NEW HIGH-PRESSURE FORM OF PYRITE-TYPE SILICA UNDER MULTIMEGABAR PRESSURE

Silica (SiO_2) is one of the most important compounds across a range of sciences, along with water and hydrogen and it is the most abundant component of the Earth's crust and mantle. Therefore, the high-pressure behavior of silica has long been of great interest owing to its wide range of implications in geophysics, materials science, and solid-state physics. At relatively low pressures, Si is tetrahedrally coordinated by O in silica polymorphs. Since the discovery of stishovite (a rutile-type polymorph of silica with octahedrally coordinated silicon which is stable above ~10 GPa), there has been significant interest in the possibility of denser phases at high pressures. Previous experimental studies have shown that stishovite undergoes a second-order structural phase transition to a $CaCl_2$-type phase at around 70 GPa and 1600 K and further transforms to an α-PbO_2-type phase above 121 GPa and 2400 K without change in the coordination number of Si, in excellent agreement with the first-principles predictions. Since the theoretical calculations of Park *et al.* in 1988 [1] indicated that cubic silica should be stable at a higher pressure, a number of subsequent theoretical studies have demonstrated the phase transition from the α-PbO_2-type to a pyrite-type (modified fluorite-type) structure at around 200 GPa [2-4]. However, no experimental studies of silica have been carried out at such multimegabar pressures due to significant difficulties in compression as well as heating. Here, we report the first experimental data on the crystal structure and stability of pyrite-type silica.

We performed *in situ* X-ray observations of silica at high pressure and temperature of up to 300 GPa and 2000 K [5]. Angle-dispersive X-ray diffraction spectra were collected at beamline **BL10XU**. The high pressure and temperature conditions were generated in a laser-heated diamond anvil cell (LHDAC). Temperature was measured by the spectroradiometric method. Pressure was determined from the unit-cell volume of platinum mixed with the sample using the *P-V-T* equation of state.

The results demonstrate that the α-PbO_2-type silica is stable up to 260 GPa and 2000 K (Fig. 1). Above 268 GPa and 1800 K, eight new peaks were observed in the X-ray diffraction pattern (Fig. 2). These new peaks can be indexed by a cubic cell with lattice parameter a = 3.9299(2) Å at 271 GPa and 300 K and assigned to a pyrite-type structure (space group $Pa\bar{3}$). To determine the crystal structure, profile fitting was performed by the Rietveld method. The crystal structure of pyrite-type silica is illustrated in Fig. 3. The pyrite structure has an unusual 6 + 2 cation coordination. Rietveld analysis showed that pyrite-type silica has six Si-O bonds with a distance of 1.608 Å and two additional interpolyhedral Si-O bonds with a distance of 2.372 Å. Such interpolyhedral Si-O distance in the pyrite-type structure is considerably shorter than that in the α-PbO_2-type structure (2.726 Å when the average Si-O distance in SiO_6-octahedra is 1.649 Å) in which Si is six-coordinated. The increase in the coordination number of Si from 6 to 6 + 2 results in a large increase in density. The density of pyrite-type silica is 6.576(1) g/cm^3 at 271 GPa and

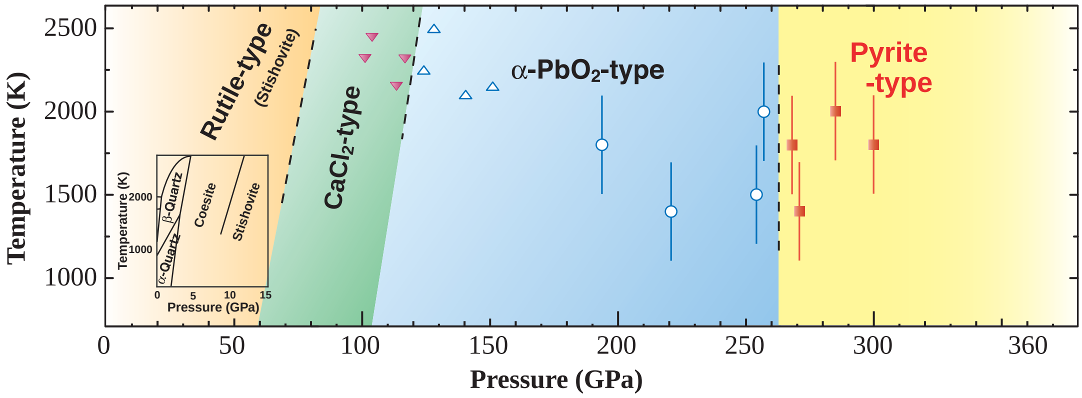

Fig. 1. Phase diagram of SiO_2. Open circles and solid squares indicate the stabilities of α-PbO_2-type and pyrite-type phases, respectively.

