



X-ray diffraction study of phase stability in SiO₂ at deep mantle conditions

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Abstract

The stability of SiO₂ phases were examined by X-ray diffraction at pressure up to 131 GPa and temperature >1300 K, corresponding to Earth's deep lower mantle conditions. Three materials, stishovite, cristobalite, and silica glass were used as starting materials, and an argon pressure-transmitting medium was loaded with the sample for five out of six sets of laser-heated diamond cell experiments. X-ray fluorescent crystals were loaded with the sample to ensure alignment of X-ray beam and heating laser. Our results from three different starting materials indicate that the CaCl₂-type phase is the stable phase throughout our studied *P–T* range. We observe the α-PbO₂-type phase for cristobalite starting material at pressures greater than 48 GPa at room temperature. However, this transforms to the CaCl₂-type structure upon heating between 72–113 GPa. Transition kinetics and metastability may be important in explaining differences in results reported above 75 GPa, and key experimental variables are discussed.

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1. Introduction

The crystal structure of SiO₂ at high pressures and temperatures has been the subject of extensive experimental and theoretical investigation. Silica serves as an analogue for the dense octahedrally coordinated

silicates that dominate the Earth's deep mantle. Free silica is expected to be locally present in the lower mantle based on experimental study of basalt compositions at lower mantle conditions [1,2]. The recognition of dense high-pressure polymorphs of SiO₂ in meteorites has also stimulated much interest in structural changes in this material [3–5].

Stishovite, the rutile-structured polymorph (P4₂/mnm) of SiO₂ undergoes a displacive transformation to an orthorhombic CaCl₂-type structure (Pnmm) near 50 GPa [6]. Theoretical studies indicate that a large

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number of structurally related phases of SiO_2 are possible at high pressures, and that many of these phases possess similar total energies [7]. Detailed studies of polymorphism in a range of AX_2 -type compounds including oxides such as GeO_2 and SnO_2 provide further insight into the probable sequence of structural changes in silica at high pressures and temperatures [8–12].

At pressures above 75 GPa there are conflicting reports about the stability of SiO_2 phases from X-ray diffraction experiments using heated diamond anvil cells. The stability of the CaCl_2 -type form was reported to ~120–128 GPa on the basis of observations of temperature-quenched samples [13–15]. Ono et al. [16] also reported in situ observation of the CaCl_2 -type phase to 92 GPa and ~2000 K. Other studies, however, have reported the formation of a polymorph related to the α - PbO_2 -type structure at pressures of ~80 GPa [17,18]. More recently, the transformation from the CaCl_2 -type structure to the α - PbO_2 -type structure (Pbcn) was reported at 121 GPa and 2400 K, and this new phase was found to be stable to 151 GPa and 2500 K [19]. Theoretical studies predict a variety of possible transformation pressures and stable phases for the SiO_2 system [7,20–23].

To further complicate the picture, there have been several reports of formation of presumably metastable high-pressure polymorphs at relatively low temperatures using externally heated diamond cells [12,18] or from different starting materials such as tridymite [24]. This is not surprising in view of the concept that there are a number of energetically similar phases that can be generated from hexagonally close packed arrays of oxygen with Si cations occupying one-half of the octahedral sites [7]. In such a case, the observed phase in an experiment could depend on starting material, deformation history, temperature, deviatoric stress, and heating duration. That is, metastable phases representing local energy minima may form depending on the initial atomic arrangement and various experimental factors. Identification of the thermodynamically stable phase becomes experimentally challenging and requires a thorough understanding of the response of SiO_2 samples to the above factors. In order to better understand phase relations in silica near and above 1 Mbar, we report new experiments using the laser-heated diamond anvil cell. Our

approach is to conduct experiments over a broad pressure–temperature range using multiple starting materials. In contrast to some earlier studies, we have emphasized collection of in situ high-temperature data and have strived to achieve uniform heating conditions both by insulating the samples from the high thermal conductivity diamond anvils and by careful alignment of the X-ray beam to the heated area. The results of this study will allow us to better characterize the conditions under which various high-pressure polymorphs, stable and metastable, form in the SiO_2 system.

