



A class of new high-pressure silica polymorphs

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Abstract

We synthesised a number of new metastable silica modifications in the electrically heated diamond anvil cells (DACs) at pressures over 100 GPa and temperatures over 1200 K. Our studies reveal the existence of a new class of silica phases with different degree of the ordering of silicon atoms. Silica polymorphs with octahedrally co-ordinated silicon known so far (stishovite, fully disordered phase with niccolite-type structure, α -PbO₂-type, and monoclinic ($P2_1/c$ space group) post-quartz phase) 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-pressure high-temperature treatment of silica, but a 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 behaviour of silica, known for more than 30 years, when at the same pressure and temperature range different phases were synthesised.

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1. Introduction

The structures, properties and high-pressure behaviour of silicon dioxide SiO₂ have been extensively investigated because of its importance in Earth and materials sciences and technology. Last decade studies revealed a number of enigmatic phenomena associated with high-pressure silica polymorphs, e.g. formation of yet unidentified phases on the compression of α -cristobalite and quartz, controversial

theoretical and experimental information on the possible post-stishovite phases, and discovery of new dense natural silica polymorphs in the Martian Shergotty meteorite (Hemley et al., 1996; Tsuchida and Yagi, 1990; Kingma et al., 1995; Gratz et al., 1993; Teter et al., 1998; Palmer et al., 1994; Yamakata and Yagi, 1997; Andrault et al., 1998; Sharp et al., 1999; Dubrovinsky et al., 1997, 2001; El Goresy et al., 2000). Despite its simple chemical composition, silica shows rich polymorphism at elevated pressures and temperatures (Hemley et al., 1996; Teter et al., 1998). In low-pressure phases, such as quartz, tridymite, cristobalite, moganite, keatite, and coesite, silicon is tetrahedrally co-ordinated by oxygen. At pressures above 8–12 GPa, depending on temperature,

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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 (Fig. 1a). At pressures above 45–50 GPa at ambient temperature tetragonal stishovite is known to undergo orthorhombic distortion and to transform to a CaCl_2 -structured phase (Kingma et al., 1995; Andrault et al., 1998; Dubrovinsky et al., 1997). In the same pressure range quartz was found (Haines et al., 2001) to transform

in He pressure medium to the monoclinic ($P2_1/c$ space group) phase built up of 3×2 kinked chains of edge-sharing SiO_6 octahedra (Fig. 1b). Compression of quartz without a pressure medium leads to formation of a mixture of phases or a complex phase (Quartz II) which so far have not been identified (Hemley et al., 1996; Haines et al., 2001). 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