300 K. It is larger by 4.7% when compared with that of the α-PbO_2-type phase at equivalent pressure. FeS_2 pyrite has relatively short S-S covalent bonds and is the cause of its metallic nature. If O-O bonds exist in pyrite-type silica, it possibly indicates a pressure-induced metallization of SiO_2. However, the Rietveld analysis showed that the shortest O-O distance in pyrite-type silica is 2.063(6) Å, which is considerably longer than the typical distance of a single covalent O-O bond (~1.5 Å). These experimental data support the argument that there are no O-O covalent bonds in pyrite-type silica [4].

Silica is the most abundant oxide component of the Earth's crust and mantle; however, the pressure required for the formation of pyrite-type silica is greater than that found in the Earth's mantle. Nevertheless, silica is also one of the most important oxide components of other planets in our solar system. The theoretical modelling of the interiors of ice giant planets suggests that both Uranus and Neptune may have a rocky core at pressures of around 800 GPa and below, and therefore, pyrite-type silica might be an important constituent of these planets. Moreover, because silicates are important oxide components in extrasolar systems and in the formation of terrestrial planets where pressures may exceed 260 GPa, the pyrite-type silica phase may be included.

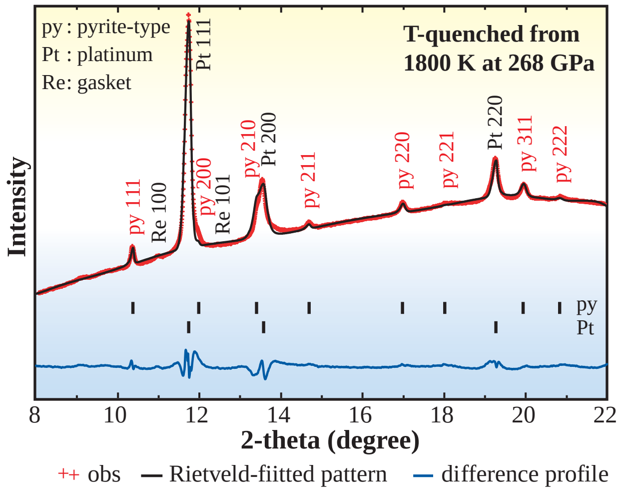

Fig. 2. XRD pattern of pyrite-type silica at 271 GPa and 300 K after heating for 1 hr at 268-271 GPa and 1400-1800 K.

The pressure and temperature conditions at the center of the Earth are 364 GPa and above ~5000 K. A study of the mineralogy at such high pressure and temperature conditions is a prerequisite for understanding the physical properties of the Earth's core; however, such extreme conditions could not be created. Our recent developments with regard to ultra-high pressure and temperature experiments will guide us toward better understanding the deep planetary interiors.

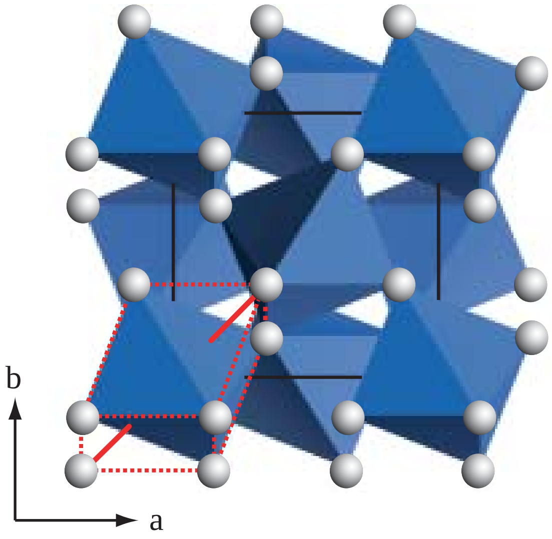

Fig. 3. Crystal structure of pyrite-type silica. The coordination polyhedra of O atoms around Si atoms are shown as octahedra. O atoms are represented by spheres. The black line indicates the unit cell, and the bold red lines indicate the interpolyhedral Si-O bonds.

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