Synthesis and X-ray diffraction structure analysis of nanocrystalline bulk SiO2 stishovite

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Abstract

The aim of this work was to synthesize nanocrystalline bulk of SiO_2 stishovite at a fixed pressure of 15.6 GPa and at temperatures between 600 and 1800°C. High- resolution x-ray diffraction measurements were carried out at P02.1 beamline at PETRA III. Full-profile analyses of the diffraction patterns were performed by Rietveld method to obtain data about structural changes in the samples with increasing synthesis temperature.

Contents

1 Introduction

Stishovite is a high-pressure polymorph of SiO2, stable at pressure above 9 GPa and is considered to be the second hardest oxide known [1]. This material can be used for industrial purposes because of its combination of very high hardness and toughness and it is relatively easy to synthesize. However, a mechanism of transition from amorphous phase SiO_2 into nanopolycrystalline stishovite remains unexplored. In addition, synthesis of fully densified bulk nanograined material is still challenging because of the difficulty of suppressing grain growth during sintering.

A series of 10 samples was synthesized under a fixed pressure of 15.6 GPa and temperature range from 600 to 1800 °C using 100ton Large Volume Press for further high-resolution X-ray diffraction measurements of structure. The aim is to get closer to understanding the mechanism of formation of nanocrystalline stishovite under high PT.

2 Synthesis of nanocrystalline stishovite

Under high-pressure and high- temperature, silicon dioxide transforms in its polymorph modification – stishovite. Stishovite is stable over a wide pressure range (10–70 GPa), which corresponds to about 300–1700 km depth in the deep mantle (Zhang et al. 1996; Ono et al. 2002). It possesses the rutile structure with each silicone atom coordinated by six oxygen atoms, forming distorted SiO6 octahedra.

For realization high PT condition, necessary for producing stishovite samples were used 1000ton Large Volume Press (LVP) (Fig. 1) .This press allows to synthesize material up to 25 GPa and 2000°C with sample size from 1 to 10 mm.

Fig 1 . 100ton Large Volume Press at HASYLAB DESY, Hamburg .

We carried out experiments using the bulk glass starting materials at different temperatures and a fixed pressure of 15 GPa.

Diagram of the experiment is shown in Fig 2. Synthesis of the samples was carried out under pressure of 15.6 GPa; time of compression was 2 hours, time of heating was 30 min, time of decompression with decreasing temperature was 3 hours.

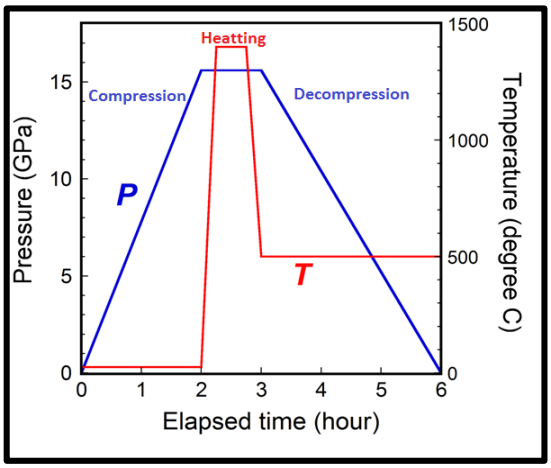
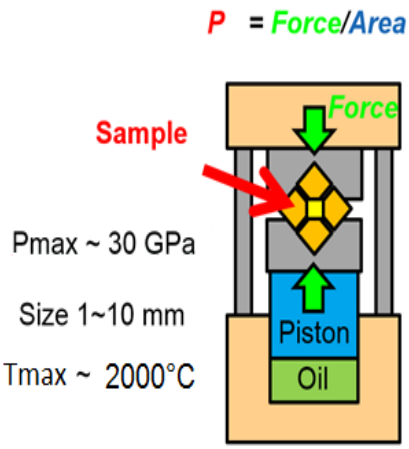


