

Pressure-induced transformations of cristobalite

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Abstract

X-ray in situ studies in electrically and laser-heated diamond anvil cells (DACs) at pressures over 80 GPa and temperatures above 2500 K were used to determine stable silica phase at extreme conditions. We demonstrate that so far unidentified phases obtained on the compression of α -cristobalite, new dense silica polymorph in the Martian Shergotty meteorite, and controversial post-stishovite phase is α -PbO₂-like silica. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Properties and behaviour of silicon dioxide SiO₂ at high pressures and temperatures are of great interest due to its wide ranging implications in fundamental physics, geophysics and material sciences. Last decade studies revealed number of enigmatic phenomenon associated with high-pressure silica polymorphs – formation of unidentified phases on the compression of α -cristobalite, controversial theoretical and experimental information on the possible post-stishovite phases, discovery of new dense natural silica polymorph in the Shergotty meteorite in the mineralogical environment (alumosilicate phases characteristic for pressure below 40 GPa) of which is inappropriate

for post-stishovite phase [1–13]. In this Letter, we present the results of in situ X-ray studies of silica in electrically and laser-heated diamond anvil cells (DACs) at pressures over 85 GPa and temperatures above 2500 K and demonstrate that the above mentioned problems could be explained from properties and behaviour of silica with α -PbO₂-type structure.

A series of phase transitions were found on cold compression of α -cristobalite. At pressures above 10 GPa, first Tsuchida and Yagi [5] and later other groups [3,4,6] reported about a phase transition to one more phase (Cristobalite XI according to [5] or Cristobalite III according to [7]). Under further compression at pressures above 40 GPa, Cristobalite XII [5,6] was found. On decompression of Cristobalite XII, a new polymorph – Cristobalite XIII formed. Little is known about the nature and structure of all these Cristobalite-‘x’ phases [6,7]. For the same pressure range (above 10 GPa), several have reported amorphisation [4,8,9]; it is

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not clear how this is related to the phase transitions mentioned above.

Recently, the α -PbO₂-like silica was experimentally obtained in a mixture with stishovite in a laser-heated DAC at pressures above 70 GPa and temperatures above 2500 K [12]. However, there is no definite theoretical and/or experimental information on the stability of the α -PbO₂-like silica [11,12,21].

Intensive studies [13] of grains of silica material from the meteorite Shergotty led to the discovery of a new natural SiO₂ polymorph. On the basis of selected area electron diffraction (SAED) data, the authors [13] suggest that the new silica polymorph is distinctly different from the ideal (with a space group *Pbcn*) or modified (with a space group *Pnc2*) α -PbO₂-type phases [10,12], but instead similar to a *Pbcn* structure produced in shock-waves experiments at 70–90 GPa [10]. It implies that the meteorite Shergotty was subjected to unlikely high shock pressure above 80 GPa [13].

2. Experimental

We conducted in situ X-ray high-pressure and high-temperature experiments at Uppsala Lab, ESRF (beam line ID30), APS (Argonne National Lab, GSECARS, Sector 13), and at BNL (beam line X-17C) using electrical and laser heating methods with white and constant wavelength radiation, energy and angle sensitive detectors [12,14,15]. In our analysis of the integrated X-ray spectra, we used the program GSAS [16] and PeakFit 4.0.

At Uppsala Lab, we have obtained powder X-ray diffraction data with a Siemens X-ray system consisting of a smart charge coupled device (CCD) area detector and a direct-drive rotating anode as an X-ray generator (18 kW). MoK α radiation (tube voltage 50 kV, tube current 24 mA, cathode gun 0.1 \times 1 mm²) focused with a capillary X-ray optical system to 40 μ m FWHM. See [12] for more details. At ESRF, powder diffraction data was collected with a fine incident X-ray beam of an approximate rectangular shape (8 \times 9 μ m²) of 0.3738 Å wavelength at the FastScan imaging plate. At APS and BNL, the X-ray beam was

collimated to the size of 12 \times 15 μ m² and diffraction spectra were collected with energy disperse Ge-detector. In experiments conducted in Uppsala and at ESRF, we heated the samples externally in a Mao-Bell type DAC [14]. At APS, we used the double sided laser heating technique with heating spot of 20–40 μ m. For temperature measurement, Kaiser holographic spectrometers together with the CCD were used [15]. Cristobalite samples were obtained by heating silica gel (99.99% purity) at 1550°C for 8 h and then quenching it.