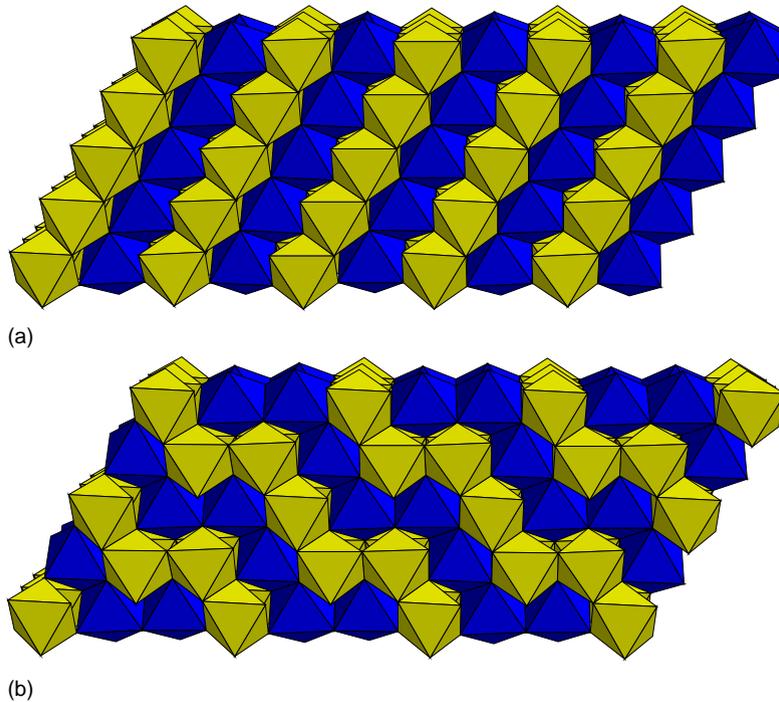


Fig. 1. Polyhedral models of: (a) stishovite (build by straight columns of edge-sharing octahedra); (b) monoclinic ($P2_1/c$ space group) post-quartz phase (Haines et al., 2001) build up of 3×2 kinked chains of edge-sharing SiO_6 octahedra; (c) α - PbO_2 -type structure made out of 2×2 kinked chains of SiO_6 octahedra; (d) Cristobalite X-I (partially or fully occupied octahedra forms 3×2 chains, partially occupied tetrahedra green). In Cristobalite X-I, fully or partially occupied edge-sharing octahedra (mean Si–O distance 1.741 Å) form 3×2 kinked chains while partially occupied tetrahedra (mean Si–O distance 1.524 Å) do not form a interconnected net; (e) Quartz II. Partially occupied tetrahedra (mean Si–O distance 1.496 Å) form 2D slabs, which connect layers that are two octahedra (mean Si–O distance 1.736 Å) thick. Octahedra in the layers are organised as pieces of 2×2 kinked chains in α - PbO_2 -type structure. The Si–O distances of octahedral sites in Cristobalite X-I and Quartz II are slightly bigger than the average Si–O distances in stishovite at corresponding pressures (Andrault et al., 1998) (1.712 Å at 34 GPa and 1.705 Å at 44 GPa), which is stable modification of silica at those conditions (Hemley et al., 1996; Andrault et al., 1998); (f) new silica phase synthesised at 112(3) GPa and 1050(30) K (fully and partially occupied octahedra are shown). A molar volume of the new phase at ambient conditions is 14.02(1) cm^3/mol , within experimental error identical to the molar volumes of stishovite (14.03 cm^3/mol), the post-monoclinic quartz-modification (Haines et al., 2001) (14.02 cm^3/mol), and α - PbO_2 -type silica (14.08 cm^3/mol) (Dubrovinsky et al., 2001). The average Si–O distances in stishovite (1.775 Å) and in the new phase (1.804 Å) are reasonably close. Considering the motif of fully or partially occupied octahedra in the new phase it is easy to notice the straight chains of octahedra like in stishovite, 2×2 and 3×2 kinked chains as in α - PbO_2 and post-quartz structures (Dubrovinsky et al., 2001; Haines et al., 2001), and more complex kinked chains predicted by geometrical structural modelling (Urusov et al., 1990) and theoretical calculations (Teter et al., 1998). Yellow and blue octahedra are placed at different height.

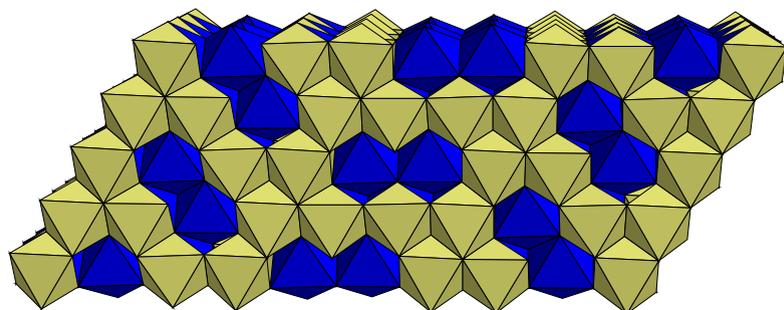
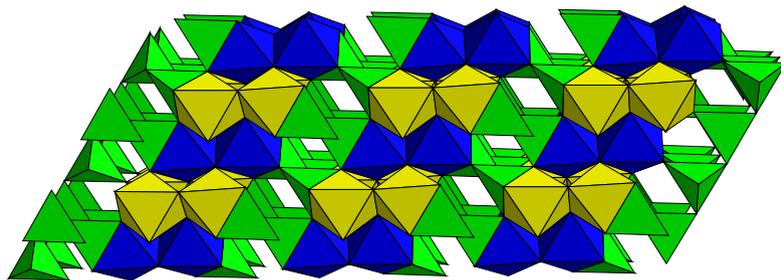
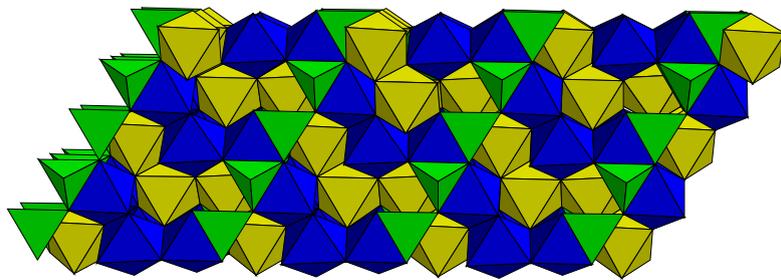
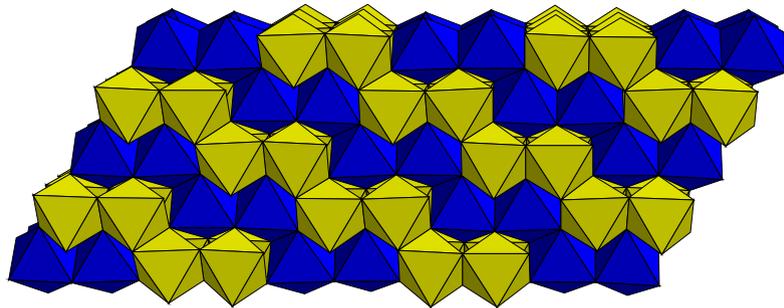


Fig. 1. (Continued).

silica at pressures between 35 and 40 GPa (Tsuchida and Yagi, 1990; Yamakata and Yagi, 1997; Dubrovinsky et al., 2001; Yagi and Yamakata, 2000) through a series of intermediate phases with still unknown structures. In the α -PbO₂-type structure the edge-shearing SiO₆ octahedra form a “zigzag” of 2×2 kinked chains (Fig. 1c). In shock wave compression (Sekine et al., 1987) and laser-heated DAC experiments (Liu et al., 1978), 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 -PbO₂-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.