2. Experiment

Three starting materials, stishovite, silica glass, and cristobalite, were used in this study. The stishovite was synthesized in a 2000-ton split-sphere multianvil apparatus at SUNY Stony Brook. Powdered samples were examined by X-ray diffraction and determined to be pure stishovite with $a=4.181(3)$ Å and $c=2.664(6)$ Å and $V=46.58(9)$ Å³, which are in good agreement with previous values [25]. The cristobalite of unknown origin was also examined by X-ray diffraction and confirmed to be pure cristobalite with $a=4.946(7)$ Å and $c=6.92(2)$ Å, also in agreement with expected values [25]. The silica glass sample was obtained from Quantum Optics Co. and was checked by Raman spectroscopy. Samples were compressed using a pair of 150- or 200- μm beveled diamond anvils in a symmetric-type diamond anvil cell. Powdered samples (1–3 μm) of each starting material were mixed with 10 wt.% Pt, which served as a laser absorber and internal pressure standard. The sample mixtures were compressed into a ~7–10- μm thick disc and loaded in a 70–90- μm diameter rhenium gasket chamber, which was preindented to a thickness of 20–25 μm . In all but one experiment, argon was loaded cryogenically as a thermal insulator, pressure-transmitting medium, and secondary pressure standard [26]. Several sample chips were placed above and below the sample foil so that Ar could flow under the sample when loaded cryogenically. A total of six experimental runs were performed (Table 1).

In situ angle-dispersive X-ray diffraction was carried out at beamline 13-ID-D of the GSECARS, sector of the Advanced Photon Source. The monochromatic

Table 1
Summary of experimental conditions for SiO₂ samples

Run	Starting material	Pressure transmitting medium	Pressure range (GPa)	X-ray wavelength (Å)	X-ray beam dimensions (μm)
StB	Stishovite	Ar	73–76	0.4246	5 × 6
StE	Stishovite	Ar	88–104	0.4246	10 × 11
StG	Silica-glass	Ar	86–92	0.3311	5 × 7
StH	Stishovite	–	107–131	0.3311	5 × 7
CrA	Cristobalite	Ar	79–113	0.4246	10 × 11
CrB	Cristobalite	Ar	77–80	0.3311	5 × 7

All experiments used a Re gasket and Pt as an internal pressure standard.

X-ray beam was focused to a size ranging from about 5 to about 11 μm in the six different runs (Table 1). A liquid-N₂ cooled CCD detector was used for recording two-dimensional X-ray diffraction images. Two X-ray wavelengths, either 0.3311 Å or 0.4246 Å, were used in this study (Table 1). A CeO₂ standard was used to calibrate the sample-to-detector distance and to correct for tilting of the detector. The two-theta range of the diffraction patterns was constrained by the opening angle and hole size of the supporting seat of the diamond anvil and the height of the diamond. In some cases, tilting of the diamond cell by 2–5° or moving the detector off center by 40 mm was used to extend two theta to a wider range and to measure the *d*-spacings down to ~1 Å. However, off-center movement restricts the 2-D image to quarter rings instead of complete rings. The program Fit2D [27] was used to process the CCD images and to obtain an integrated one-dimensional diffraction pattern. The CCD exposure time for diffraction images varied from 1 to 5 min.

To achieve high temperatures, Nd:YLF lasers with a combination of TEM₀₀ and TEM₀₁ modes were employed using the double-sided laser heating method [28–30]. In most cases, the visible heating spots are more than 20 μm in diameter, which are greater than the X-ray beam size. Temperatures were reported on the basis of the average of the center 20 μm of thermal radiation from both sides in the cases where a pressure medium was used. For the run without a pressure medium (StH) most temperature measurements were only obtained from one side. The heating spots in this run were still near or larger than 15 μm, which is greater than the X-ray beam (~5 × 7 μm). The heating

conditions were not as stable in these experiments due to the absence of an insulation medium. In general, the recorded temperatures were at or above 1300 K and the temperature uncertainty was about 100–400 K. The total heating time was about 30 min for most of the individual heating cycles.

The pressure measurement was based on the equation of state of platinum [31] using at least four individual peaks of platinum (111, 200, 220, and 311). At room temperature, the pressure uncertainties were in the range of 1–4 GPa for experiments with pressure media and 2–7 GPa for that without a pressure medium (StH). During laser heating additional pressure uncertainty results from the temperature uncertainty through the thermal pressure term. For a maximal temperature error of 400 K, this corresponds to a 3 GPa error in pressure. In addition, there is also systematic error in the Pt equation of state, which is derived from shock data. A comparison of various Au and Pt equations of state found differences of ~10% at 100 GPa and room temperature [32].