3. Results and discussion

We did not follow the phase transition from cristobalite I (or α -cristobalite) to cristobalite II (\sim 1.5 GPa according to [7]) and compressed samples directly to 10–12 GPa (Fig. 1). At that pressure, cristobalite I transforms to cristobalite XI (Fig. 1). At pressures above 37 GPa, new reflections started growing and the phase transition was completed by 45 GPa. On further compression to 89 GPa at room temperature, we did not observe any other phase transitions (Fig. 1).

The *d*-values and relative intensities of reflections of the phase obtained in the present Letter at high pressure from α -cristobalite as a starting material, and those from the substance synthesised in a laser-heated DAC at 69 GPa [12,17,18] are in quantitative agreement (Table 1). Such a comparison allows us to identify the phase which we obtained from low cristobalite at pressures above 45 GPa as the α -PbO₂-like silica (Fig. 2). Moreover at 53 GPa, our diffraction data and the data reported by Tsuchida and Yagi [5] for the same pressure are close (Table 1). The lattice parameters of the α -PbO₂-like silica obtained in the present study at 53(1) GPa are $a = 4.3268(5)$ Å, $b = 3.9354(6)$ Å, $c = 4.8037(6)$ Å, while by indexing reflections reported in [5] in terms of an orthorhombic lattice of the α -PbO₂-like structure, we have $a = 4.407(5)$ Å, $b = 3.884(7)$ Å, $c = 4.821(4)$ Å. In other words, the Cristobalite XII phase found by Tsuchida and Yagi [5] is the α -PbO₂-like silica phase.

On gradual decompression from 64(1) GPa, we did not observe any phase transformations, trace

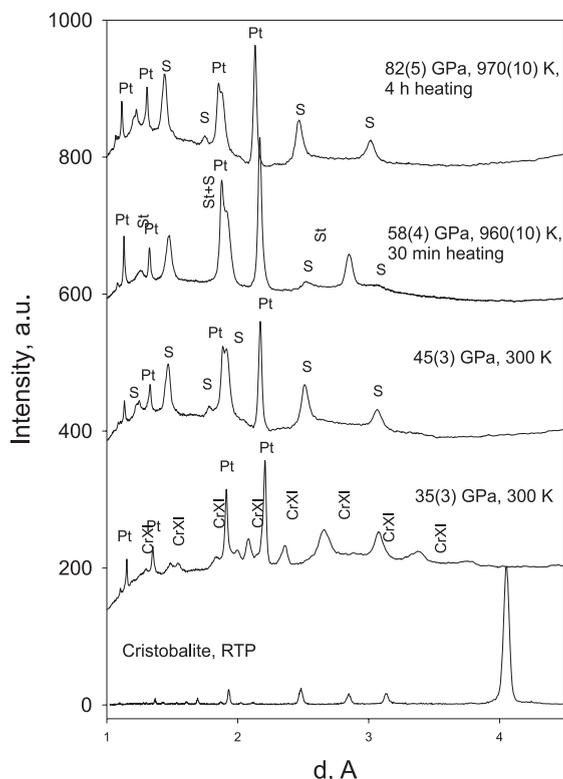


Fig. 1. Examples of diffraction patterns collected on compression at room temperature of α -cristobalite (three bottom lines) and on the heating of α -PbO₂-like silica (two upper lines). The initial material (bottom line) is low-cristobalite ($a = 4.9733(3)$ Å, $c = 6.9234(4)$ Å). At pressures above 10 GPa, α -cristobalite transforms to Cristobalite XI [5] ('CrXI', second line from bottom). At pressures above 37 GPa, new reflections start growing and phase transition to α -PbO₂-like structure ('S') is completed by 45 GPa. On further compression to 89 GPa at room temperature, we did not observe any other phase transitions. After heating for 30 min in electrically heated DAC at 58(4) GPa and 960(10) K, reflections of α -PbO₂-like silica phase almost disappeared and instead stishovite reflections ('St') grew. But when at the same temperature (~ 950 K) pressure was increased to 82 GPa and the sample was heated for approximately 4 h, stishovite reflections disappeared and α -PbO₂-like silica phase reflections were recovered. In other words, at 58(4) GPa and 960(10) K, stishovite is stable phase (in good agreement with [5,6]), while at 82(5) GPa and 970(10) K, stable silica phase has α -PbO₂-like structure. Platinum reflections are marked as 'Pt'.