The goal of the present work was to study the behaviour of silica at pressures above 100 GPa and temperatures above 1000 K.

2. Experimental

Cristobalite samples were obtained by heating a silica gel (99.99% purity) at 1550 °C for 8 h and then quenching it or by annealing of silica sol–gel glass (Prokopenko et al., 2001). 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 (Dubrovinsky et al., 2000; Talyzin et al., 2002). 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 μ m \times 50 μ m (beam line BM01), and at ID30 we used MAR345 or Bruker CCD area detectors and a highly focused beam of 10 μ m \times 15 μ m of 0.3738 Å wavelengths. The detector-to-sample distance varied in different experiments from 170 to 350 mm. The modified Merrill-Basset (three- and four-pin) cells have been used. Diamonds with 250 or 300 μ m culets were mounted on the seats made of B₄C or cubic BN 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 LeBail fits of powder X-ray diffraction data were carried out using the GSAS program (Larson and Von Dreele, 1994). 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 μ m 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).

For details of the lattice dynamic simulations, see Dubrovinsky et al. (1997, 1998) and Dubrovinskaia et al. (2001). We used the empirical and ab initio Si–O interatomic potentials models (Dubrovinsky et al., 1997, 1998). All calculations were performed at 300 K using a 64-point mesh in the Brillouin zone. No symmetry restrictions were used in the calculations.

3. Results

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. Fig. 2 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 (1990) as Cristobalite X–I, appeared and persisted on compression at room temperature to 37–40 GPa (Tsuchida and Yagi, 1990; Dubrovinsky et al., 2001; Prokopenko et al., 2001) (Figs. 2 and 3). If at pressures between 30 and 40 GPa temperature increases to 700–900 K, Cristobalite X–I 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 X–I slowly evolved—the reflections at about 1.24, 1.45, and 1.85 Å are growing, while other reflections diminish (Fig. 2). At the same time, long heating at pressures above 75–80 GPa results in crystallisation of the α -PbO₂-structured phase (Fig. 2), in agreement with previous observations (Dubrovinsky et al., 1997, 2001) and theoretical predictions (Teter et al., 1998; Dubrovinsky et al., 1997). Based on experiments with

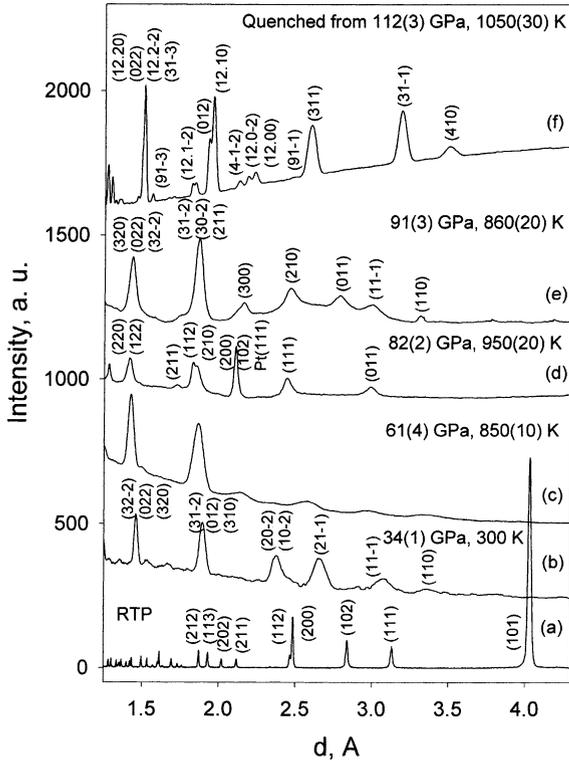


Fig. 2. Examples of the diffraction patterns collected in high-pressure high-temperature experiments with α -cristobalite as a starting material. All observed reflections of the initial material (a) belong to the low-cristobalite tetragonal structure with lattice parameters $a = 4.9733(3) \text{ \AA}$ and $c = 6.9234(4) \text{ \AA}$. (b) On compression in Ar pressure medium to 34(1) GPa at ambient temperature Cristobalite X-I phase was formed (indexes for monoclinic unit cell with lattice parameters $a = 7.473(3) \text{ \AA}$, $b = 3.961(1) \text{ \AA}$, $c = 4.993(2) \text{ \AA}$, $\beta = 120.08(2)^\circ$); heating at 850(1) K and 61(4) GPa (c) during 2 h produces a disordered phase, which crystallizes to the α -PbO₂-structured phase on heating during 4 h at 82(2) GPa and 950(20) K (d) (indexes for orthorhombic cell $a = 4.232(5) \text{ \AA}$, $b = 3.848(4) \text{ \AA}$, $c = 4.756(9) \text{ \AA}$). Heating at 91(4) GPa and 860(20) K at about 3 h results in appearance of new reflections (e) which can be indexed in a monoclinic cell with lattice parameters $a = 7.294(5) \text{ \AA}$, $b = 3.868(3) \text{ \AA}$, $c = 4.841(7) \text{ \AA}$, $\beta = 118.8(1)^\circ$. The top spectrum (f) was obtained from the initial cristobalite sample treated at 112(3) GPa and 1050(30) K during 8 h and subsequently quenched (indexes for monoclinic unit cell with lattice parameters $a = 30.553(4) \text{ \AA}$, $b = 4.1037(4) \text{ \AA}$, $c = 5.0753(9) \text{ \AA}$, $\beta = 118.61(1)^\circ$).