During sample loading, a few small (~3–5 μm) crystals of Y₃Al₅O₁₂ garnet doped with 0.05% Ce (YAG:Ce) were placed at the edge of the gasket hole away from the sample in a position where they are optically visible. The YAG:Ce crystals fluoresce in the visible (spectral emission range: 487–587 nm) in response to X-ray excitation. The sample image and the visible thermal radiation emitted by the heated sample could be viewed using an optical system and a CCD detector [28]. Thus, the location of the heating spot on the sample can be directly observed, but determining the X-ray beam position in the past has proven to be much more difficult. Previous methods relied on sample centering using X-ray absorption scans or imaging diamond/pressure medium fluorescence that is often weak and/or diffuse. Positioning uncertainties in excess of 5 μm were not uncommon, and it was not possible to verify the X-ray/heating alignment during and after heating. The YAG:Ce crystals used in this study allows for accurate (~3 μm) positioning of the X-ray beam within the center of the heated spot and also allowed us to confirm that this positioning accuracy was maintained after heating. Such alignment is important as offsets of X-ray position from the center of the heated spot can produce large temperature uncertainties when temperature gradients exist. YAG crystals were used in all

experimental runs except StB and StH (Table 1). For StB and StH runs, we relied on the image of diamond fluorescence excited by the X-ray as a reference to determine the X-ray position.

3. Results

For stishovite starting material, two sets of experiments were carried out under quasi-hydrostatic conditions and one under non-hydrostatic conditions. Our results show that stishovite transformed to CaCl₂-type structure at pressure above 60 GPa at room temperature (Fig. 1), in good agreement with previous reports (e.g., [6,13,16]). For experiments using Ar insulation, only the CaCl₂-type phase was observed at temperatures to 3060(260) K and pressures up to 104 GPa after ~60 min heating (two heating cycles) for this starting material (Fig. 1). For the non-hydrostatic experiment (StH), the sample was directly compressed to 105 GPa and then heated to above 1600 K. As

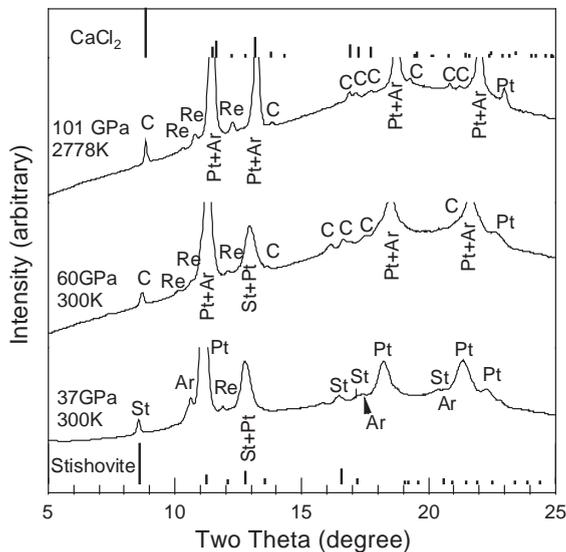
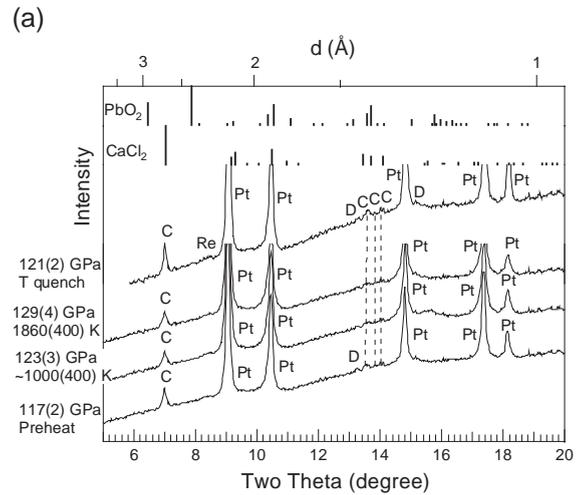


Fig. 1. The phase transformation of stishovite at elevated pressure and temperature. The CaCl₂-type phase was first observed at pressure above 60 GPa and at room temperature and persisted to 131 GPa. Abbreviations are stishovite (St), CaCl₂-type (C), platinum (Pt), argon (Ar), and rhenium (Re). The vertical bars near the bottom represent the expected diffraction peak locations for stishovite at 37 GPa using its equation of state (EOS) [40]. The expected peak positions for the CaCl₂-type phase at 101 GPa and 2778 K are shown at the top (using parameters from [7] and assuming its EOS is same as stishovite).



