

# Post-stishovite phase boundary in SiO<sub>2</sub> determined by in situ X-ray observations

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## Abstract

A laser heating diamond anvil cell experiment, with an angle-dispersive X-ray diffraction using synchrotron radiation source at the SPring-8, has been developed to observe the phase transition in silica (SiO<sub>2</sub>) between the *P4<sub>2</sub>/mmm* (rutile-type) and *Pnnm* (CaCl<sub>2</sub>-type) up to pressures of 100 GPa and at temperatures up to 2200 K. The transition was observed in the vicinity of 55 GPa at room temperature, and showed a positive temperature dependence of the transition pressure. The phase boundary was determined to follow the equation  $P$  (GPa) =  $(51 \pm 2) + (0.012 \pm 0.005) \times T$  (K). Our result gives a transition pressure of near 80 GPa and a depth of 1900 km at an expected lower mantle temperature of 2000–2500 K. Therefore, this SiO<sub>2</sub> transition is not the cause of recent observations of seismic anomalies between 800 and 1600 km depth in the mid–lower mantle. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** silica; stishovite

## 1. Introduction

The physical properties and structural evolution of SiO<sub>2</sub> at high pressures have attracted attention in the geophysical community because stishovite is one of the minerals in the oceanic crust which seems to subduct into the lower mantle [1,2]. Recently some groups have claimed a disproportionation of Mg-perovskite into MgO and SiO<sub>2</sub>

takes place [3]. If the break down of orthorhombic Mg-perovskite occurs in the lower mantle, then SiO<sub>2</sub> could play a key role in the structure and dynamics of the lower mantle.

The possibility of a pressure-induced tetragonal–orthorhombic phase transition in stishovite was first suggested by crystal chemical arguments [4]. The transition occurs in the vicinity of 50 GPa at room temperature, and has now been investigated from both experimental [5–7] and theoretical perspectives [8–10]. Although detailed knowledge has accumulated on the high-pressure behavior of SiO<sub>2</sub>, most data have been limited to those obtained at room temperature and high

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pressure. The second-order rutile-type to  $\text{CaCl}_2$ -type transition that occurs at high pressure and temperature has been studied in  $\text{GeO}_2$  [11,12], which is regarded as an analogue of  $\text{SiO}_2$ . In situ observation at high pressure and high temperature is required to determine the phase boundary of the high-pressure phases, because the orthorhombic ( $\text{CaCl}_2$ -type) phase does not exist on quenching, and converting to the tetragonal (rutile-type) phase on release of pressure.

In this study, we used a laser-heated diamond anvil cell (LHDAC), which made it possible to acquire precise data on a sample under high- $P$ - $T$  conditions, using intense X-ray from a synchrotron radiation source. We report on the results of in situ X-ray observations on the high-pressure phases of  $\text{SiO}_2$ . We also comment on the phase boundary between the tetragonal rutile-type and the orthorhombic  $\text{CaCl}_2$ -type phase.

## 2. Experimental procedure

The high-pressure X-ray diffraction experiments were performed using an LHDAC high-pressure apparatus [11]. Synthetic powdered quartz-type  $\text{SiO}_2$  (purity 99.9%) was loaded into a 100  $\mu\text{m}$  diameter hole drilled into a rhenium gasket that was pre-indented to a thickness of 50–100  $\mu\text{m}$ . Platinum powder was mixed with the sample to absorb the laser radiation for heating, and to provide an internal pressure calibrant. The samples were heated with a multimode continuous wave Nd:YAG laser employing a double-sided laser heating technique that minimized any temperature gradients across the heated area [13]. The size of the heating spot was about 70–100  $\mu\text{m}$ . The sample temperature was measured on one side of the sample using the spectroradiometric method [14]. A pressure medium was not used in our experiments, because the diffraction of a pressure medium would interfere with that of the sample. Although accurate diffraction patterns of the sample could be acquired without a pressure medium, the temperature gradient across the sample was large. It was difficult to measure the axial temperature gradient, because it varied with each experimental conditions. However, other studies have

