 for NaCl and 1:20 for metals. In some experiments Au wire of 5 µm in diameter placed in the centre of the pressure chamber was used as an internal pressure standard. All loadings of DAC were made in inert atmosphere (Ar or He).

RESULTS AND DISCUSSION

We conducted a series of experiments in electrically heated diamond anvil cells (DACs) in order to determine the behaviour of silica at pressures above 100 GPa and temperatures above 1000 K. Figure 1 shows a typical sequence of diffraction patterns obtained in high-pressure high-temperature experiments with α-cristobalite as a starting material. On compression in Ar pressure medium above 10–12 GPa a new phase, first described by Tsuchida and Yagi [7] as Cristobalite XI, appeared and persisted on compression at room temperature to 37–40 GPa [7, 9, 14] (Fig. 1). If at pressures between 30 and 40 GPa temperature increases to 700–900 K, Cristobalite XI reflections could be observed on the compression at high temperature to at least 65 GPa. However, upon heating at pressures above 35 GPa the diffraction pattern of Cristobalite XI slowly evolved – the reflections at about 1.24 Å, 1.45 Å, and 1.85 Å are growing, while other reflections diminish (Fig. 1). At the same time, long heating at pressures above 75–80 GPa results in crystallization of the α-PbO_2-structured phase (Fig. 1), in agreement with previous observations [5, 9] and theoretical predictions [2, 9]. Based on experiments with pre-synthesized α-PbO_2-type silica [9] conducted at pressures below 85 GPa it was proposed that α-PbO_2-structured silica is a stable post-stishovite phase. However, long heating at pressures above 90 GPa and temperatures above 850 K results in

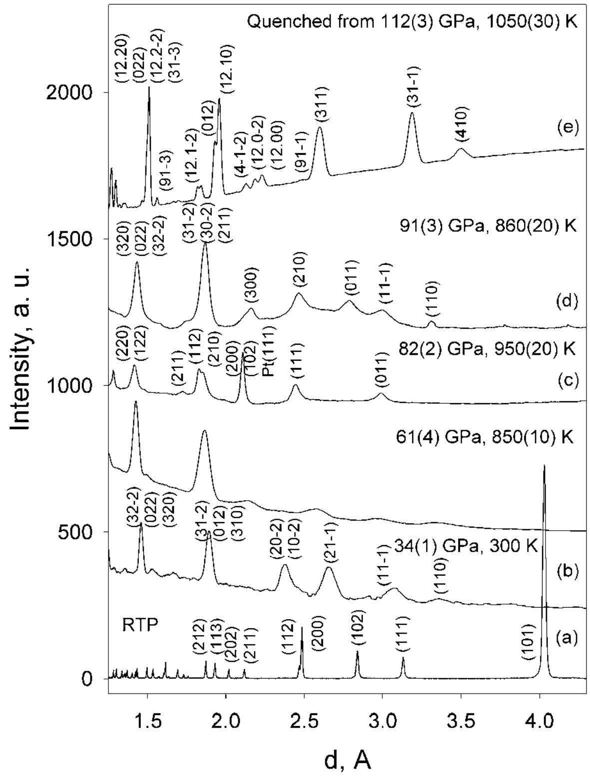

FIGURE 1 Examples of the diffraction patterns collected in high-pressure high-temperature experiments with α-cristobalite as a starting material. All observed reflections of the initial material (a) belong to the low-cristobalite tetragonal structure with lattice parameters $a = 4.9733(3)$ Å and $c = 6.9234(4)$ Å. (b) On compression in Ar pressure medium to 34(1) GPa at ambient temperature Cristobalite XI phase was formed (indexes for monoclinic unit cell with lattice parameters $a = 7.473(3)$ Å, $b = 3.961(1)$ Å, $c = 4.993(2)$ Å, $\beta = 120.08(2)°$); heating at 850(1) K and 61(4) GPa (c) during two hours produces a disordered phase, which crystallizes to the α-PbO_2-structured phase on heating during 4 hours at 82(2) GPa and 950(20) K (d) (indexes for orthorhombic cell $a = 4.232(5)$ Å, $b = 3.848(4)$ Å, $c = 4.756(9)$ Å). Heating at 91(4) GPa and 860(20) K at about 3 hours results in appearance of new reflections (e) which can be indexed in a monoclinic cell with lattice parameters $a = 7.294(5)$ Å, $b = 3.868(3)$ Å, $c = 4.841(7)$ Å, $\beta = 118.8(1)°$. The top spectrum was obtained from the initial cristobalite sample treated at 112(3) GPa and 1050(30) K during 8 hours and subsequently quenched (indexes for monoclinic unit cell with lattice parameters $a = 30.553(4)$ Å, $b = 4.1037(4)$ Å, $c = 5.0753(9)$ Å, $\beta = 118.61(1)°$).

appearance of new reflections which cannot belong to α-PbO_2-type SiO_2 (Fig. 1). Moreover, the diffraction pattern from a quenched sample treated at pressures above 110 GPa and 1050 K during 8 hours is quite different from the diffraction patterns of quenched α-PbO_2-type silica [9].

A key for understanding the nature of the described above transformations of cristobalite at high pressures and temperatures is provided by the diffraction pattern shown in Figure 1(c). The most intense diffraction peaks closely resemble the pattern reported by Liu *et al.* [15] for quartz heated above 1000 °C at pressures between 35 and 40 GPa. It was interpreted as the hexagonal disordered niccolite structure [11, 15]. Our lattice dynamics simulations for pressure 60 GPa and temperature 1000 K for hexagonal close packed configuration of oxygen atoms and silicon atoms statistically distributed over octahedral interstitials indicate that the unit cell should be monoclinic with the parameters $a = 7.32$ Å, $b = 3.87$ Å, $c = 4.81$ Å, $\beta = 117.6°$. Using this unit cell we can reproduce the diffraction pattern collected in experiments with cristobalite at 850(1) K and 61(4) GPa after about two hours of heating (Fig. 1(c)).