(b)

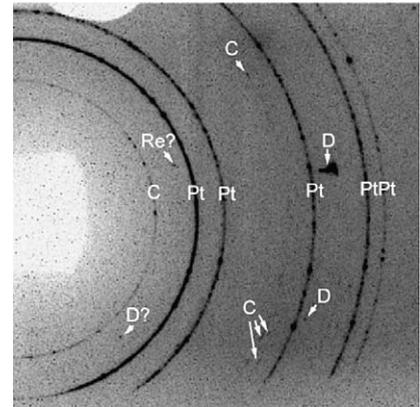


Fig. 2. (a) Selected X-ray diffraction patterns of stishovite at high P - T and non-hydrostatic conditions. The lower vertical bars at the top represent the expected diffraction peak locations for CaCl₂-type phase at 121 GPa and those for the α -PbO₂-type phase are shown at the top (assuming EOS is same as stishovite). The dashed lines are guides to the eye. (b) A typical CCD exposure (121 GPa, quench, same as top spectrum shown in (a)). Abbreviations are C for CaCl₂-type phase, Pt for platinum, Re for rhenium and D for diamond.

discussed above, the heating quality was not as good for these experiments and the temperature uncertainties are larger (± 200 – 400 K). Again, only the CaCl₂-type phase was observed in this experiment that covered pressures of 107–131 GPa at high temperatures (Fig. 2). The d -spacings of the CaCl₂-type structure obtained from this study in general agree with previous reports [7,13–17]. For example, at ~121 GPa, the diagnostic peak of CaCl₂-type structure, (110) obtained from the StH run is 2.7108 Å, which is in agreement with those of Andrault et al. [14] (at 120.4

GPa, $d_{110}=2.7138$ Å) and Murakami et al. [19] (at 124 GPa, $d_{110}=2.7108$ Å).

We note that some unknown peaks were observed in two runs, at pressure above 67 GPa (StB) and 90 GPa (StE) for temperature-quenched samples under quasi-hydrostatic conditions. In the case of the StB run, we observed a peak over a narrow ($\sim 10^0$) portion of the ring from the 2-D image and its d spacing was 3.258 Å at 70 GPa. In the case of the StE run, three peaks at 3.230 Å, 1.936 Å, and 1.484 Å were observed at 95 GPa. Again, only localized spots were observed for these unknown peaks, which indicate strong preferred orientation. These peaks were not observed under in situ high-temperature conditions. The peak locations are inconsistent with those expected for the α -PbO₂-type phase at this pressure.

Another set of experiments involved cristobalite starting material loaded in an argon pressure medium. The α -PbO₂-type phase was first observed at $\sim 48(2)$ GPa at room temperature and remained upon further compression to 77(2) GPa at room temperature, consistent with Dubrovinsky et al. [34] and Prakapenka et al. [12]. Upon heating, the CaCl₂-type peaks appeared and grew slowly stronger, and those of the α -PbO₂-type phase diminished, although the α -PbO₂-type peaks remained after heating for 30 min (Fig. 3). The diagnostic features for the appearance of CaCl₂-type phase are located at 2θ near 9° and 17° (Fig. 3). The sample was then further compressed to 96(2) GPa and heated again to 101(2) GPa and 1500 K. The CaCl₂-type peaks became even stronger, but weak peaks associated with the α -PbO₂-type phase persisted (Fig. 3). The total heating time at the second loading step was also about 30 min. The sample was further compressed and another heating cycle was conducted. The coexistence of CaCl₂-type and α -PbO₂-type phase was also observed at pressure to 113(4) GPa and 1800 K, however, the peaks of α -PbO₂-type phase became very weak. The growth of the CaCl₂-type phase suggests that it is likely to be the stable phase under these conditions (but see caveats discussed below). However, the transition between the two phases appears to be very sluggish. Our room-temperature results are consistent with Dubrovinsky et al. [34] who first reported the formation of the α -PbO₂-type structure upon room-temperature compression of cristobalite. However, at high temperatures, our results are in contrast to the findings by Dubro-