all reflections of the α -PbO₂-like silica to an ambient pressure and obtained phase with lattice parameters $a = 4.547(2)$ Å, $b = 4.099(3)$ Å, $c = 5.018(4)$ Å. A comparison of our X-ray data for

the quenched α -PbO₂-like silica phase with data published by Tsuchida and Yagi [5] for Cristobalite XIII (Table 2) clearly shows that d -spacings, relative intensities of reflections, and lattice parameters for the two phases are close. Close agreement in X-ray data for our quenched samples and for the samples of Tsuchida and Yagi [5] (especially taking into account the different methods of synthesis of the samples, different maximum pressures, possible differences in decompression rates, etc. [3,6]) allows us to conclude that Cristobalite XIII [5] is the α -PbO₂-like silica quenched from high pressure.

According to the molecular dynamics calculations with semi-empirical potentials and ab initio pseudopotential calculations [11], α -PbO₂-like silica phase belongs to $Pbcn$ (or $Pnca$ in another setting) space group. On the other hand, lattice dynamics with empirical potentials and full-potential linear muffin tin orbital (FP-LMTO) [12,18] calculations indicate that the symmetry of α -PbO₂-like silica could be lower and described by space group $Pnc2$. The theoretically predicted difference between ideal and distorted α -PbO₂-like silica is too small to be unambiguously resolved by X-ray powder diffraction [12,18]. The space group $Pbcn$ is centrosymmetric and materials which crystallise in this space group cannot have piezoelectric properties. We measured piezoelectric properties of polycrystalline sample of α -PbO₂-like silica synthesised at 82(2) GPa and 950(25) K and subsequently decompressed to ambient conditions. Indentation technique [19] was used. Fig. 2 shows the experimental set-up. A small piece of an α -quartz X-plate was used to calibrate the system. A sample of polycrystalline α -PbO₂-like silica demonstrated direct piezoelectric effect with coefficient $e = 1.2(4)$ C/m² and it unambiguously excludes centrosymmetric $Pbcn$ (or $Pnca$) space group in favour of $Pnc2$ (Fig. 3). Note that stishovite (centrosymmetric space group $P4_2/mmm$) sintered between 42 and 45 GPa at 900(25) K does not show any sign of piezoelectric effect (Fig. 4).

Table 2 shows that position of reflections and zone relations, observed for the newly discovered silica polymorph in the meteorite Shergotty [13] by SAED (SAED), could be easily explained in terms of the α -PbO₂-like silica structure with $Pnc2$ space

Table 1

Comparison of d -values obtained in present study on compression of cristobalite at room temperature and 53(1) GPa and 69(2) GPa with earlier reported diffraction patterns of silica polymorphs at similar conditions [5,12]

53(1) GPa				69(2) GPa			
This study		Phase XII [5]		This study		α -PbO ₂ -like (Pnc2-phase) [12]	
d^a (Å)	I (%)	d^b (Å)	I^c (%)	d^d (Å)	I (%)	d^e (Å)	I (%)
3.046	12			3.014	21	3.013	19
2.491	39	2.493	W	2.464	45	2.472	52
				2.139	5	2.145	^f
2.100	5	2.114	VW	2.076	5	2.069	6
1.896	81	1.917	M	1.875	85	1.894	100
1.853	100	1.859	M	1.833	100	1.830	^f
1.764	16			1.744	13	1.742	11

^a $a = 4.3268(5)$ Å, $b = 3.9394(6)$ Å, $c = 4.8037(6)$ Å.

^b $a = 4.407(5)$ Å, $b = 3.884(7)$ Å, $c = 4.821(4)$ Å.

^c M, medium; W, weak; VW, very weak.

^d $a = 4.277(4)$ Å, $b = 3.901(3)$ Å, $c = 4.749(4)$ Å.

^e $a = 4.300(1)$ Å, $b = 3.899(2)$ Å, $c = 4.698(4)$ Å [12].

