

High-pressure Hexagonal Phase of SiO₂

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Introduction

Silica, a major component of the earth's interior, shows rich polymorphs at high pressures and high temperatures. There are a number of theoretical and experimental studies on the behavior of various high-pressure silica phases: keatite, coesite, stishovite, CaCl₂, α -PbO₂, *I2/a*, baddeleyite, fluorite, and pyrite types. First-principle simulations for specific structures provide an explanation for a number of recent high-pressure results for crystalline silica [1]. However, the experimental determinations of phase boundaries are still controversial, and different groups reported inconsistent results on phase transformations at high pressures when different silica polymorphs were used as starting materials: cristobalite [low-temperature tetragonal, space group or S.G.: *P4₁2₁2*], tridymite (hexagonal, S.G.: *P6₃/mmc*), α -quartz (trigonal, S.G.: *P3₂21*), or glass (amorphous network) [2-7].

The experimental results show that the high-pressure behavior of silica depends on the starting material because of its strong kinetic effects on phase transitions. Ideally, to synthesize a stable high-pressure, high-temperature polymorph, we should melt material at high pressure first and then gradually reduce the temperature to obtain a thermodynamically stable crystalline phase. Currently, however, such experiments are challenging. As an alternative, we synthesized sol-gel amorphous silica with a very disordered network [8]. At each pressure, we gradually heated the sample to induce crystallization. The use of amorphous silica minimizes the effect of starting materials on the stability field of high-pressure polymorphs. Here, we report on the observation of a distorted-NiAs phase that is likely metastable. A detailed description of the results can be found in Prakapenka et al. [10].

Methods and Materials

Amorphous silica with a highly disordered network was synthesized by the sol-gel technique [2]. In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Hydrolysis of the metal alkoxide produces reactive monomers, which, through polycondensation reactions, promote cross-linking, leading to a 3-D matrix. The silicon atoms are bound to oxygen atoms in an irregular, noncrystalline network, forming a gel. Thus, the sol-gel amorphous structure of a very disordered silica network can be used as model material

for SiO₂. The sol was prepared from a mixture of tetraethoxysilane/water/ethanol/hydrochloric acid in a molar ratio of 1:4:6:0.3. After drying at 60°C for 24 hours, the xerogel was heated to 650°C for 4 hours in air to remove all organic solvents [2].

High pressure was generated by a symmetrical diamond anvil cell (DAC). The samples were loaded in 100 to 150- μ m holes in stainless steel or rhenium gaskets preindented to a thickness of 30 to 40 μ m. Pt, Fe, TiC, or B powder (1-3 at. %) was mixed with the SiO₂ in order to absorb laser radiation for heating and to measure pressures at high temperatures from the equations of state of Pt and Au [11, 12]. Ruby luminescence was also used for pressure measurements at room temperature [13].

High-resolution angle-dispersive x-ray diffraction experiments were performed at GeoSoilEnviroCARS (GSECARS) sector 13 at the APS by using an on-line imaging plate or a charge-coupled device (CCD) detector. The double-sided laser-heating technique with a laser spot of 20-40 μ m was used in high-temperature experiments [14]. Details of the experiments are described in Prokopenko et al. [2].

Results

Figure 1 shows the diffraction spectra of temperature-quenched silica collected at 58 GPa after laser heating for ~10 minutes at each temperature. The gradual temperature-induced transformation of the amorphous silica into a new crystalline structure (peak positions at 1.233, 1.444, 1.874, 2.134 Å) was observed at a temperature range of 1000-1300K. At 1400 \pm 100K, the CaCl₂-type phase of SiO₂ started to grow, and above 1800 \pm 100K, only the CaCl₂-type phase was detected. The x-ray diffraction spectra were collected in both conditions: *in situ* at both high temperatures and high pressures and at room temperature and high pressure on temperature-quenched samples across the heated area. Our x-ray beam (~8 μ m in diameter) was smaller than the laser-heated spot (~25 μ m in diameter). On the boundary of the heated area, we observed no other phases; we observed only the relative intensity of diffraction peaks from the new crystalline phase changed.

Rietveld full-profile refinement of the d-NiAs-type phase at 53 GPa after annealing at 1200 \pm 100K is shown in Fig. 2. The structure of the new phase can be described as hcp oxygen with cations randomly filling

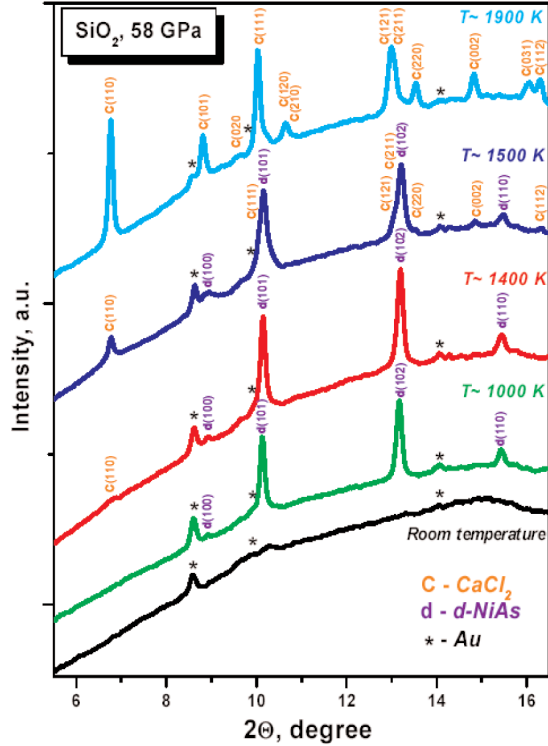


FIG. 1. Temperature-induced phase transformation of sol-gel amorphous silica to CaCl₂-type structure through an intermediate d-NiAs phase (shown by indices).