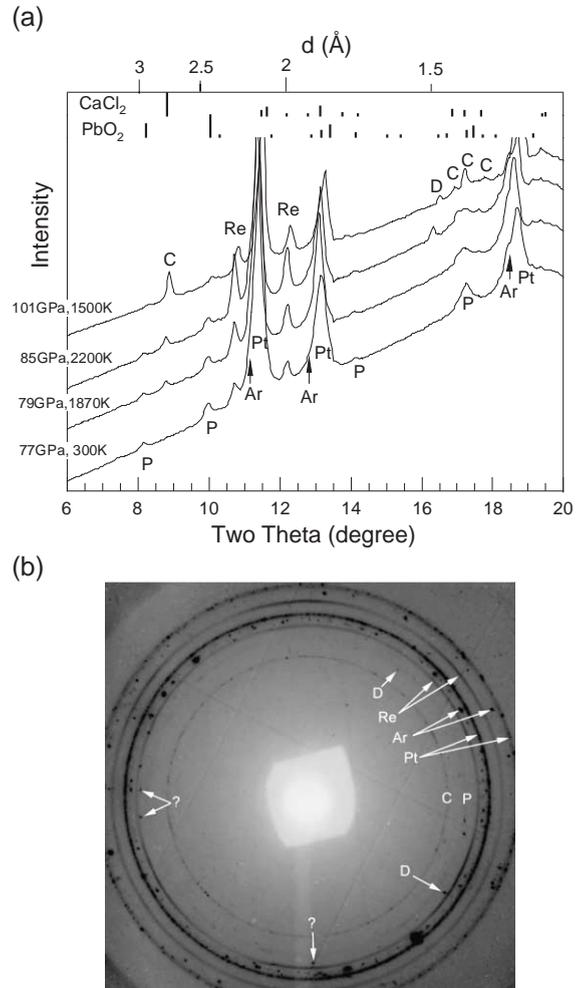


Fig. 3. (a) Selected X-ray diffraction patterns obtained from cristobalite starting material at various P - T conditions. The bottom three spectra were obtained during heating at a single compression step while the top spectrum was obtained after further compression. (b) The 2-D image obtained after temperature quenching of the final heating cycle (top spectrum of (a)). Abbreviations are same as in Figs. 1 and 2. ? denotes unknown phase.

vinsky et al. [34] who reported that the α -PbO₂-type phase was stabilized relative to stishovite after 4 h heating at 82 GPa and 950 K. Prakapenka et al. [12] also reported that the α -PbO₂-type phase remained stable when heated to 900 K at pressures up to 90 GPa. We shall also note that some unknown spots ($d \sim 2.30$ Å) were observed from the quenched patterns (108(2) GPa, 300K) of our final heating cycle for CrA (Fig. 3b). Coincidentally, Murakami et al. [19] also observed unknown peak (Fig. 1c, at 128 GPa,

300K) with a similar d -spacing. However, this peak cannot be assigned to any reported high-pressure silica phases, pressure medium, pressure standard, or diamond.

Our results using silica glass as a starting material cover only a limited P – T range. We found that the CaCl_2 -type phase was the stable phase at 86–92 GPa and 1370–1830 K, which is in good agreement with our observations using other starting materials in this P – T range.

4. Discussion

4.1. Comparison with previous studies

Our results are consistent with the experiments of Andrault et al. [13,14] in which quartz was used as a starting material and samples were examined after laser annealing at pressure up to 128 GPa. No pressure-transmitting medium was used in those experiments. Angle-dispersive diffraction patterns above ~60 GPa were found to be consistent with the CaCl_2 -type structure, and no evidence for a post- CaCl_2 phase was reported to 120–128 GPa [13,14]. Tsuchida and Yagi [15] and Ono et al. [16] also reported the stability of the CaCl_2 -type phase at pressures up to 124 and 93 GPa, respectively, from quartz or amorphous silica starting material. These experiments also used no pressure-transmitting/insulating medium.