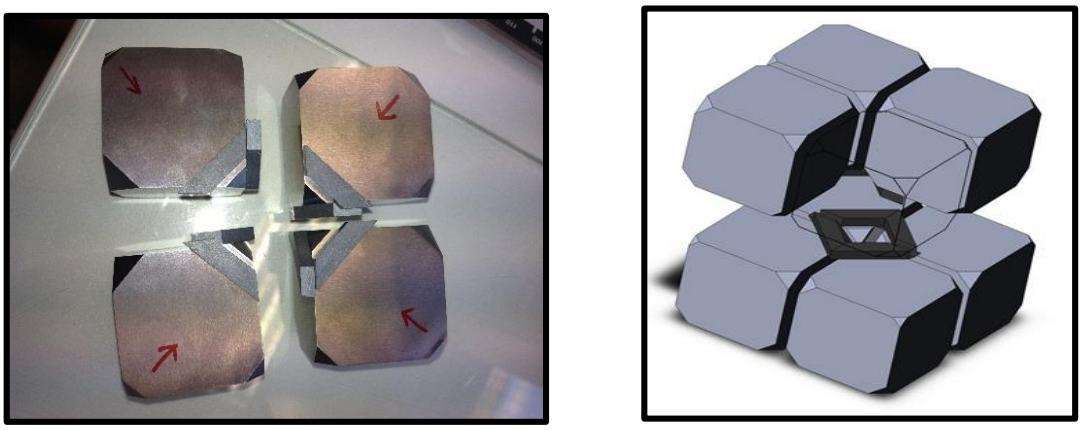
Fig 2 . Diagram of the experiment



2.1 Design of multi-anvil device and cell assembly for high-pressure experiment

For synthesis of styishovite under high-pressure multi-anvil device were used. This system employs six tool-steel outer-anvils and eight tungsten carbide cubic inner-anvils to focus an applied load on an octahedral high-pressure chamber formed as a result of corner truncations on the inner-anvils [2]. The three main outer-anvils define an inner cubic cavity of 100mm edge-length in which the eight second-stage tungsten carbide inner-anvils are compressed. The special form of the cell helps to produce pressure in 8 directions, that prevents from deformation and additional stress in a sample.

Divers sample-pressure ranges can be attained by using various corner truncation size of the inner-anvils. In this experiment were used anvil with the size of the truncated angle of about 7 mm, which allows for pressure to and to obtain samples of 1 mm diameter. This system has been designed with the aim of providing significantly larger sample volumes .



(a) **(b)**

Fig. 3(a) (b) Tungsten carbide cubic inner-anvils with gaskets forming octahedral high-pressure chamber

Internal arrangement of cell assembly for stishovite represents a complicated structure diagram of this assembly is shown in Fig. 4. In order to avoid reaction or eutectic melting between various ceramic materials at high temperature, MgO surrounds the LaCrO3 furnace and the thermocouple sleeve, which is normally Al2O3, is also made from MgO. A thin ZrO2 sleeve for thermal insulation is inserted around the furnace, but is separated from it by an MgO sleeve. A single crystal MgO sample capsule is employed,

which is particularly effective in keeping metallic liquids enclosed due to the absence of wet table grain boundaries [1].

The bulk of SiO2 is placed in the center of the cell and the construction is settled in the octahedral pressure medium.

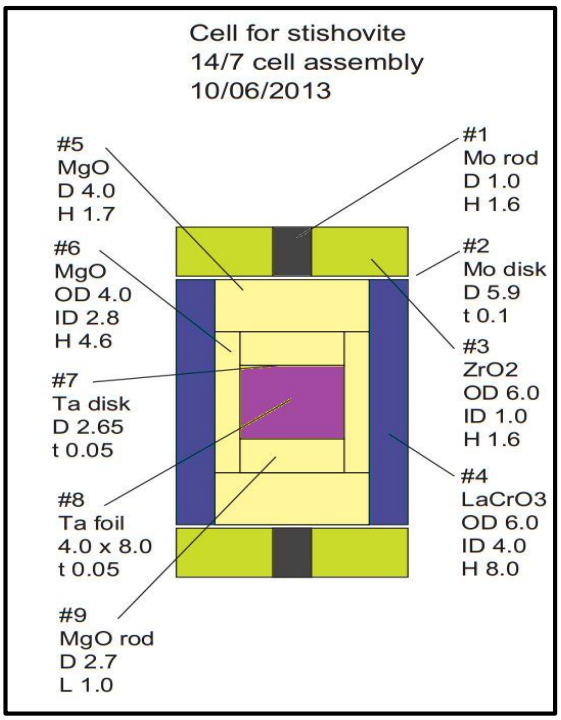


Fig. 4 Diagram of cell assembly for stishovite.