pre-synthesised α -PbO₂-type silica (Dubrovinsky et al., 2001) conducted at pressures below 85 GPa it was proposed that α -PbO₂-structured silica is a stable post-stishovite phase. However, long heating

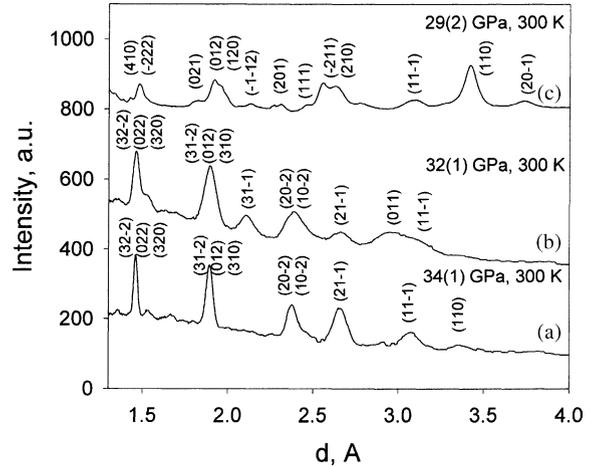


Fig. 3. Examples of the diffraction patterns of “Cristobalite X-I” obtained in different experimental conditions—compression in argon pressure medium (a), in nitrogen pressure medium (b) and without pressure medium (c). In all experiments, α -cristobalite was used as a starting material. Indexing was made for monoclinic unit cells with following lattice parameters: (a) $a = 7.473(3) \text{ \AA}$, $b = 3.961(1) \text{ \AA}$, $c = 4.993(2) \text{ \AA}$, $\beta = 120.08(2)^\circ$; (b) $a = 7.485(4) \text{ \AA}$, $b = 3.967(3) \text{ \AA}$, $c = 4.989(4) \text{ \AA}$, $\beta = 120.0(1)^\circ$; (c) $a = 7.377(9) \text{ \AA}$, $b = 4.002(4) \text{ \AA}$, $c = 5.025(9) \text{ \AA}$, $\beta = 116.7(2)^\circ$.

at pressures above 90 GPa and temperatures above 850 K results in appearance of new reflections, which cannot belong to α -PbO₂-type SiO₂ (Fig. 2). Moreover, the diffraction pattern from a quenched sample treated at pressures above 110 GPa and 1050 K during 8 h is quite different from the diffraction patterns of quenched α -PbO₂-type silica (Dubrovinsky et al., 2001).

4. Discussion

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 Fig. 2c. The most intense diffraction peaks closely resemble the pattern reported by Liu et al. (1978) for quartz heated above 1000 °C at pressures between 35 and 40 GPa. It was interpreted as the hexagonal disordered niccolite structure (Sekine et al., 1987; Liu et al., 1978). Our lattice dynamics simulations for pressure 60 GPa and temperature 1000 K for hexagonal close packed configuration