In contrast, Dubrovinsky et al. [17] reported the synthesis of an α - PbO_2 -like form (Pnc2) of SiO_2 from dried silica gel and quartz starting material after heating near 80 GPa and 2000 K for several dozen minutes. The peaks of the new phase coexisted with those of the CaCl_2 -type phase, and it was reported that the new peaks were preferentially observed near a metal foil used for laser absorption. The formation of α - PbO_2 -related structures has not been observed at high temperatures in this study and several subsequent experiments that have probed similar P – T conditions [13,14,16,18].

Murakami et al. [19] have recently reported synthesis of the α - PbO_2 form of SiO_2 at 121–151 GPa. We have not observed this phase at pressures to 131 GPa and at temperatures that overlap within uncertainty (Fig. 4). Two important differences between our

results and those of Murakami et al. [19] involve the starting material and length of heating. Our experiments in this pressure range used stishovite as starting material whereas Murakami et al. [19] used synthetic amorphous SiO_2 . Our results are in agreement at ~101–104 GPa, where Murakami et al. [19] observed formation of the CaCl_2 -type phase after heating silica glass for 0.5 h. However, at 124–128 GPa and 2250–2500 K, the α - PbO_2 -type phase was observed only after heating the silica glass for more than 1 h. In a third experiment at 113–117 GPa and 2160–2320 K, diffraction peaks of both CaCl_2 -type and α - PbO_2 -type of similar intensity were observed after only 5 min of heating. It is not clear why the length of heating time required before the appearance of the diffraction peaks is so different at similar temperatures for the same starting material. For the third experiment, upon heating after further compression above 130 GPa, it was observed that α - PbO_2 -type peaks continued to grow relative to peaks of the CaCl_2 -type phase, suggesting the former is the stable phase. Nevertheless, the transition is apparently sluggish as the intensity of the CaCl_2 -type peaks remained comparable to those of the α - PbO_2 -type phase more than 20 GPa above the proposed phase boundary after 4.5 h of heating at ~2100 K.

In our experiments, total heating times were approximately 30 min. We conducted several runs at 110–120 GPa and ~1700–2200 K, conditions overlapping those at which the α - PbO_2 phase was observed after only 5 min of heating in the experiments of [17].

4.2. Comparison of transformation rates in silicates and germanates

GeO_2 undergoes a similar series of phase transitions as SiO_2 at lower pressure and is thus believed to be a good analogue for SiO_2 . In previous experiments [35], which used quartz-type starting material and NaCl insulation, complete transformation to the α - PbO_2 -type phase was reported above 50 GPa after only 2–5 min of heating. On the other hand, Praka-penka et al. [12], in experiments with no insulation medium, observed that the CaCl_2 -type– α - PbO_2 -type transition in GeO_2 was more sluggish, and some portion of the low-pressure phase persisted even after laser heating at about 20 GPa above its first appear-