^f Not resolved with Pt reflections.

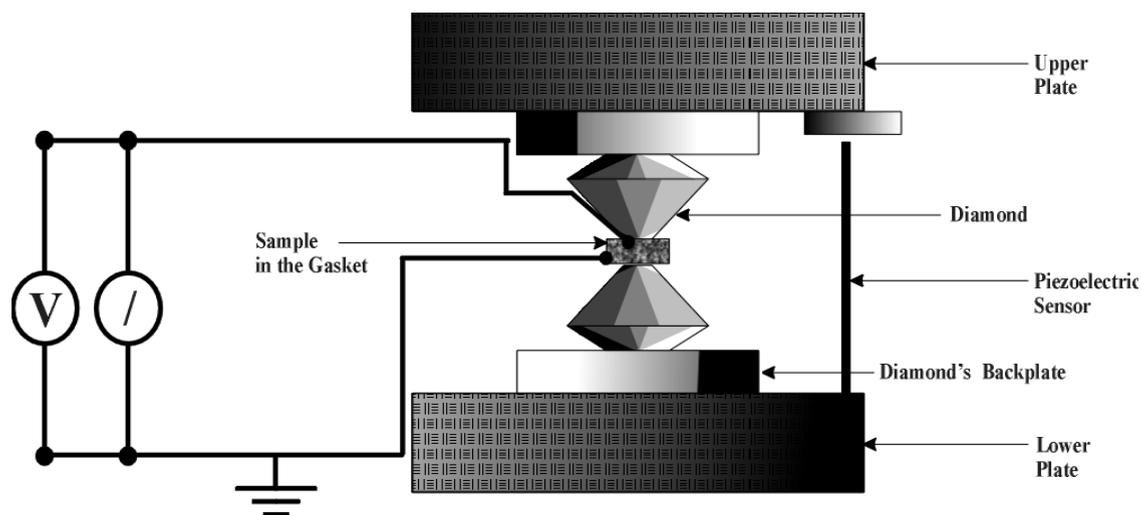


Fig. 2. Experimental set-up used for piezoelectric measurements. Sample is located in the hole (150–200 μm in diameter) drilled in the metallic gasket (acting also as electrode). Second electrode (flattened thin Pt wire) attached to upper diamond and electrically isolated from the gasket.

group described above. The ratio of lattice parameters for the silica mineral from Shergotty meteorite ($a/c = 0.890(9)$, $b/c = 0.814(12)$) are comparable to those of the α -PbO₂-like silica phase obtained on decompression ($a/c = 0.906(1)$, $b/c = 0.816(1)$). The reasonable small differences in the lattice parameters could be due to the different history of the synthetic and natural samples

and due to the small amount of Na₂O (0.4 wt%) and Al₂O₃ (1.12 wt%) in silica grains from the meteorite. Issuing from the presence of Na₂O and Al₂O₃ in the SiO₂ grains and their morphology, the authors [13] suggested that the low-pressure precursor phase was tridymite. Indeed, compression of tridymite at ambient temperature to pressures above 40 GPa and further quenching led to the

Table 2
Diffraction data for some silica polymorphs^a

This study, quenched from 64(1) GPa		Tsuchida and Yagi [5] Phase XIII ^b		Sharp et al., [13] ^c	<i>hkl</i>
<i>d</i> (Å)	<i>I</i> (%)	<i>d</i> (Å)	<i>I</i> (%)	<i>d</i> (Å)	
				4.54 ^d	100
				3.41 ^d	101
3.173	26	3.166	W	3.22	011
				3.09 ^d	110
		2.966 ^c	VW		
2.605	100	2.595	S	2.62	111
2.272	6	2.244	VW	2.28	200
2.197	5	2.244	VW		102
1.989	35	1.972	W	1.97	210
1.936	65	1.933	W		112
1.848	16	1.834	VW		211
1.499	45	1.494	M		122

^a Samples studied outside the DAC with oscillation around ω -axis of goniometer. Synthetic cristobalite as a starting material; slowly quenched sample from maximum pressure 64 GPa; Lattice parameters of quenched α -PbO₂-like phase are $a = 4.547(2)$ Å, $b = 4.099(3)$ Å, $c = 5.018(4)$ Å.