calculated the temperature gradient in a LHDAC (e.g. [15–17]). According to these studies, the estimated uncertainty of temperature in the present study would be higher than 400 K at the high temperatures. The heated samples were probed by the angle-dispersive X-ray diffraction technique using the synchrotron beam line BL10XU (operating at 8 GeV and 70–80 mA) at SPring-8, at the Japan Synchrotron Radiation Research Institute (JASRI) in Japan. A monochromatic incident X-ray beam at a wavelength  $\lambda=0.4127 \text{ \AA}$  was used. The X-ray beam size was collimated to a diameter of 16–20  $\mu\text{m}$ . The angle-dispersive X-ray diffraction patterns were obtained on an imaging plate. The observed intensities on the imaging plates were integrated as a function of  $2\theta$  to provide the conventional one-dimensional diffraction profiles. The pressure was determined from the observed unit cell volume of platinum using the equation of state (EOS) for platinum by Holmes et al. [18]. The uncertainty in the pressure value was related to the experiment temperature, because of the use of the platinum EOS. However, there are discrepancies between various reference EOS values (e.g. [19,20]). Moreover, the pressure gradient could have existed in the sample, even at high sample temperatures. Therefore, the maximum pressure error was greater than 4 GPa at the high temperatures used.

## 3. Results

In the LHDAC experiments, the X-ray diffraction data were acquired at several temperatures along a heating cycle at fixed press loads. We conducted two runs at pressures between 47 and 93 GPa, and temperatures between 300 and 2150 K. The typical diffraction patterns of the rutile-type ( $P4_2/mnm$ ) and the  $\text{CaCl}_2$ -type ( $Pnmm$ ) phases are reproduced in Fig. 1. The exposure times of the diffraction patterns were typically 1–3 min. The pressure was calculated from the EOS of platinum using the  $111$ ,  $200$ , and  $220$  diffraction lines.

In the first run, the sample was compressed to 20 GPa, and then heated to synthesize the rutile-type  $\text{SiO}_2$  (stishovite). After synthesis of the ru-

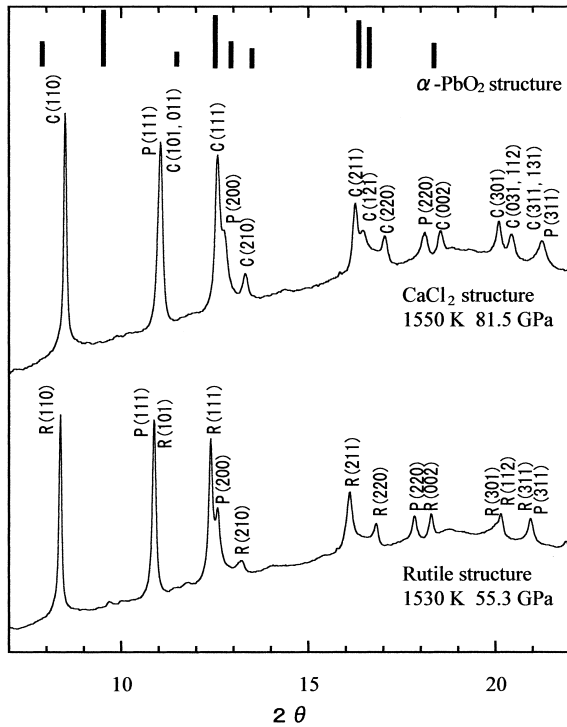


Fig. 1. Examples of X-ray diffraction patterns for  $\text{SiO}_2$  phases obtained in this study using the angle-dispersive technique with DAC experiments. Abbreviations of peaks are as follows: R, Rutile-type  $\text{SiO}_2$ ; C,  $\text{CaCl}_2$ -type  $\text{SiO}_2$ ; P, platinum.  $\alpha$ - $\text{PbO}_2$ -type  $\text{SiO}_2$  was reported by Dubrovinsky et al. [6].