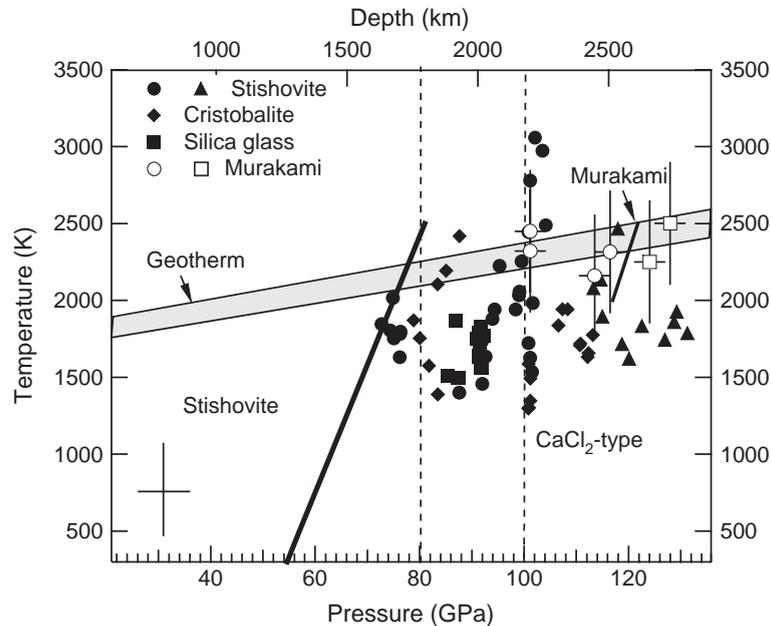


Fig. 4. Pressure and temperature conditions for SiO_2 experiments. Solid symbols are data of this study (different symbols correspond to different runs (Table 1)) for which the CaCl_2 -type phase was observed to be stable. The open symbols are from Murakami et al. [19]; circles are CaCl_2 -type phase and squares are $\alpha\text{-PbO}_2$ -type phase. The solid bold lines are phase boundary for stishovite- CaCl_2 -type [16] and CaCl_2 -type- $\alpha\text{-PbO}_2$ -type [19]. Theoretical estimates (vertical dashed lines) of CaCl_2 -type to $\alpha\text{-PbO}_2$ -type transition are from Dubrovinsky et al. [17], Karki et al. [20], and Teter et al. [7]. A representative error bar (1σ) is plotted at the lower left corner. An estimated geotherm [41] is also shown.

ance. Nevertheless, the appearance of the $\alpha\text{-PbO}_2$ -type phase was fast (within a few minutes) in both experiments. Notably, the two studies [12,35] also differ on the first appearance of the high-pressure phase: Prakapenka et al. [12] reported appearance of the $\alpha\text{-PbO}_2$ -type phase in GeO_2 at 41 GPa and also reported reversal of the transformation near this pressure. Ono et al. [35] did not observe the new phase below 52.6 GPa. Despite these differences, observations for GeO_2 consistently indicate that only short heating periods are needed before the $\alpha\text{-PbO}_2$ -type phase becomes detectable in X-ray diffraction patterns. In the case of MgGeO_3 compositions, it was also observed that transformation to a post-perovskite (Cmcm -type) phase near 70 GPa [36] occurred much more rapidly than that of an $(\text{Mg,Fe})\text{SiO}_3$ composition near 110 GPa. [37].

A multitude of factors can govern nucleation and growth rates including temperature, overpressure, and details of the growth mechanism. Currently reported observations of kinetic factors for the post- CaCl_2 -type phase transformations in GeO_2 and SiO_2 provide evi-

dence for sluggish kinetics even above 2000 K and suggest transformations in silica samples are more sluggish than germania samples. But they are not sufficiently robust at present to allow us to explain differences between our observations and those of Murakami et al. [19] in the 120–130 GPa range.

4.3. Role of starting material

The different behavior exhibited by cristobalite starting material compared with others indicates that starting material can be an important factor in SiO_2 phase transitions. Theoretical studies have shown that there are many possible polymorphs of SiO_2 with similar total energies [7]. Static experiments at relatively low temperatures (<1000 K) have reported a variety of different metastable polymorphs at different pressures [16,20,21]. In particular, it is notable that metastable phases have been synthesized at low pressures (30–60 GPa) and modest temperatures (1000–1300 K) using amorphous SiO_2 starting material [12]. Shock compression experiments and observations of

natural meteorites also provide support for the existence of intermediate or metastable polymorphs in the SiO₂ system under dynamic compression [4,5,24]. The atomic configurations presented by some starting materials in combination with differences in stress and temperature and loading may provide pathways for the formation (or persistence) of metastable phases that are not available to others. The atomic rearrangements required to form the α -PbO₂-type phase from the CaCl₂-type phase are large [21,38]. The failure to form the α -PbO₂-type phase from the CaCl₂-type phase in molecular dynamics simulations suggests that the transformation may be significantly more difficult for CaCl₂-type material compared with SiO₂ glass or cristobalite [21]. This is one possible explanation for differences between our results and those of Murakami et al. [19]. On the other hand, as discussed above, the α -PbO₂-type phase in GeO₂ appears after only a few minutes of heating of the CaCl₂-type phase. The failure to form the α -PbO₂-type phase in the theoretical calculations could also be due to the short duration of those simulations.