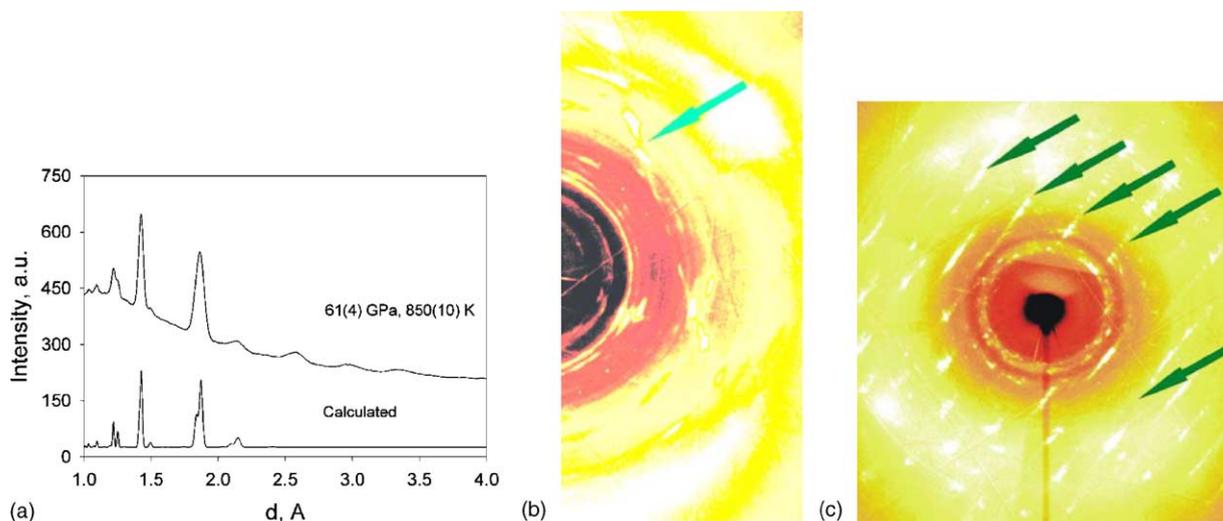


Fig. 4. (a) Comparison of calculated (bottom line) and experimentally observed (upper line) diffraction patterns at 61(4) GPa and 850(10) K. Calculations were made for the structure in which oxygen atoms are hexagonally closed packed and silicon atoms statistically distributed over all possible octahedral positions. Lattice parameters used in calculations are $a = 7.32 \text{ \AA}$, $b = 3.87 \text{ \AA}$, $c = 4.81 \text{ \AA}$, $\beta = 117.6^\circ$. Broad peaks between 2.5 and 3.5 \AA from untransformed low-pressure material. 2D diffraction images of post-quartz (b) at 39(3) GPa and post-tridymite (c) at 9(1) GPa with diffusive scattering lines (arrows).

of oxygen atoms and silicon atoms statistically distributed over octahedral interstitials indicate that the unit cell should be monoclinic with the parameters $a = 7.32 \text{ \AA}$, $b = 3.87 \text{ \AA}$, $c = 4.81 \text{ \AA}$, $\beta = 117.6^\circ$. 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 2 h of heating (Figs. 2c and 4). 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 (Hemley et al., 1996; Yamakata and Yagi, 1997; Dubrovinsky et al., 2001; Haines et al., 2001; Yagi and Yamakata, 2000; Prokopenko et al., 2001). The post-quartz phase discovered by Haines et al. (2001) (Fig. 1b) 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 (Figs. 3–5). This observation allows us to suggest that all “post-tetrahedrally-co-ordinated” (post-quartz,

post-cristobalite, post-tridymite) silica phases are based on hexagonal close packing of oxygen atoms as was predicted by theoretical work (Dmitriev et al., 1998). Broadening of diffraction lines as observed by us (Figs. 2, 3 and 5) and reported earlier (Haines et al., 2001; Hemley et al., 1996) could associate with statistical disorder of silicon atoms among octahedral voids (Giacovazzo, 1992). Moreover, the presence of the diffuse scattering lines (Fig. 4b and c) on the 2D diffraction images of post-quartz and post-tridymite phases provides a direct evidence for the disordered nature of those phases (Giacovazzo, 1992; Vainshtein et al., 1982).

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 X-I (Fig. 6a) at 34(1) GPa assuming that 27% of silicon atoms are still in tetrahedral positions, and a diffraction pattern of Quartz II (Fig. 6b) at 44(2) GPa with 50% of silicon in tetrahedral and 50% in octahedral positions of a distorted *hcp* oxygen lattice.

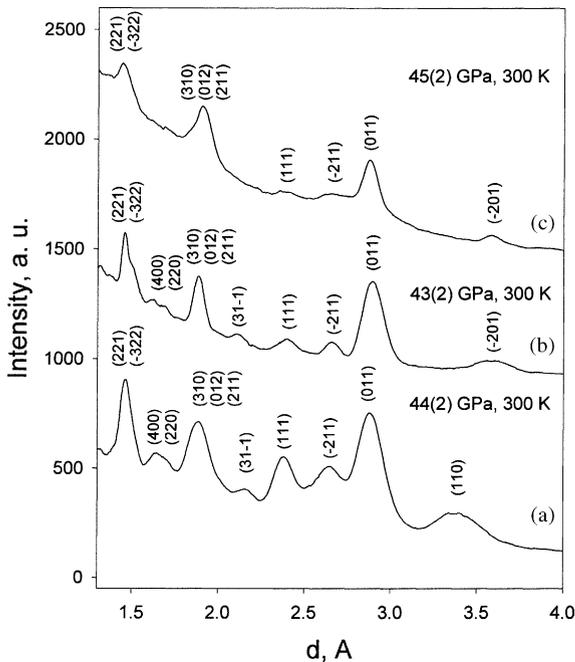


Fig. 5. Examples of the diffraction patterns of quartz compressed in different pressure media: in argon (a), in nitrogen (b), and without a pressure medium. Indexing was made for monoclinic unit cells with following lattice parameters: (a) $a = 7.593(5) \text{ \AA}$, $b = 3.956(4) \text{ \AA}$, $c = 4.834(4) \text{ \AA}$, $\beta = 119.7(1)^\circ$; (b) $a = 7.504(6) \text{ \AA}$, $b = 3.968(4) \text{ \AA}$, $c = 4.888(6) \text{ \AA}$, $\beta = 120.1(1)^\circ$; (c) $a = 7.520(4) \text{ \AA}$, $b = 3.923(3) \text{ \AA}$, $c = 4.965(9) \text{ \AA}$, $\beta = 118.96(42)^\circ$.

