Structural origin of the anomalous properties of SiO_2 glass under pressure reveled by *in situ* high-pressure pair distribution function measurement

Understanding the structural origin of the anomalous properties of tetrahedral liquids and amorphous materials at high pressure and/or high temperature conditions is of great interest in wide range of scientific fields. In particular, since SiO_2 is ubiquitous in the Earth, understanding the SiO_2's anomaly is fundamental not only in physics, but also in geophysics to understand nature of silicate magmas in the Earth and planet, and in materials science as a prototype network-forming glass. It has been reported that SiO_2 liquid shows anomalous density and compressibility behaviors at high temperatures and high pressures [1]. In addition, SiO_2 glass also shows compressibility maximum (bulk modulus minimum) at high pressure of ~2–3 GPa under room temperature condition [2].

Theoretical studies of SiO_2 liquid suggests that the second shell structure of silicon is the key to understanding the anomalous properties of SiO_2 liquid at high temperatures and high pressures. A structural parameter z ($z = \delta_{ji} - \delta_{j'i}$, where δ_{ji} and $\delta_{j'i}$ is the distance from each silicon atom i to the fifth nearest silicon neighbor j and to the fourth nearest oxygen neighbor j') was developed to investigate the second shell structure in SiO_2 liquid [1]. The theoretical study found a bimodal distribution in the structural parameter z with varying temperature, and the S and ρ states are assigned to the high and low distributions in the parameter z, respectively. The low-density S state in SiO_2 liquid consists of four silicon neighbor atoms in the first shell and exhibits high tetrahedral order with clear separation between the first and second shell. The fraction of the S state with high tetrahedrality is considered to be the controlling parameter of the anomalous properties of SiO_2 liquid at high temperatures and high pressures in theoretical study [1]. However, there has been no experimental observation of the structure of the silicon's second shell in SiO_2 liquid and/or glass at *in situ* high pressure and/or high temperature conditions.

In this work [3], we carried out *in situ* high-pressure pair distribution function measurement of SiO_2 glass by utilizing high flux and high energy X-rays from undulator sources at SPring-8 **BL37XU** and **BL05XU** (Fig. 1(a)). The structure of SiO_2 glass was measured at *in situ* high pressure conditions up to 6.0 GPa in a Paris-Edinburgh (PE) cell (Fig. 1(b)) by high-energy X-ray diffraction measurement with a collimation setup to obtain signals only from the SiO_2 glass sample. We obtained the Faber-Ziman structure factor, $S(Q)$, of SiO_2 glass at the wide range of the momentum transfer Q up to 19 $Å^{-1}$ at BL37XU and up to 20 $Å^{-1}$ at BL05XU (Fig. 2), which is almost two times larger than that in conventional high-pressure angle-dispersive X-ray diffraction measurements.

By combining the high-pressure experimental $S(Q)$ precisely determined at a wide range of Q up to 19–20 $Å^{-1}$ with the MD (molecular dynamics simulation)-RMC (reverse Monte Carlo) modeling, we were able to investigate in detail the structural behavior of SiO_2 glass beyond the nearest neighbor distances under *in situ* high pressure conditions. We found bimodal feature in the translational order of the silicon's second shell in terms of the structural parameter z (Fig. 3(c)). The bimodal feature is consistent with that simulated in SiO_2 liquid with varying temperature in the theoretical study [1].

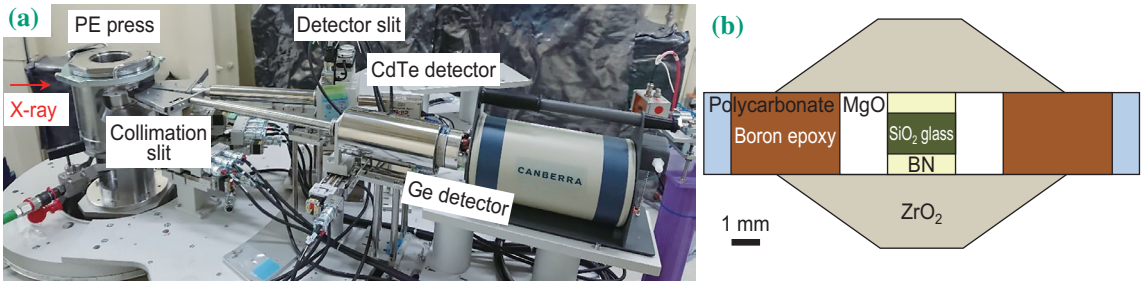

Fig. 1. *In situ* high-pressure pair distribution function measurement at SPring-8 BL05XU **(a)**, and design of the Paris-Edinburgh (PE) cell assembly for the SiO_2 glass experiment up to 6.0 GPa under room temperature condition **(b)**.

