Newly-Developed High-Pressure Small-Angle X-Ray Scattering System at BL-18C Reveals Inhomogeneity in Silica Glass during Structural Transformation

Glass is usually considered to be homogeneous, but it is also known to show phase transformations called "polyamorphism" during which it could be inhomogeneous. To detect nanoscale inhomogeneity, we have developed a high-pressure small-angle X-ray scattering system at BL-18C and succeeded in detecting the signal from the transient state of pressure-induced phase transformation of silica glass. The data suggests that the size of inhomogeneity is sub-nanometer (~6 Å) and the boundary between low- and high-density domains is unsharp.

Silica glass is one of the most studied noncrystalline materials. Despite its simple chemical composition, this material shows interesting behaviors such as anomalous elasticity, permanent densification, and gradual structural changes in short-range order [1]. These phenomena are related to some amorphous-amorphous phase transformations (polyamorphism). However, little is known about the intermediate state of pressure-induced polyamorphism because of the lack of suitable experimental techniques.

The gradual phase transformation in short-range order of silica glass occurs between 20 and 35 GPa and is accompanied by a ~30% increase in density [2]. Despite such large changes in density, silica glass remains optically homogeneous during the transformation. X-ray diffraction reveals that the average silicon coordination number gradually increases from four to six as the transformation proceeds. However, no information on the inhomogeneity has been obtained because X-ray diffraction only provides information on the average atomic arrangement of noncrystalline materials. Small-angle X-ray scattering is a method that covers the length scale between optical microscopy (micron scale) and X-ray diffraction (angstrom scale). It provides information about the inhomogeneity of a sample on a nanometer scale. In this study, we developed small-angle X-ray scattering techniques to study the inhomogeneity of glass at high pressures, and used them to unveil the intermediate state of the transformation in silica glass.

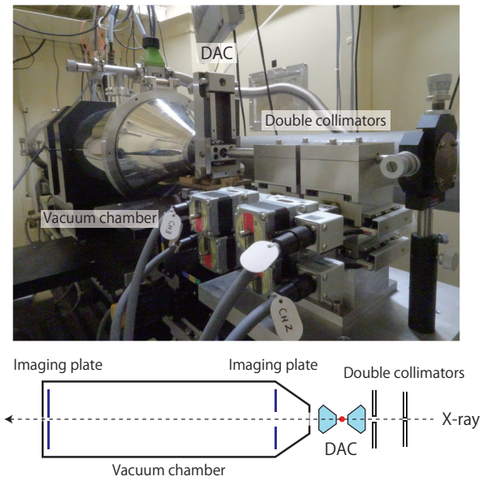

Figure 1: High-pressure small-angle X-ray scattering system at BL-18C.

High-pressure in-situ small-angle X-ray scattering experiments for silica glass were conducted using a newly-developed system at BL-18C [3]. **Figure 1** shows the setup for measuring X-ray scattering in the low-Q range for samples in diamond-anvil high-pressure cells (DAC). The system is very simple with two collimators and a vacuum chamber. The lower limit of the Q range is about 0.1 Å^{-1}. The X-ray energy was set to around 15 keV considering the X-ray absorption and glitches of the anvils.

Figure 2(a) shows the pressure dependence of the scattering intensity averaged over the low-Q range (I_{av}) and the position of the first sharp diffraction peak (FSDP). Upon compression, the position of the FSDP changes monotonically with pressure, whereas I_{av} shows a maximum at ~25 GPa. Upon decompression, the position and the height of the FSDP change drastically between 15 and 10 GPa. This is accompanied by a more obvious maximum in I_{av}. These drastic changes observed upon decompression can be attributed to the transformation from the sixfold-coordinated structure to the fourfold-coordinated structure. As the pressure-induced transformation in short-range order of silica glass occurs mainly between 20 and 35 GPa, the increase in the intensity of the small-angle X-ray scattering provides definitive evidence of a heterogeneous intermediate state during the transformation.