2.2 Results of synthesis

As a result, 10 samples of diameter 1.2-1.5mm with thickness 0.5 and 1 mm were synthesized under pressure 15, 6 GPa and in the range of temperature 600-1800**°C.** As seen in Fig. 5, an increase in temperature leads to the following visible changes like a change of color and increasing transparent properties of stishovite indentation. In the samples synthesized at temperatures 1100**°C** 1200**°C,** heterogeneity of textures and some blotches were found.

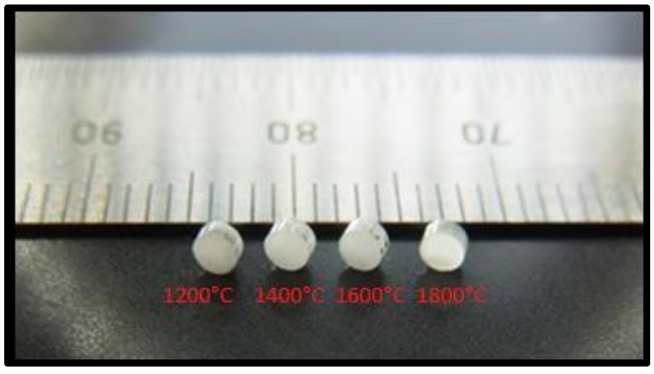


Fig. 5 Nanocrystalline bulk of stishovite syntezed at 15.6 GPa and 1200, 1400, 1600, 1800 °C.Changes of color and icreasing of transparent properties with growing of temperature.

3 X-ray diffraction measurement of nanocrystalline bulk SiO_2 stishovite.

For subsequent full-profile analysis of the structure of nanocrystalline stishovite by Rietveld method, the high-resolution X-ray diffraction data were collected on P02.1 beamline, DESY Hamburg. Diffraction pattern were measured in transmission geometry with using 2D detector Perkin Elmer with a fixed photon energy of 60 KeV, λ=0,20727Å. Time of exposure was 10 sec. Integration of two-dimensional diffraction patterns was carried out using the program FIT2D.

3.1 Description of beamline

Beamline P02.1 is located in sector 2 of the new synchrotron PETRA III at DESY. This beamline is focused on the Hard X-Ray diffraction experiments at high time-resolution using high-energy x-rays. P02.1 operates at a fixed photon energy of 60 keV. Its dispersive monochromator produces a highly intense and highly collimated beam of very narrow energy bandwidth. These excellent beam characteristics turn P02.1 into an ideal instrument for many different kinds of experiments, ranging from high resolution powder diffraction of polycrystalline materials for structure refinement and microstructure analysis to the study of nanocrystalline and disordered materials to determine their local structure[3].