The structure of SiO_2 glass with the characteristic distribution of the parameter z at 2.4 Å shows a tetrahedral symmetry structure formed from the nearest four silicon atoms in the first shell, and the first and second shells are clearly separated as the fifth neighbor silicon atom locates in the second shell (Fig. 3(b)). The structural feature corresponds to the low-density *S* state structure reported in the theoretical study of SiO_2 liquid [1]. On the other hand, the structure of SiO_2 glass with the characteristic distribution of z at 1.7 Å shows that the fifth neighbor silicon atom locates in the first shell (Fig. 3(a)), which indicates collapse of the second shell onto the first shell and breaking of local tetrahedral symmetry. SiO_2 glass mainly consists of the low-density *S* state with tetrahedral symmetry structure at low pressures. On the other hand, the local tetrahedral symmetry structure breaks at high pressures, and the fraction of the *S* state in SiO_2 glass decreases under pressure, as well as theoretical observation in SiO_2 liquid at high temperatures and high pressures.

The new experimental technique of high-pressure pair distribution function measurement particularly using the high-flux pink beam at BL05XU beamline opens new way to investigate structural behavior of liquids and amorphous materials at *in situ* high pressure and high temperature conditions. The PE cell enables us to conduct high-pressure experiments not only for glass but also for liquid up to 7 GPa and 2000°C [4]. These techniques would have wide ranging application not only in scientific fields such as physics, chemistry, geoscience, and materials science but also engineering and industry processes.

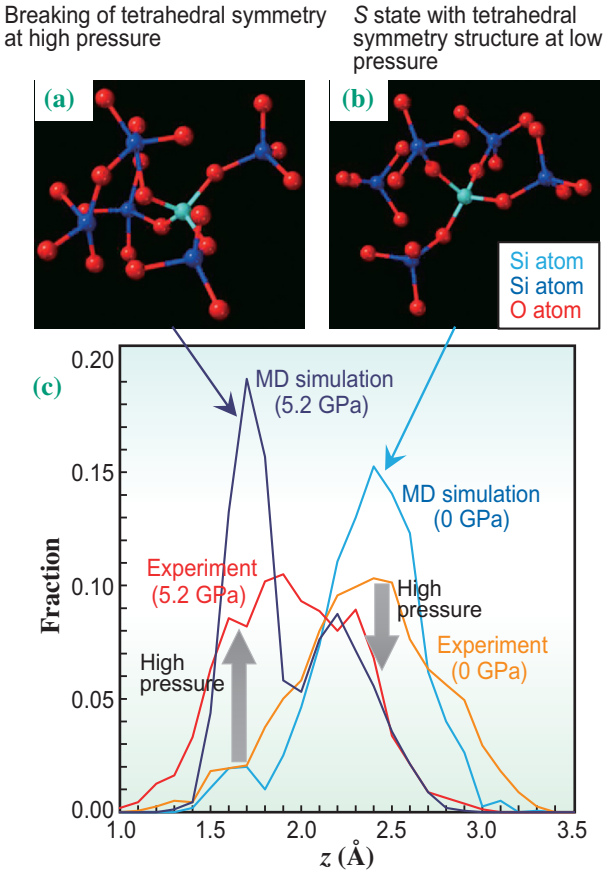

Fig. 3. The structural features in SiO_2 glass with the characteristic distribution of z = 2.4 Å **(b)** and z = 1.7 Å **(a)**. Translational order in SiO_2 glass as a function of the parameter z obtained in our experiment with MD-RMC modeling and MD simulation with BKS model at 0 and 5.2 GPa **(c)**.

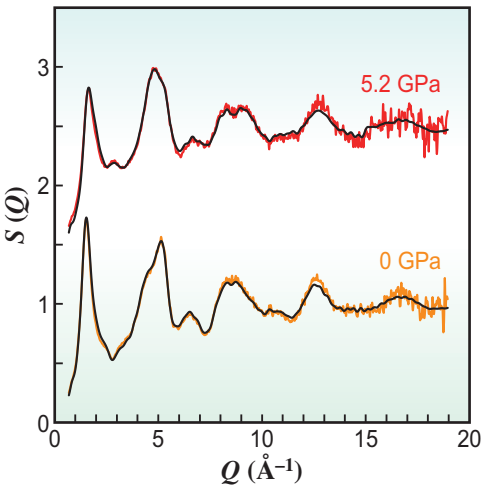

Fig. 2. Structure factor [$S(Q)$] of SiO_2 glass measured at 0 GPa (orange) and 5.2 GPa (red). Black lines show $S(Q)$ of the MD-RMC structure model derived based on the experimentally observed $S(Q)$ at each pressure condition. $S(Q)$ at 5.2 GPa is displayed by a vertical offset of +1.5.

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References

[1] R. Shi and H. Tanaka: Proc. Natl. Acad. Sci. USA **115** (2018) 1980.
[2] A. Yokoyama *et al.*: J. Appl. Phys. **107** (2010) 123530.
[3] *Y. Kono, K. Ohara, N. M. Kondo, H. Yamada, S. Hiroi, F. Noritake, K. Nitta, O. Sekizawa, Y. Higo, Y. Tange, H. Yumoto, T. Koyama, H. Yamazaki, Y. Senba, H. Ohashi, S. Goto, I. Inoue, Y. Hayashi, K. Tamasaku, T. Osaka, J. Yamada and M. Yabashi: Nat. Commun.* ***13*** *(2022) 2292.*
[4] Y. Kono *et al.*: Phys. Earth. Planet. Inter. **228** (2014) 269.