^b Calculated lattice parameters are $a = 4.508(5)$ Å, $b = 4.070(7)$ Å, $c = 5.044(11)$ Å.

^c Calculated lattice parameters are $a = 4.55(1)$ Å, $b = 4.16(3)$ Å, $c = 5.11(4)$ Å.

^d Reflection is forbidden for *Pnca* or *Pnc2* space groups but present in SAED data [13] as a result of dynamical diffraction effects.

^e Corresponds to (110) 100% intensity reflection of stishovite.

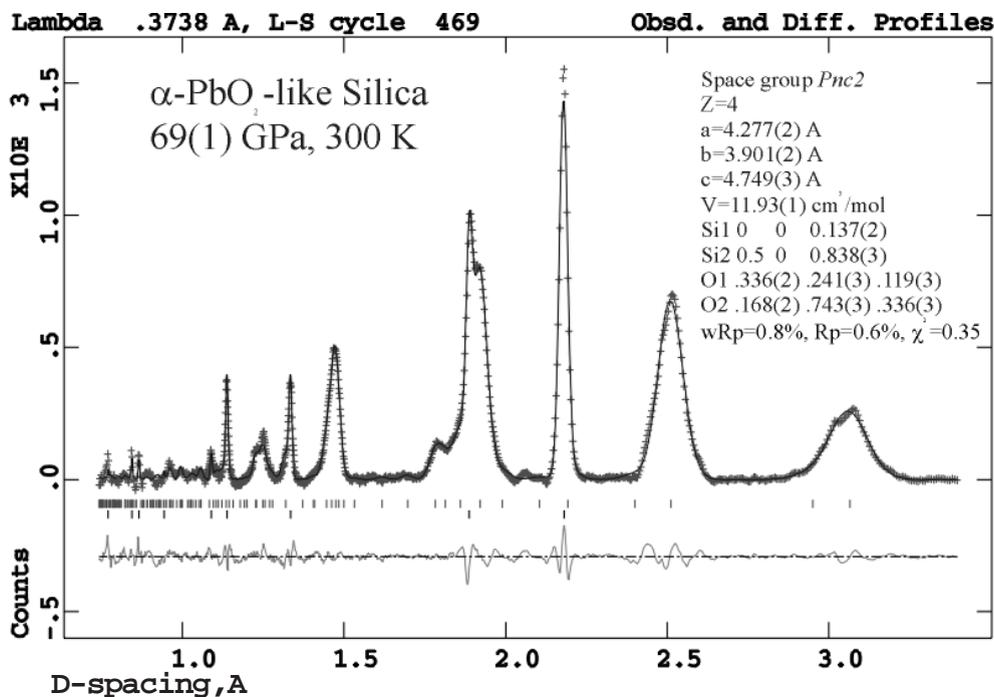


Fig. 3. Typical example of analysed integrated patterns of the spectrum collected at 61(1) GPa and ambient temperature. GSAS program package [16] was used. The lower ticks mark positions of Pt pressure calibrant and upper one – the α -PbO₂-like silica phase. Background was subtracted.

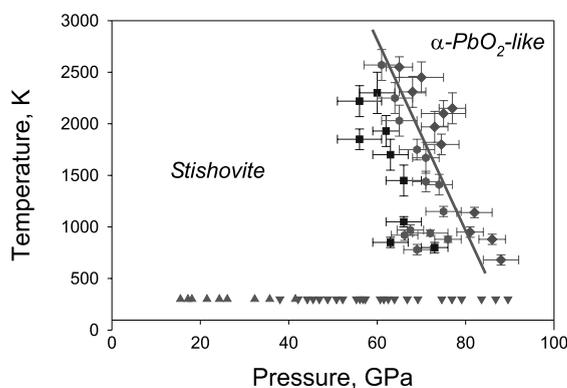


Fig. 4. High pressures and temperatures relations of SiO_2 . Triangles and inverse triangles show conditions at which Cristobalite XI [5] and $\alpha\text{-PbO}_2$ -like silica (respectively) were observed on the compression at ambient temperature of α -cristobalite. Blue squares represent conditions at which stishovite is a stable phase, red diamonds – $\alpha\text{-PbO}_2$ -like silica is a stable phase, and green circles mixed region. The line shows tentative phase boundary between stishovite and $\alpha\text{-PbO}_2$ -like silica.

formation of $\alpha\text{-PbO}_2$ -like silica phase with lattice parameters $a = 4.548(1)$ Å, $b = 4.112(1)$ Å, $c = 5.053(2)$ Å, values fairly close to those obtained for natural SiO_2 crystals from the Shergotty meteorite. Our studies show that the silica phase discovered by Sharp et al. [13] is actually a naturally occurring $\alpha\text{-PbO}_2$ -like silica phase.