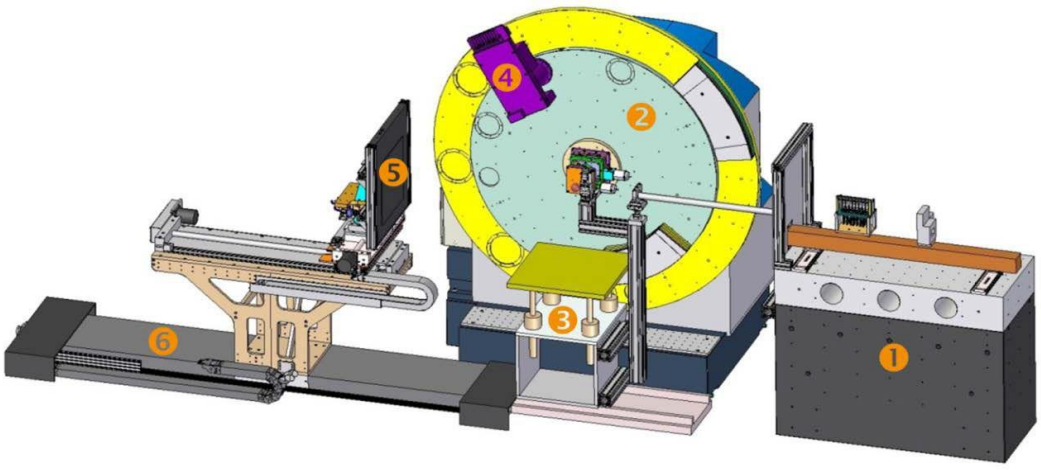


Fig. 6 Schematic layout of the P02.1 beamline: (1) granite support for optical components; (2) three-circle diffractometer; (3) sample environment support table; (4) high resolution detector; (5) area detector; (6) table track for area detector

3.2 Results of diffraction measurement.

Figure 7 showes X-ray diffraction patterns of recovered samples synthezied at temperature from 600 to 1800 °C and fixed pressure 15.6 GPa . As we can see sample synthesized at temperatures of 600°C represents a completely amorphous substance glass-SiO2,increase temperature leads to a gradual crystallization in the sample. As can be seen from the figure peaks widths became narrower with increasing the temperature and appear to increase with increasing 2Ɵ angle. Amorphous component is observed in the samples synthesized in the range from 600 to 1200 °C. After temperature of synthesize 1200 °C silicon dioxide completely transforms in its polymorph modification –stishovite .

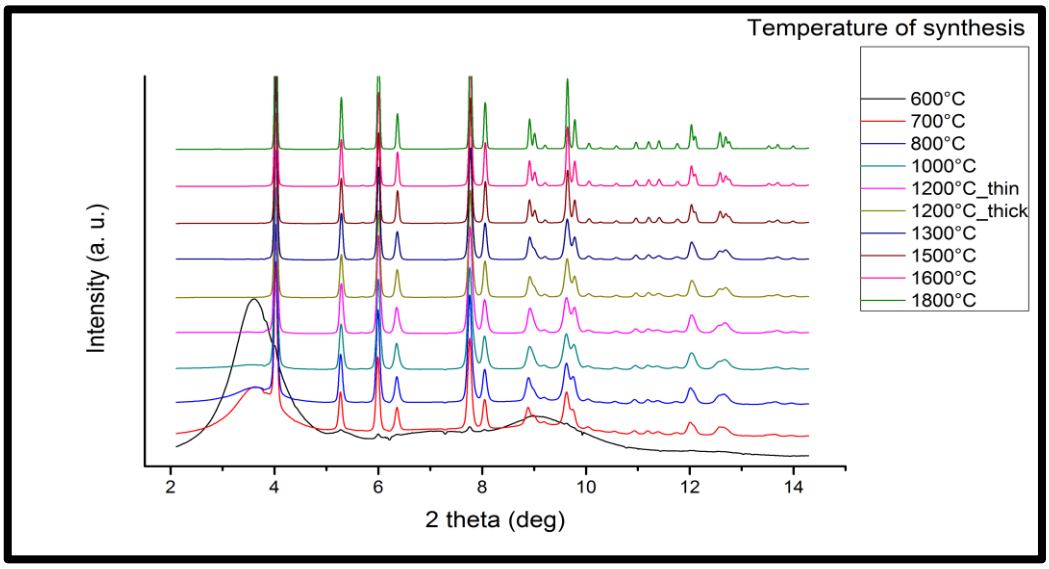


Fig.7 Experimental data of X-ray diffraction messurements . X-ray diffarction pattaerns of recovered samples sy nthezied at 15 Gpa and temperature from 600 to 1800 °C

Two peaks 111 and 040 with low intensity corresponding to coesite structure were observed for samples synthesizied at temperature 1100°C and 1200°C (Fig. 8).

