

High-Pressure Transformation of SiO₂ Glass

We have developed synchrotron X-ray diffraction and absorption techniques for measuring the structure and density of noncrystalline materials at high pressures and have applied them to SiO₂ glass. SiO₂ glass transforms from a fourfold- to a sixfold-coordinated structure between 20 and 35 GPa, and then behaves as a sixfold-coordinated amorphous polymorph at least up to 100 GPa. It is suggested that the density of SiO₂ glass does not exceed that of crystalline polymorphs even at 100 GPa. SiO₂-rich melts in the deep mantle may be much more incompressible than currently thought.

The high-pressure behavior of SiO₂ glass has attracted considerable attention because of its importance not only in condensed-matter physics but also in materials science and geophysics. Numerous studies, including Raman scattering, infrared absorption, Brillouin scattering, and X-ray diffraction, have suggested the occurrence of the structural transformation of SiO₂ glass in the short-range order, i.e. the change in the coordination number from four to six [1]. However, details of the transformation remain unclear because of experimental difficulties. The pressure dependence of density is one of the most fundamental and important pieces of information in high-pressure physics, but density measurements of SiO₂ glass were limited to pressures up to about 10 GPa. X-ray diffraction measurements are essential for discussing the structure of amorphous materials, but were also limited up to about 40 GPa. We have developed new experimental techniques for high-pressure *in situ* structure and density measurements of noncrystalline materials consisting of low-Z (low atomic

number) elements, and succeeded in measuring the structure factor and density of SiO₂ glass up to 100 GPa and up to above 50 GPa, respectively [2-5].

Structure measurements of SiO₂ glass were carried out at BL-14C2 by an energy-dispersive X-ray diffraction method with 20–65 keV white X-rays using slits and solid-state detector systems [3-5]. The shapes of structure factor $S(Q)$ and pair distribution function $g(r)$ are significantly different below and above 27 GPa and show no significant changes above 35 GPa (Fig. 1a). The first peak of $g(r)$ corresponds to the nearest neighbor Si-O pair. The Si-O bond length and the coordination number show drastic changes between 20 and 35 GPa (Fig. 1b). It is strongly suggested that SiO₂ glass transforms from a fourfold- to a sixfold-coordinated structure at pressures between 20 and 35 GPa, and then no major structural changes occur at least up to 100 GPa. Below 20 GPa, the structural transformation occurs mainly in the intermediate-range order, which is not associated with the increase in the coordination number.

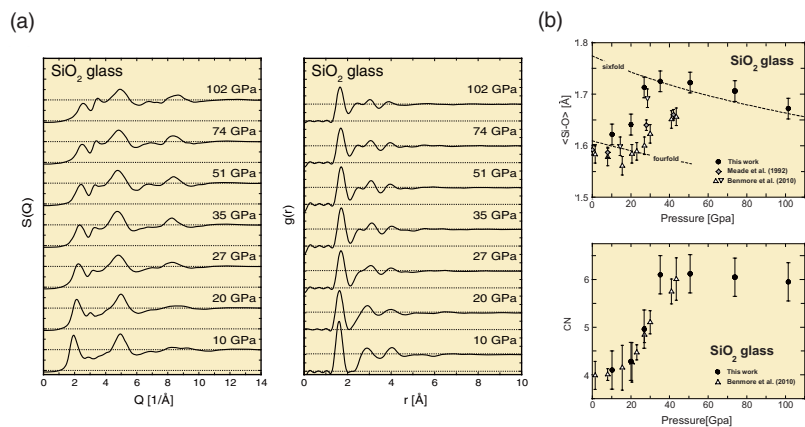


Figure 1 (a) Pressure dependence of $S(Q)$ and $g(r)$ of SiO₂ glass. (b) Pressure dependence of the Si-O bond length $\langle\text{Si-O}\rangle$ and the coordination number CN of SiO₂ glass. Estimated bond lengths of fourfold- and sixfold-coordinated crystalline phases are shown as dotted lines for comparison.

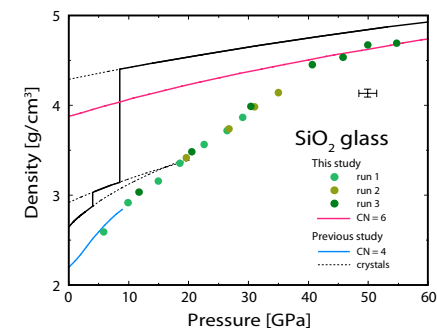


Figure 2 Pressure dependence of the density of SiO₂ glass. Uncertainties have been estimated as indicated by the error bar. The solid black line represents the pressure dependence of the density of thermodynamically stable crystalline polymorphs of SiO₂. The red line represents the estimated equation of state for the sixfold-coordinated amorphous polymorph of SiO₂.

Density measurements of SiO₂ glass were carried out at BL-18C by an X-ray absorption method with 10-keV monochromatic X-rays using a photodiode [2, 3]. The density of SiO₂ glass increased greatly and almost linearly from 10 to 40 GPa, and then relatively slightly above 40 GPa (Fig. 2). The equation of state for the sixfold-coordinated amorphous polymorph was estimated based on the density data above 45 GPa with the constraint from sound-velocity data available in the literature. It is suggested that the density of SiO₂ glass does not exceed that of crystalline polymorphs even at 100 GPa. The results of density measurements are consistent with those of structure measurements, except for the slight difference in the pressure range where the transformation to a sixfold-coordinated structure is completed. It is presumed that the irradiation of white X-rays may have relaxed the structure and deviatoric stresses of SiO₂ glass in structure measurements.

Glasses can be considered to be analog materials that reflect the structure and density of melts. Based on extrapolation of the equations of state determined by the data measured under the conditions of the shallow mantle, the compressibility of SiO₂-rich melts was considered to be high in the deep mantle. However, considering the

fact that SiO₂ glass shows a much lower compressibility after the transformation to a sixfold-coordinated structure is completed, it is suggested that the compressibility of SiO₂-rich melts in the deep mantle may be much lower than that estimated by extrapolation of the equations of state of melts in the shallow mantle [6].

REFERENCES

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BEAMLINES

14C2 and 18C

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