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X-ray diffraction study of phase stability in SiO_2 at deep mantle conditions

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Abstract

The stability of SiO_2 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 staring materials indicate that the $CaCl_2$-type phase is the stable phase throughout our studied *P–T* range. We observe the α-PbO_2-type phase for cristobalite starting material at pressures greater than 48 GPa at room temperature. However, this transforms to the $CaCl_2$-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.

Keywords: silica; $CaCl_2$-type structure; high-pressure; laser-heating; mantle

1. Introduction

The crystal structure of SiO_2 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 SiO_2 in meteorites has also stimulated much interest in structural changes in this material [3–5].

Stishovite, the rutile-structured polymorph ($P4_2/mnm$) of SiO_2 undergoes a displacive transformation to an orthorhombic $CaCl_2$-type structure (Pnnm) 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 $V = 46.58(9)$ Å^3, 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