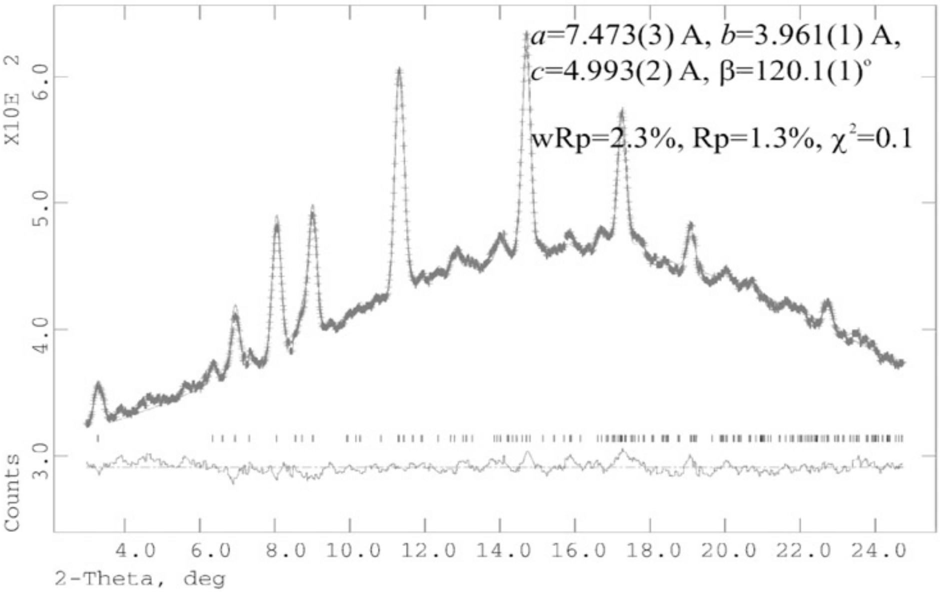

FIGURE 2 Profile-fitted X-ray diffraction data of different silica phases obtained at 34(1) GPa (starting phase α-cristobalite). The GSAS program package was used in the refinement. For structural parameters see Table I.

It is well known that depending on the conditions of experiments (hydrostaticity of the pressure medium, speed of compression, duration time of high-pressure treatment, starting material, etc.) different silica phases appear on compression [1, 6, 8–10, 14]. The post-quartz phase discovered by Haines *et al.* [6] has a monoclinic unit cell with dimensions close to those we found for disordered silica. In our experiments on cristobalite and quartz in dependence on the experimental conditions we observed different phases at pressures between 25 and 50 GPa, but all diffraction patterns could be indexed in a framework of the proposed monoclinic unit cell. This observation allows us to suggest that all "post tetrahedrally-coordinated" (post-quartz, post-cristobalite, post-tridymite) silica phases are based on hexagonal close packing of oxygen atoms as was predicted by theoretical work[28].

It is logical to propose that at moderate pressures between 10 and 35 GPa silicon atoms may be distributed over both tetrahedral and octahedral sites of the *hcp* oxygen sublattice, while at higher pressures silicon atoms occupy mostly octahedral positions. Indeed, we could quantitatively reproduce a diffraction pattern of one of modifications of Cristobalite XI (Fig. 2) at 34(1) GPa assuming that 27% of silicon atoms are still in tetrahedral positions (Tab. I).

TABLE I Structural Parameters for Cristobalite XI Synthesized at 34(1) GPa (Space Group $P2_1/c$, Lattice Constants are: $a = 7.473(3)$ Å, $b = 3.961(1)$ Å, $c = 4.993(2)$ Å, $\beta = 120.08(2)°$).

	x	*y*	*z*	*Site occupancy*
Si1	0.5	0.0	0.0	1.0
Si2	0.164(2)	0.508(4)	0.979(2)	0.603
Si3	0.268(3)	0.125(3)	0.307(3)	0.397
O1	0.046(2)	0.248(1)	0.655(3)	1.0
O2	0.721(2)	0.240(2)	0.173(3)	1.0
O3	0.386(2)	0.237(1)	0.659(3)	1.0

CONCLUSIONS

At low pressure the variety of silica polymorphs is related to the flexibility of the Si—O—Si bonding angle between corner-shearing SiO_4 tetrahedra. At high pressure the diversity of silica modifications is associated with the ability of silicon atoms to occupy various interstices in the monoclinically distorted *hcp* oxygen lattice. Our studies reveal the existence of the class of silica phases with different degree of the ordering of silicon atoms. Silica polymorphs with octahedrally coordinated silicon known so far (stishovite, fully disordered phase with niccolite-type structure [11, 15], α-PbO_2-type [9], and monoclinic ($P2_1/c$ space group) post-quartz phase [6]) are members of this class. The details of the silicon distribution among free positions in the oxygen network strongly depend on the starting material and the conditions of high-P, T treatment of silica, but the general trend is that at pressures above 40–45 GPa most of the silicon atoms are placed in octahedral positions. Our structural model provides a key for an explanation of the mysterious behavior of silica, known for more than 30 years, when at the same pressure and temperature range different phases were synthesized.

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