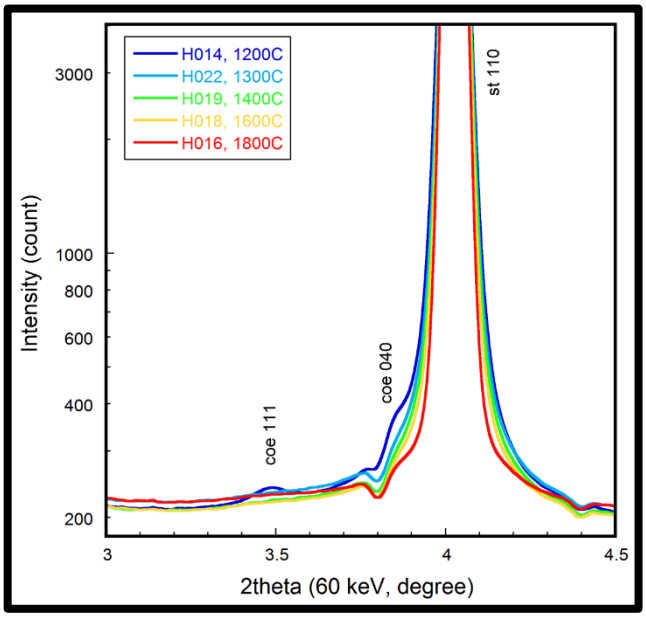


Fig.8 X-ray diffarction pattaerns of samples synthezied at 15 Gpa and temperature from 1200 to 1800 °C.

4 Full-profile analysis of the diffraction patterns by the Rietveld method

- Full profile analyses by Rietveld method were performed for diffraction patterns of the sample synthesized at 700-1800 °C. Rietveld method - iterative procedure to minimize the deviation between the experimental and calculated diffraction patterns.

$$\Phi = \sum_i w_i \left(I_{obs} - I_{calc}\right)^2$$

i – number of experimental point

Peaks intensity according to the angle derived from the following parameters:

$$I(2\theta) = B(2\theta) + k\sum_{h,k,l} p_{hkl} \times \left|F_{hkl}\right|^2 \times LPG \times T_{hkl} \times P_{hkl}(2\theta_{hkl} - 2\theta)$$

$I(2\theta)$ – Intensity as a function of angle

$B(2\theta)$ – Background as a function of angle

k – Proportionality factor (Scale factor)

p_{hkl} – Repeatability factor

$\left|F_{hkl}\right|^2$ – Structure amplitude

LPG – Lorentz + Polarization factors

T_{hkl} – Texture factor

$P_{hkl}(2\theta_{hkl} - 2\theta)$ – Profile function

Minimizing the deviation between the experimental and calculated diffraction patterns was done by varying the following parameters:

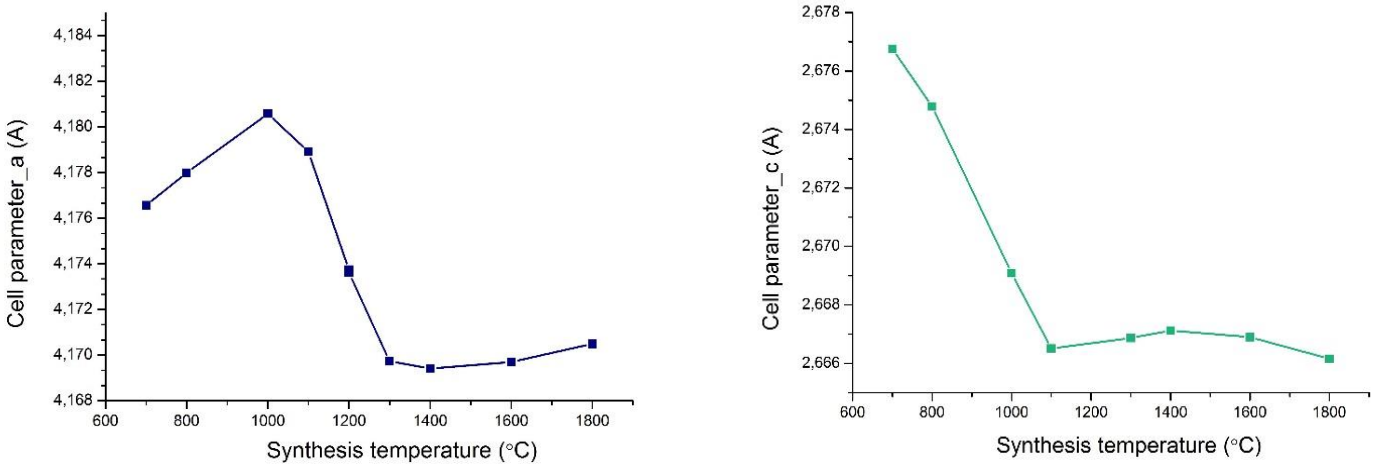
- Scale factor, background parameters
- Lattice parameters, zero shift
- Profile parameters (Gauss and Lorentz)
- Asymmetry parameters
- Texture parameters
- Atomic coordinates