tile-type phase, the sample was compressed with a load corresponding to a pressure of 77 GPa, which was in the stability field of the  $\text{CaCl}_2$ -type phase, and then heated. The duration of heating was typically 5–10 min at each  $P$ – $T$  condition at which the X-ray diffraction data were acquired, yielding a total heating duration of 0.5–1.5 h under the fixed loads of the press. At this fixed load, the  $\text{CaCl}_2$ -type phase of  $\text{SiO}_2$  was observed at temperatures of 1770–2140 K, and at pressures of 86–93 GPa. After a temperature quench, the fixed load was decreased to a pressure of 54 GPa, and the sample was then reheated. The rutile-type was observed at temperatures between 1190 and 1530 K, and at pressures of 55–57 GPa. The observed changes in the 211–121 and 301–031 peaks from double into single peaks indicate that the  $\text{CaCl}_2$ -type phase has transformed

into the rutile-type phase (Fig. 1). Although a mixed phase region may exist because of the temperature gradient in the sample, it could not be identified in this study. After decreasing the temperature, the fixed load was increased again to a pressure of 73 GPa and the sample was again reheated. The  $\text{CaCl}_2$ -type phase was again observed in the temperature range of 1510–2070 K, and the pressure range of 77–85 GPa. After a temperature quench, the  $\text{CaCl}_2$ -type phase remained on cooling to 300 K (see Table 1). A similar heating method was used in the second run.

Our results and previous study [7] of the rutile-type and  $\text{CaCl}_2$ -type stability fields are summarized in Fig. 2. The transition boundary in Fig. 2 is represented by the linear equation:

$$P \text{ (GPa)} = (51 \pm 2) + (0.012 \pm 0.005) \times T \text{ (K)}$$

Our results yield a transition pressure of 55 GPa

Table 1

Observed and calculated X-ray diffraction pattern of  $\text{CaCl}_2$  structure at 74 GPa and 300 K

$hkl$	$d_{\text{obs}}$ (Å)	$d_{\text{cal}}$ (Å)	$\Delta d$	$I_{\text{obs}}$
110	2.7775	2.7775	0.0002	84
101	2.1398	2.1523	−0.0058	100
011	2.1398	2.1306	0.0043	100
200		1.9985		
020		1.9312		
111	1.8807	1.8801	0.0003	19
210	1.7768	1.7750	0.0010	15
120		1.7389		
211	1.4574	1.4576	−0.0002	28
121	1.4367	1.4374	−0.0005	17
220	1.3892	1.3888	0.0003	21
002	1.2772	1.2772	0.0001	23
310	1.2589	1.2595	−0.0005	7
130	1.2257	1.2255	0.0002	7
221	1.2187	1.2201	−0.0011	1
301	1.1822	1.1813	0.0008	19
112	1.1605	1.1604	0.0001	25
031	1.1499	1.1497	0.0002	3
311		1.1296		
131		1.1049		
320		1.0967		
230		1.0823		
202	1.0762	1.0762	0.0000	5
022		1.0652		

Calculated  $d$  spacings are based on orthorhombic unit cell dimensions of  $a = 3.997(2)$  Å,  $b = 3.862(2)$  Å,  $c = 2.554(1)$  Å, and  $V = 39.43(4)$  Å<sup>3</sup>.

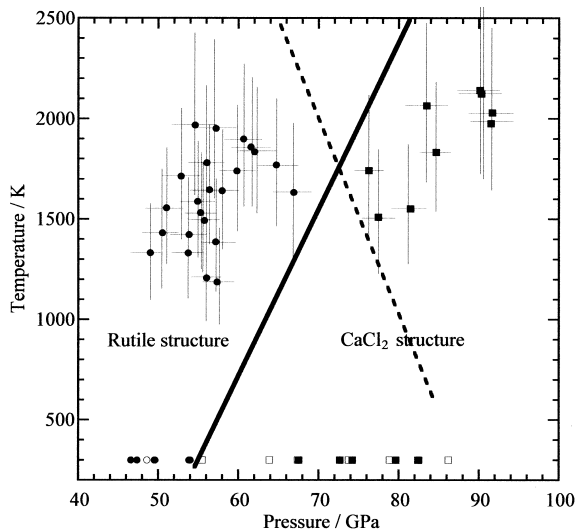


Fig. 2. Experimental results and a phase boundary determined by in situ observation. Solid circles and squares represent conditions where rutile-type and  $\text{CaCl}_2$ -type  $\text{SiO}_2$  were stable in this study. Open symbols represent data from Andraut et al. [7]. Solid line is the inferred phase boundary between rutile-type and  $\text{CaCl}_2$ -type  $\text{SiO}_2$ . Dashed line shows tentative phase boundary between rutile-type and  $\alpha\text{-PbO}_2$ -type  $\text{SiO}_2$  reported by Dubrovinsky et al. [26].

