Phase Boundary of Silicon Dioxide SiO_2 under High-pressure and -temperature Determined by *In Situ* DAC Laser Heating Technique

The physical properties and structural evolution of silicon dioxide (SiO_2) at high pressure and high temperature have attracted attention in geophysical science because silicon dioxide is a primary component of minerals in the interior of the Earth. The mantle of the Earth consists of mostly SiO_2, MgO, FeO, Al_2O_3, and CaO components. Therefore, there is a possibility that SiO_2 plays key role in the structure and dynamics of the Earth's mantle. The possibility of a pressure-induced tetragonal-orthorhombic (*$P4_2/mnm$-Pnnm*) phase transition in SiO_2 was suggested by crystal chemical arguments [1]. The transition occurs in the vicinity of 50 GPa at room temperature and has now been investigated from both experimental [2,3] and theoretical perspectives [4,5]. Although detailed knowledge has been accumulated on the high-pressure behavior of SiO_2, most studies have been limited to room temperature. The second-order tetragonal-to-orthorhombic transition at high pressure and high temperature has been studied in GeO_2 [6], which is regarded as an analogue of 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 phase in SiO_2 is unquenchable, converting to the tetragonal phase on decrease of temperature and release of pressure.

An *in-situ* X-ray diffraction measurement system under high pressure and temperature with use of a diamond anvil cell (DAC) apparatus has been set up at beamline **BL10XU** [7]. The samples were heated with a multimode continuous wave Nd:YAG laser using double-sided laser heating techniques, which minimized the temperature gradients of the heated area. The sample temperature was measured from one side of the sample using the spectroradiometric method. The heated samples were probed by angle-dispersive X-ray diffraction technique. The incident X-ray beam was

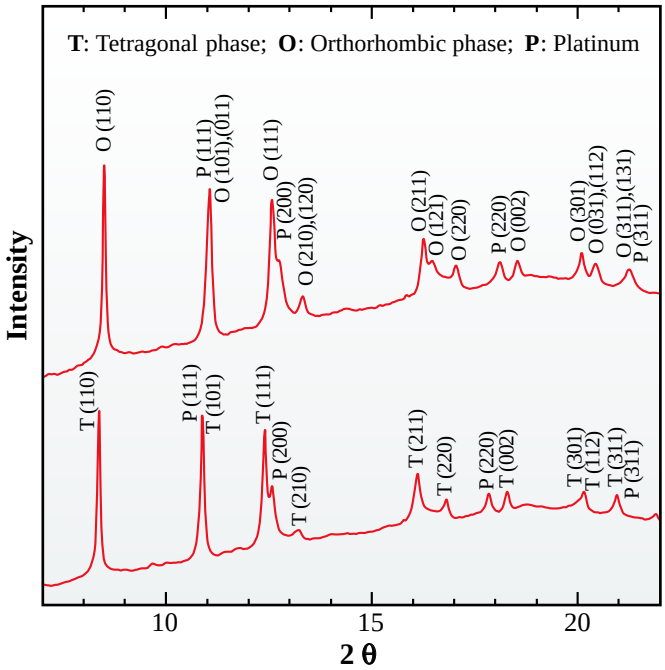

Fig. 1. X-ray diffraction patterns for silicon dioxide phases using angle-dispersive technique with DAC experiments.

monochromatized to wavelength of 0.4127 Å. The X-ray beam size was collimated to 16 - 20 μm diameter. Pressure was determined from the measured unit cell volume of platinum using the equation of state for platinum mixed with the sample.

We conducted two runs at pressures between 45 to 92 GPa and at temperatures between 300 K to 2200 K. The typical diffraction patterns of the tetragonal ($P4_2/mnm$) and the orthorhombic ($Pnnm$) phases are reproduced in Fig. 1. The changes from double peaks in the orthorhombic phase (*211-121* and *301-031*) to single peaks in the tetragonal phase indicated that the orthorhombic phase transformed to the tetragonal phase. Our determinations of the tetragonal and orthorhombic stability fields are summarized in Fig. 2. Zhang *et al.* [8] reported that an equilibrium phase boundary between coesite (monoclinic) and stishovite (tetragonal) of SiO_2 at about 10 GPa could not be determined below 1273 K because of the kinetics of the phase transition. However, the second-order phase transition between the tetragonal and orthorhombic phases in GeO_2 occurs without pressure and temperature hysteresis [6]. Therefore, it was possible to determine the phase boundary between the tetragonal and orthorhombic phase of SiO_2 at low temperature in this study.

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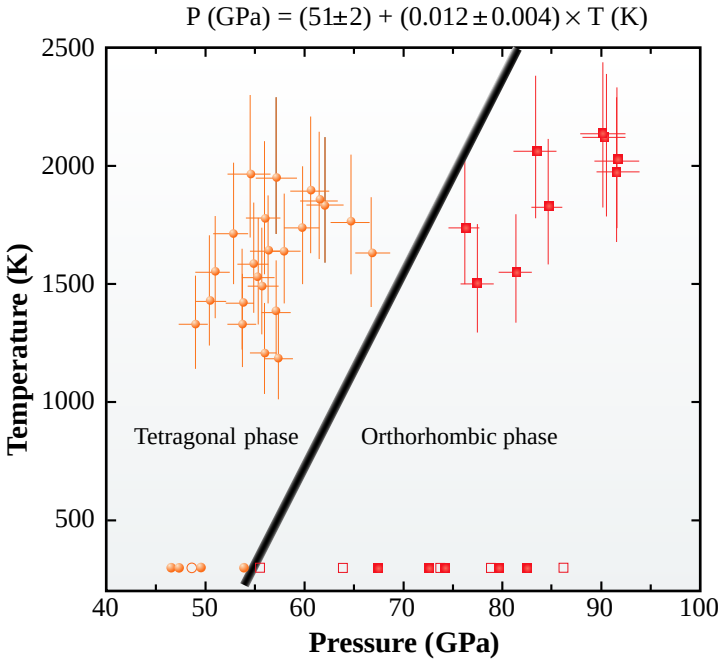

Fig. 2. The experimental results and a phase boundary determined by in situ observation. The solid circles and squares represent conditions where the tetragonal and orthorhombic phases were stable [9]. The open symbols represent data from Andrault et al. [3]. The solid line is the inferred phase boundary between the tetragonal and orthorhombic phases in silicon dioxide.

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