- Site occupancy factors (unstoichiometric samples)
- ADP- Atom Displacement Parameters

(temperature factors + static displacement)

4.1 Results

Dependence of lattice parameters, microstrains and crystallite size on the synthesis temperature were found as a result of full-profile analysis by Rietveld method.



(a) **(b)**

Fig.9 (a) (b) dependence of lattice parametrs at 15.6GPa on synthesis temperature

In Fig 9(a) we can see the sharp decrease the value of lattice parameter in trhe temperature range 1000-1300 °C because of up to synthesis tempreture 1200°C samples represent a not pure stishovite, SiO_2 glass does not completely transform in its high-pressure polymorph.

It was supposed that the lattice parameter c would undergo minor changes with increasing synthesis temperature, however we can see sharp changing of this parameter in the temperature range 600 -1100 °C.

The lattice parameters are located on the constant after synthesis temperature 1200°C that indicate that after the synthesis temperature 1200 degree the pure stishovite is formed.

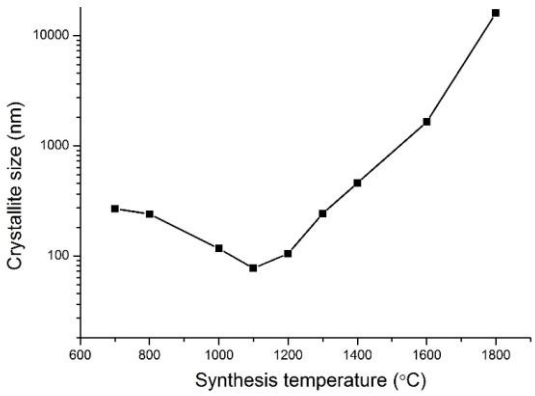


Fig.10 at 15.6GPa dependence of crytallite size on synthesis temperature

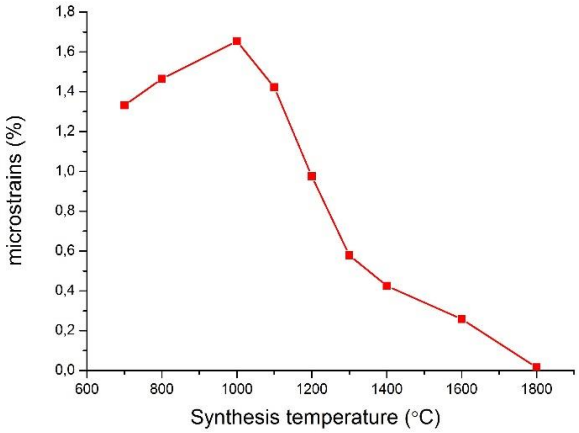


Fig. 11 at 15.6GPa dependence of microstrains on synthesis temperature

With increasing synthesis temperature, the increase of crystallite size from 100 nm to 15 μm and calculated microstrain decreases.

Acknowledgements

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References

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