4.4. Other relevant experimental factors

Finally, it should be noted that pressure determination above 120 GPa is subject to substantial uncertainties, and thus error in pressure could also be a source of the discrepancy. However, both of these studies used Pt as a primary standard referenced to the same equation of state, although we did not include the electronic thermal pressure contribution used by Murakami et al. [19]. Temperature uncertainties are also large, and these uncertainties translate into a pressure uncertainty through the thermal pressure calculation. In our study, we used measured temperature profiles over a 20- μ m range on both sides of the sample and computed an averaged temperature including temporal variation during the X-ray exposure. Special care was also taken to align the X-ray and laser position. However, the temperature calculation assumes perfect alignment of X-ray and laser positions. Murakami et al. [19] provided limited details about their temperature measurements so it is difficult to evaluate any differences. Axial temperature gradients will also contribute to temperature and hence pressure error.

The growth of α -PbO₂ peaks relative to CaCl₂-type peaks can also be an ambiguous criterion for thermodynamic stability especially in experiments without any insulation medium. In such experiments, temperatures vary axially from close to 300 K at the anvil surface [39] to a maximum in the middle of the sample. The CCD image integrates the diffraction intensity along this axial gradient. The slow growth of one phase over a long time period could represent the slow crystallization of a phase, possibly metastable, in the low temperature region of the cell. Indeed, there have been several observations that indicate that the α -PbO₂-type phase can form metastably in the stability field of the CaCl₂-type phase. These include its formation at 300–900 K from cristobalite above 45 GPa [12,33, this study], the observations of Murakami et al. [19] at 113–117 GPa, and the observation of an α -PbO₂-type phase in natural shocked meteorites [4,5].

As the duration of a laser heating experiment increases, other problems can present themselves. We have observed migration of laser absorption material (Pt) away from the heated spot during long (>0.5 h) heating runs. This can change the temperature distribution within the sample. Prolonged heating of laser optics and the diamond cell can result in relative movement of the X-ray and laser spots such that the X-ray probed region could shift to lower averaged temperatures. Even small misalignments can result in large changes of the average temperature in the heated area. The low temperature regions in experiments without insulation media may also sustain larger shear stresses, which could also affect crystallization of phases. Thus, careful characterization of the high pressure–temperature environment in the laser-heated diamond anvil cell is necessary to delineate phase relationships in SiO₂ at conditions close to the Earth's core–mantle boundary.

5. Conclusions

We have performed laser heating experiments on SiO₂ using stishovite, cristobalite, and fused silica starting materials at pressures above 60 GPa and temperatures above 1300 K. Our results show that CaCl₂-type phase is the stable phase at 73–131 GPa and $T > 1300$ K. These results are in agreement with a

number of earlier studies [13–16] that also concluded the CaCl_2 -type structure is stable to as high as 128 GPa. Our results strengthen this conclusion by reporting data obtained using Ar insulation to provide a more homogeneous temperature distribution (up to 113 GPa), by reporting in situ X-ray diffraction measurements to 131 GPa, and by obtaining consistent results using three different starting materials.

Above 120 GPa, we observe continued stability of the CaCl_2 -type structure to 131 GPa whereas Murakami et al. [19] reported the formation of the α - PbO_2 -type structure above 120 GPa. Neither our highest P – T data (StH run) nor Murakami et al. [19] used an insulation medium for experiments, which means the X-ray diffraction patterns integrated material over a range of temperatures. There are several potentially important differences between the studies that warrant further study. These include the nature of the starting material and length of heating, which could play a role due to transformation kinetics and metastability. While extended length of heating may be beneficial, it also has the potential to introduce complications particularly when no insulation medium is used.

For cristobalite starting material, we observe formation of the α - PbO_2 -type structure above 48 GPa at room temperature in agreement with earlier results [12,34]. However, upon heating, we observe the emergence and growth of peaks of the CaCl_2 -type phase in contrast to Dubrovinsky et al. [34]. Since our experiments for cristobalite used an insulation medium (argon), the growth of CaCl_2 -type peaks is a better indicator of thermodynamic stability because the temperature distribution in the sample is more uniform and we avoid the formation of a low-temperature region in our sample near the diamond anvils.

There is now growing evidence both from experiment and natural samples that transformations among high P – T SiO_2 phases can be sluggish and metastable phases may develop. The complex behavior of this fundamental material and model silicate represents a continued challenge for high-pressure experiments and theory.

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