Visual similarities of the diffraction patterns of Cristobalite X–I and Quartz II and the diffraction patterns obtained in experiments (in situ and quenched) at pressures above 90 GPa (Figs. 2–5) suggest that silica phases observed at corresponding conditions are also distorted. The main, most intense reflections are close to those of α - PbO_2 -type silica, but some of them (for example, at $\sim 3.5 \text{ \AA}$ in a quenched sample, Fig. 2e), as well as relative intensities of reflections are clearly distinct from those of the diffraction pattern of the α - PbO_2 structure (Dubrovinsky et al., 2001). We indexed all reflections of the sample treated at 112(3) GPa and 1050(30) K during 8 h in a framework of a monoclinic unit cell with lattice parameters $a = 30.553(4) \text{ \AA}$, $b = 4.1037(4) \text{ \AA}$, $c = 5.0753(9) \text{ \AA}$, $\beta = 118.61(1)^\circ$ (Figs. 2e and 6c). The a lattice parameter is about four times bigger than the corresponding lattice parameter of monoclinic unit cells

of the post-quartz modification (Haines et al., 2001), Cristobalite X–I and Quartz II. As in all those silica modifications, oxygen in the new high-pressure phase forms *hcp* sublattice while silicon atoms fully or partially occupy octahedral positions (Figs. 1 and 6c). This structure could be described as a concentration modulation of the silicon sublattice over the monoclinically distorted *hcp* oxygen sublattice (Fig. 1d–f). The origin and lattice parameters of this modulated structure can be understood considering the atomistic mechanism of densification of the cristobalite structure (Dmitriev et al., 1998), which can be formulated in terms of the neighbouring oxygen layers collapse. The oxygen atoms belonging to the successive couples of layers perpendicular to the $[0\ 1\ 2]$ direction of the tetragonal α -cristobalite structure, collapse thus forming the ABAB ... stacking order of hexagonal close packed layers. In order to fit experimental data appropriate monoclinic distortions should be taken into account resulted into the Cristobalite X–I superstructure. However, the silicon atoms still kept an initial motif, which corresponds to the tetragonal α -cristobalite. One can see that the latter is commensurable with c of the Cristobalite X–I structure and quadrupled a (Figs. 1 and 6).

At low pressure the variety of silica polymorphs is related to the flexibility of the Si–O–Si bonding angle between corner-sharing SiO_4 tetrahedra. At high pressure, the diversity of silica modifications is associated with the ability of silicon atoms to occupy varies interstices in the monoclinically distorted *hcp* oxygen lattice. Our studies reveal the existence of the new class of silica phases with different degree of the ordering of silicon atoms. Silica polymorphs with octahedrally co-ordinated silicon known so far (stishovite, fully disordered phase with niccolite'-type structure (Liu et al., 1978), α - PbO_2 -type (Dubrovinsky et al., 2001), and monoclinic ($P2_1/c$ space group) post-quartz phase (Haines et al., 2001) 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-pressure high-temperature 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 behaviour of silica, known for more than 30 years, when at the same pressure and