Lattice parameters and molar volume of the $\alpha\text{-PbO}_2$ -like silica phase were determined at pressures between 20 and 70 GPa at room temperature. The result of the fit with the third-order Birch–Murnaghan equation of state [20] gave $K_{300,1} = 313(5)$ GPa, $K'_{300,1} = 3.43(11)$, and $V_{300,1} = 14.08(2)$ cm³/mol. For the $\alpha\text{-PbO}_2$ -like silica, the values of bulk modulus and molar volume are slightly higher, and pressure derivatives of bulk modulus lower than the corresponding values for stishovite [21] ($K_{300,1} = 291(1)$ GPa, $K'_{300,1} = 4.3(1)$, and $V_{300,1} = 14.04$ cm³/mol). At pressures above 80 GPa and ambient temperature, the density of the $\alpha\text{-PbO}_2$ -like silica becomes higher than that of stishovite and it indicates that the former could be more stable than the latter.

To determine the relative stability of the $\alpha\text{-PbO}_2$ -like silica and stishovite at different pressures and temperatures, we conducted a series of

experiments in externally electrically heated and internally laser-heated DACs. Fig. 1 shows examples of the patterns collected during an experiment with electrical heating. A mixture of platinum powder (served as an internal pressure standard) and a presynthesised $\alpha\text{-PbO}_2$ -like silica was compressed to 45 GPa. On heating to 950 K, the pressure rose to 58 GPa. After heating for 30 min, the reflections of the $\alpha\text{-PbO}_2$ -like silica phase almost disappeared, and instead stishovite reflections grew (particularly the (110) characteristic reflection of stishovite can be observed quite clearly, see Fig. 1). But when at the same temperature (~ 950 K), the pressure was increased to 82 GPa, and the sample was heated for approximately 4 h, stishovite reflections disappeared and the $\alpha\text{-PbO}_2$ -like silica phase reflections were recovered. In other words, at 58(4) GPa and 960(10) K, stishovite is a stable phase (in good agreement with [5,6]), while at 82(5) GPa and 970(10) K, a stable silica phase has the $\alpha\text{-PbO}_2$ -like structure. Fig. 4 summarizes the results of the different experiments and shows phase boundary between stishovite and the $\alpha\text{-PbO}_2$ -like phase.

We did not observe the CaCl_2 -type silica phase reported earlier at pressures above 45 GPa and ambient temperature [7,12,21] (Fig. 1). First, we did not use stishovite as a starting material in our experiments, and stishovite synthesised during experiments could not be well crystallised. Thus, it could be more difficult to recognize formation of CaCl_2 -type structure. Another reason, why CaCl_2 -type phase did not appear in our experiments could be that in electrically heated DAC, we had practically stress-free conditions, while the stishovite – CaCl_2 -type silica phase transition is very sensitive to stress conditions [17]. It is also possible that CaCl_2 -structured silica is a metastable phase similarly to the same polymorph of PbO_2 [22]. Further studies are required to resolve this issue.

4. Conclusions

In summary, X-ray in situ studies show that on compression at ambient temperature α -cristobalite transforms to Cristobalite XI at pressures above 10 GPa. On further compression above 40 GPa at

room temperature, Cristobalite XI transforms to an α -PbO₂-like silica phase, which is observed to be 89 GPa. The α -PbO₂-like silica phase is stable with respect to stishovite above 80 GPa at high temperature. We demonstrated that SiO₂ in the earth's lower mantle would have a post-stishovite α -PbO₂-like structure. Based on the high-pressure and temperature studies we conclude that the silica mineral discovered in the meteorite Shergotty has the α -PbO₂-like structure.

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