one-half of the octahedral sites that adopt the disordered niccolite (d-NiAs-type) structure with S.G. $P6_3/mmc$ (#194). The d-NiAs-type structure is meta-quenchable and gradually transforms to stishovite at ambient conditions over time (in ~20-60 hours), which could explain why this phase has not been found in nature.

The d-NiAs-type structure as a possible metastable post-rutile phase of SiO₂ was reported on the basis of static and shock-wave experiments on vitreous silica glass [15, 16]. In this study, we determined that the d-NiAs-type structure precedes rutile/CaCl₂-type structures and can be synthesized only from disordered materials at the narrow temperature range of 1000-1300K and at pressures above 30 GPa to at least 60 GPa (the maximum pressure in this study). The stishovite- and CaCl₂-type phases are found to be denser than the d-NiAs-type phase, contrary to the predicted higher density for d-NiAs at high pressures [15]. In experiments at pressures of 30 GPa and 55 GPa after laser heating at 1200 ± 100K for ~10 minutes, the molar volumes of d-NiAs are 13.22 cm³/mol and 12.45 cm³/mol, respectively — larger by 1.3-2% than stishovite (12.95 cm³/mol and 12.29 cm³/mol, respectively) synthesized by heating the same samples

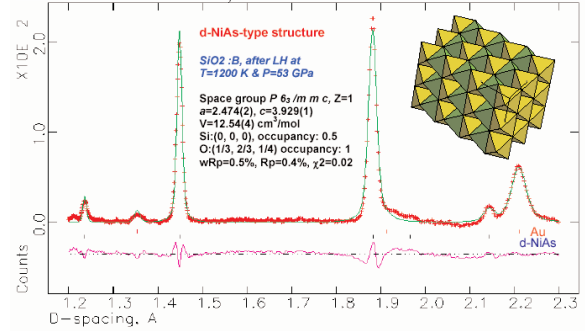


FIG. 2. Rietveld full-profile refinement of the d-NiAs-type phase of SiO₂ at 53 GPa after laser annealing at 1200 ± 100K for 20 minutes.

at higher temperatures (1800 ± 100K) for ~10 minutes at those pressures.

Discussion

The observed d-NiAs structure in laser-heated DACs could be synthesized only when amorphous starting material was used. The presence of a small amount of the d-NiAs phase together with other phases (rutile- or CaCl₂-type structures and untransformed material) when α -quartz is the starting material has been observed in shock-wave experiments [16] and DAC experiments after laser heating [15]. According to our data, the d-NiAs is a pre-rutile/CaCl₂-type phase that can be formed only by heating disordered structures. We interpret the presence of the d-NiAs phase in experiments when α -quartz is used as the starting material as follows. During compression, some crystalline part of the sample may transform to a disordered network [17], especially at room temperature and on grain boundaries. The effectiveness of the disordering process depends on the crystal size, high-pressure history, and stress conditions (i.e., compression rate and pressure gradient). Temperature-induced transformation of this partially disordered crystalline structure to rutile-type or CaCl₂-type structures may be accompanied by the formation of a d-NiAs structure at temperatures below 1400K. The shocked quartz actually shows the presence of ~5% glass [16], which can be a source for the hexagonal d-NiAs-type phase. The co-existence of both phases — mainly rutile/CaCl₂-type structures and a much lower-percentage of d-NiAs-type structures — in these experiments [15, 16], confirms our interpretation.

The success of full-profile refinement for the d-NiAs-type phase can be obtained only for cations that randomly occupy one-half of the octahedral sites in the ratio of Wyck positions of $2a/4e$ ~0.3 and cannot be fitted by any of CdI₂ structure types that are based on ordered cations in an hcp network of anions. Hence, the

d-NiAs-type can be synthesized only from the disordered amorphous phase and cannot be obtained from crystalline phases with ordered cations. For example, the laser heating of the stishovite or CaCl₂-type phases at conditions where the d-NiAs-type phase was synthesized from amorphous phase (1000-1300K and 30-60 GPa) does not produce any structural changes. On the other hand, the density of the d-NiAs type is less than the densities of rutile- or CaCl₂-type structures. Thus, we think that the hexagonal phase of SiO₂ could be a metastable intermediate phase prior to the rutile- or CaCl-type phase at high pressure in a narrow temperature interval of 1000-1300K, where energy is insufficient to overcome the kinetic barrier to order cations inside an hcp oxygen network.

In summary, we found that at relatively low temperatures, kinetics still plays an important role in high-pressure transformation. For the first time, we isolated the d-NiAs-type phase of SiO₂, which allowed us to define the lattice parameters by using Rietveld full-profile refinement at different pressures and temperatures. The temperature-induced formation of the d-NiAs phase can be used as an indicator of the presence of a cation-disordered network in SiO₂ at high pressure before heating.

Acknowledgments

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