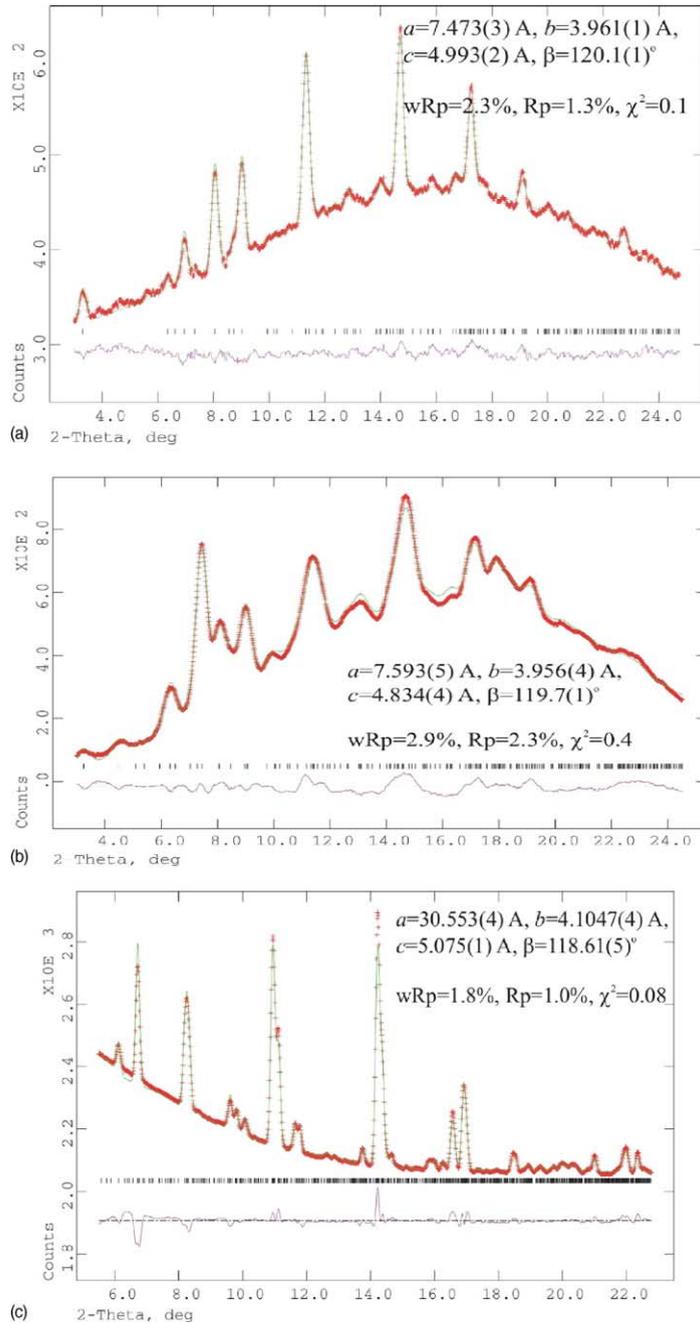


Fig. 6. Profile-fitted X-ray diffraction data of different silica phases obtained: (a) at 34(1) GPa (starting phase α -cristobalite), (b) at 44(2) GPa (starting phase α -quartz), and (c) at ambient conditions after treatment of initial α -cristobalite sample at 112(3) GPa and 1050(30) K during 8 h. The GSAS program package (Larson and Von Dreele, 1994) was used in the LeBail fit. Structural parameters available from authors. Refinement done assuming $P1$ space group. Monoclinic lattice is fixed during the fitting of the atomic coordinates. “Pseudo-monoclinic” symmetry of atomic coordinates (space group $P2_1/c$) derived from lattice dynamics simulations is preserved. Thermal parameters of all atoms are fixed on the value 0.025.

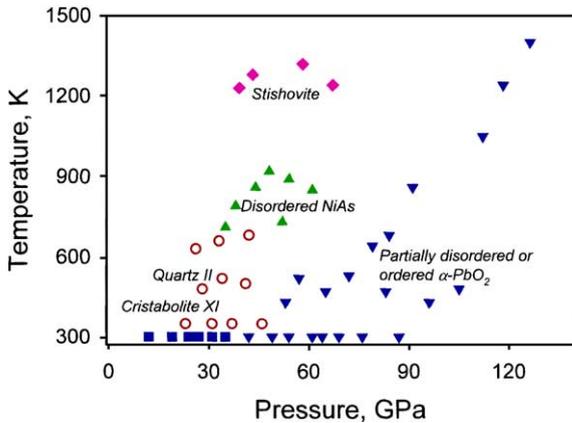


Fig. 7. Phases observed in electrically-heated DAC experiments with α -cristobalite (filled symbols) and α -quartz (open symbols) as starting materials. All partially ordered phases with silicon in tetrahedral and octahedral coordination produced from α -quartz combined under name “Quartz II” (open circles). All phases with silicon atoms partially or fully ordered in octahedral voids in *hcp* oxygen lattice designated as “partially disordered or ordered α -PbO₂” (inverse triangles). Stishovite: diamonds, disordered NiAs structure: triangles, Cristobalite X–I: squares.

temperature range different phases were synthesised (Hemley et al., 1996; Tsuchida and Yagi, 1990; Gratz et al., 1993; Yamakata and Yagi, 1997; Andraut et al., 1998; Dubrovinsky et al., 1997, 2001; Liu et al., 1978; Prokopenko et al., 2001). Silica phases with tetrahedrally co-ordinated silicon demonstrate a significant diversity in densities—from 1.77 g/cm³ in open framework zeolite-like structures to 2.90 g/cm³ of coesite (Heaney et al., 1996), while high-pressure modifications of silicon dioxide with hexagonal close packing of oxygen and octahedrally co-ordinated silicon have practically the same densities (\sim 4.28 g/cm³) at ambient conditions (quenched metastable phases), and very close densities at a megabar pressure range (difference just about 1–1.5% from CaCl₂- to α -PbO₂-type and disordered SiO₂ phases).

5. Conclusions

We found that starting from different low-pressure silica polymorphs (quartz, trydimite, cristobalite) depending on history and conditions of treatment in electrically-heated DAC different metastable and stable phases can be synthesised (Fig. 7). All these phases,

as well as known high-pressure silica modifications (stishovite, fully disordered phase with niccolite-type structure, α -PbO₂-type, and monoclinic ($P2_1/c$ space group) post-quartz phase) belong to the same class of silica phases with different degree of the ordering of silicon atoms within (distorted) hexagonal close packing of oxygen atoms. The details of the silicon distribution among free positions in the oxygen network strongly depend on the starting material and the conditions of high-pressure high-temperature treatment of silica, but a general trend is that at pressures above 40–45 GPa most of the silicon atoms are placed in octahedral positions.