at room temperature, which is in good agreement with that observed in previous studies [5,7]. Lattice dynamics calculations that reproduce the measured vibrational spectrum predict a weak, positive temperature dependence of the transition pressure ( $dP/dT \sim 0.004$  GPa/K) [5]. A positive temperature dependence was confirmed in this study, but the gradient of  $dP/dT$  from this study ( $0.012$  GPa/K) is larger than  $0.004$  GPa/K. Recently, molecular dynamics computations calculated a transition pressure of  $52.5$  GPa at room temperature, and a  $dP/dT$  gradient of  $0.0167$  GPa/K [21]. This calculated boundary agrees quite well with our results. We did not observe a mixed phase region, as the difference in the diffraction patterns between the two structures was very small. If the mixed region existed in this study, the uncertainty of the estimated  $dP/dT$  gradient is not small.

Zhang et al. [22] reported that an equilibrium phase boundary between the coesite and stishovite forms of  $\text{SiO}_2$  could not be determined below  $1273$  K, because of the kinetics of the phase tran-

sition. However, in the case of the second-order phase transition between the rutile-type and the  $\text{CaCl}_2$ -type phases, the pressure hysteresis is not large when heating is used to relax the deviatoric stress in the sample [11,12]. Therefore, the phase boundary between the rutile-type and the  $\text{CaCl}_2$ -type of  $\text{SiO}_2$  could be determined at the lower temperatures used in this study.

#### 4. Discussion

It is widely recognized that lithospheric slabs are transported by subduction into the lower mantle. The basaltic (MORB) component in the slab crystallizes into an Mg-perovskite+Ca-perovskite+Al-rich phase+stishovite assemblage in the lower mantle [1,2]. The  $\text{Al}_2\text{O}_3$  content in the stishovite increases with increasing temperature [23], and stishovite in the subducted slab seems to contain several wt%  $\text{Al}_2\text{O}_3$ . Therefore, the phase boundary of stishovite containing  $\text{Al}_2\text{O}_3$  in the lower mantle may be different from that of pure  $\text{SiO}_2$  stishovite.

The high-pressure transition from the  $\text{CaCl}_2$  to the  $\alpha\text{-PbO}_2$  structure of  $\text{SiO}_2$  is predicted to occur above  $80$  GPa [9,10]. Such transition is predicted to involve a volume discontinuity, which would destabilize the silicate perovskite. A new  $\text{SiO}_2$  phase with the  $\alpha\text{-PbO}_2$ -like structure has been reported in the Martian meteorite Shergotty [24]. There is experimental evidence for such a transition [6], but other data indicate the persistence of the  $\text{CaCl}_2$  structure to at least  $120$  GPa [7]. Silica is known to follow different transition paths under high pressure at room temperature depending on the starting material [5,25,26]. Although experimental reports have been controversial, the  $\alpha\text{-PbO}_2$ -like phase was not observed in this study.

There is evidence for seismic structure in the mid-lower mantle. Kawakatsu and Niu [27] reported a seismic discontinuity at a depth of about  $1000$  km, low-velocity anomalies at depths of  $1400$ – $1600$  km [28], and the observation of reflectors at depths of  $800$ – $1200$  km [29]. The phase boundary between the rutile and  $\text{CaCl}_2$  structure determined by our results indicates a transition pressure near  $80$  GPa, corresponding to a depth

of 1900 km at an expected lower mantle temperature of 2000–2500 K. Therefore, this discrepancy in depths suggests that any transition in SiO<sub>2</sub> should not be considered in the interpretation of these particular seismic observations.

The existence of free silica would have consequences for a number of geophysical and geochemical questions relating to large-scale structure, dynamics, and thermal state of the mantle. A recently proposed model for a change in composition in the bottom 1000 km of the mantle attempts to satisfy geodynamic, seismological, and mineral thermoelasticity consideration, as well as the apparent need for isolated geochemical reservoirs [30,31]. The experimental reports on the subducted oceanic crust suggested that the slab, which contains free silica, might stagnate at depths of 1500–2000 km [2]. Therefore, in order to understand the chemical reactions and the dynamics of the subducted slab in the lower mantle, transitions in the SiO<sub>2</sub> phases should be quantitatively clear.

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