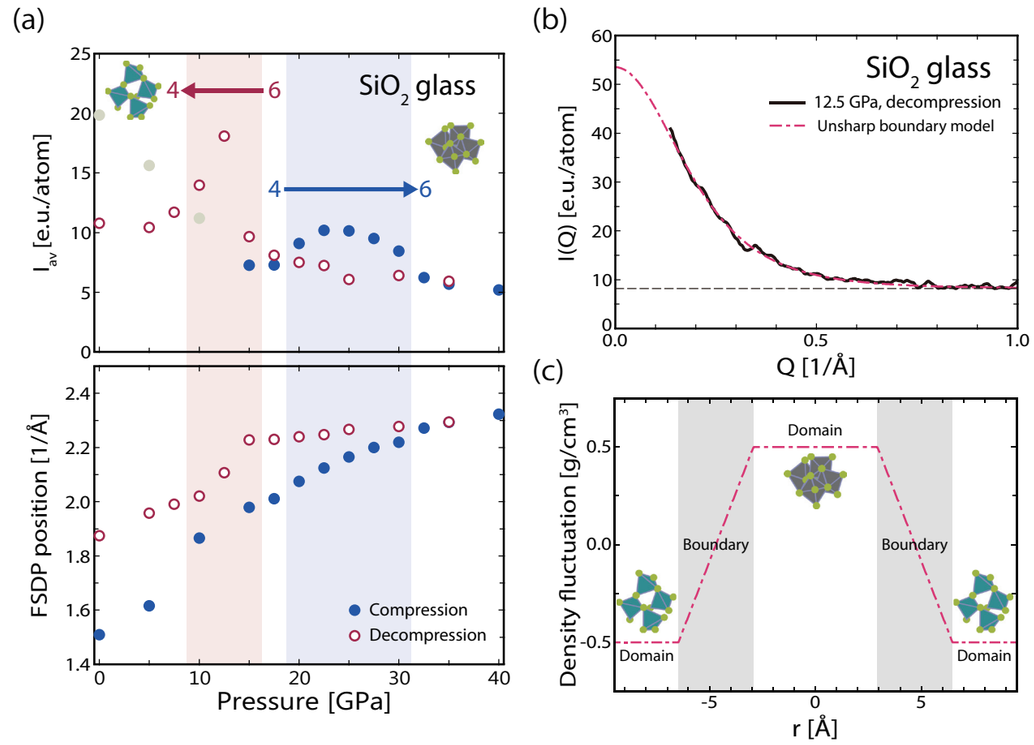

Figure 2: (a) Pressure dependence of I_{av}, the average scattering intensity at Q = 0.14–0.60 Å^{-1}, and the position of the FSDP. Gray symbols for I_{av} denote the data upon compression affected by the tail of the FSDP. **(b)** Low-Q X-ray scattering pattern of silica glass at 12.5 GPa upon decompression and **(c)** corresponding one-dimensional density-fluctuation model.

Figure 2(b) shows the low-Q X-ray scattering pattern of silica glass at 12.5 GPa on decompression. We have fitted the data with the two-phase mixing model extended to the case of an unsharp domain boundary [3] and obtained the parameters of the correlation length ξ and the boundary width E. **Figure 2(c)** shows the one-dimensional density-fluctuation model with the best-fitted parameters. The average domain size and boundary width are estimated to be ~6 Å and 3–4 Å, respectively. Considering that the Si-O bond length is 1.6–1.7 Å both in the fourfold-coordinated structure and the sixfold-coordinated structure, several SiO_4 tetrahedrons and SiO_6 octahedrons likely form one domain. The structure in the boundary region may be classified as a fivefold-coordinated structure. The result well explains the lack of heterogeneous features such as grain boundaries and cracks in optical microscopy, although the two structures coexist in silica glass during the transformation. First, optical microscopy cannot identify domains that are smaller than the wavelength of visible light. Second, the broad boundary region with an intermediate structure likely works as a buffer.

REFERENCES

[1] T. Sato and N. Funamori, *Phys. Rev. B* **82**, 184102 (2010).
[2] T. Sato and N. Funamori, *Phys. Rev. Lett.*, **101**, 255502 (2008).
[3] T. Sato, N. Funamori, D. Wakabayashi, K. Nishida and T. Kikegawa, *Phys. Rev. B* **98**, 144111 (2018).

BEAMLINE

BL-18C

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