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References

- Andraut, D., Fiquet, G., Guyot, F., Hanfland, M., 1998. Pressure-induced Landau-type transition in stishovite. *Science* 282, 720–724.
- Dmitriev, V.P., Toledano, P., Torgashev, V.I., Salje, E.K.H., 1998. Theory of reconstructive phase transitions between SiO₂ polymorphs. *Phys. Rev. B* 58, 11911–11921.
- Dubrovinskaia, N.A., Dubrovinsky, L.S., Ahuja, R., Dmitriev, V., Weber, H.P., 2001. Experimental and theoretical identification of new high-pressure TiO₂ polymorph. *Phys. Rev. Lett.* 87, 5501–5504.
- Dubrovinsky, L.S., Saxena, S.K., Lazor, P., Ahuja, R., Eriksson, O., Wills, J.M., Johansson, B., 1997. Experimental and theoretical identification of a new high-pressure phase of silica. *Nature* 388, 362–365.
- Dubrovinsky, L.S., Saxena, S.K., Ahuja, R., Johansson, B., 1998. Theoretical study of the stability of MgSiO₃-perovskite in the deep mantle. *Geophys. Res. Lett.* 25, 4253–4256.
- Dubrovinsky, L.S., Saxena, S.K., Tutti, F., Le Bihan, T., 2000. X-ray study of thermal expansion and phase transition of iron at multimegabar pressure. *Phys. Rev. Lett.* 84, 1720–1723.
- Dubrovinsky, L.S., Dubrovinskaia, N.A., Saxena, S.K., Tutti, F., Rehi, S., Le Bihan, T., Shen, G., Hu, J., 2001. Pressure-induced transformations of cristobalite. *Chem. Phys. Lett.* 333, 264–270.
- El Goresy, A., Dubrovinsky, L., Sharp, T.G., Saxena, S.K., Chen, M., 2000. A new monoclinic post-stishovite polymorph of silica in the SNC meteorite Shergotty. *Science* 288, 1632–1634.
- Giacovazzo, C., 1992. *Fundamentals of Crystallography*. Oxford University Press, New York, 654 pp.

- Gratz, A.J., DeLoach, L.D., Clough, T.M., Nellis, W.J., 1993. Shock amorphization of cristobalite. *Science* 259, 663–666.
- Haines, J., Leger, J.M., Gorelli, F., Hanfland, M., 2001. Crystalline post-quartz phase in silica at high pressure. *Phys. Rev. Lett.* 87, 155503.
- Hemley, R.J., Prewitt, C.T., Kingma, K.J., 1996. High pressure behaviour of silica. *Rev. Miner.* 29, 41–81.
- Heaney, P.J., Prewitt, C.T., Gibbs, G.V. (Eds.), 1996. *Silica*. *Rev. Miner.* 29, 606.
- Kingma, K.J., Cohen, R.E., Hemley, R.J., Mao, H.K., 1995. Transformation of stishovite to a denser phase at lower-mantle pressures. *Nature* 374, 243–245.
- Larson, A.C., Von Dreele, R.B., 1994. Los Alamos National Laboratory (LAUR), p. 86.
- Liu, L., Basset, W.A., Sharry, J., 1978. New high-pressure modifications of GeO₂ and SiO₂. *J. Geophys. Res.* 83, 2301–2305.
- Teter, D.M., Hemley, R.J., Kresse, G., Hafner, J., 1998. High pressure polymorphism in silica. *Phys. Rev. Lett.* 80, 2145–2148.
- Tsuchida, Y., Yagi, T., 1990. New pressure-induced transformations of silica at room temperature. *Nature* 347, 267–269.
- Palmer, D.C., Hemley, L.W., Prewitt, C.T., 1994. Raman spectroscopic study of high-pressure phase transitions in cristobalite. *Phys. Chem. Miner.* 21, 481–488.
- Prokopenko, V.B., Dubrovinsky, L.S., Dmitriev, V., Weber, H.-P., 2001. Raman spectroscopy and X-ray diffraction in situ characterization of phase transitions in cristobalite under high pressure. *J. Alloys Comp.* 327, 87–95.
- Sharp, T.G., El Goresy, A., Wopenka, B., Chen, M., 1999. A post-stishovite SiO₂ polymorph in Shergotty: implication for impact events. *Science* 284, 1511–1513.
- Sekine, T., Akaishi, M., Setaka, N., 1987. Fe₂N-type SiO₂ from shocked quartz. *Geochem. Cosmochem. Acta* 51, 379–381.
- Talyzin, A.V., Dubrovinsky, L.S., Le Bihan, T., Jansson, U., 2002. In situ Raman study of C₆₀ polymerization at high pressure high temperature conditions. *J. Phys. Chem.* 116, 2166–2174.
- Vainshtein, B.K., Fridkin, V.M., Indenbom, V.L., 1982. *Modern Crystallography*, vol. II. Springer, Berlin, 340 pp.
- Urusov, V.S., Dubrovinskaia, N.A., Dubrovinsky, L.S., 1990. *Construction of Possible Crystal Structures (in Russian)*. MGU, Moscow, 160 pp.
- Yagi, T., Yamakata, M., 2000. Effect of hydrostaticity on the phase transformations of cristobalite. In: Aoki, H., et al. (Eds.), *Physics Meets Mineralogy*. Cambridge University Press, pp. 242–255.
- Yamakata, M., Yagi, T., 1997. New stishovite-like phase of silica formed by hydrostatic compression of cristobalite. *Proc. Jpn. Acad.* 73B, 6, 85–88.