In situ high-pressure pair distribution function measurement of liquid and glass by using 100 keV pink beam

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**ABSTRACT**

Understanding the pressure-induced structural changes in liquids and amorphous materials is fundamental in a wide range of scientific fields. However, experimental investigation of the structure of liquid and amorphous material under **in situ** high-pressure conditions is still limited due to the experimental difficulties. In particular, the range of the momentum transfer (Q) in the structure factor [S(Q)] measurement under high-pressure conditions has been limited at relatively low Q, which makes it difficult to conduct detailed structural analysis of liquid and amorphous material. Here, we show the **in situ** high-pressure pair distribution function measurement of liquid and glass by using the 100 keV pink beam. Structures of liquids and glasses are measured under **in situ** high-pressure conditions in the Paris–Edinburgh press by high-energy x-ray diffraction measurement using a double-slit collimation setup with a point detector. The experiment enables us to measure S(Q) of GeO$_2$ and SiO$_2$ glasses and liquid Ge at a wide range of Q up to 20–29 Å$^{-1}$ under **in situ** high-pressure and high-temperature conditions, which is almost two times larger than that of the conventional high-pressure angle-dispersive x-ray diffraction measurement. The high-pressure experimental S(Q) precisely determined at a wide range of Q opens the way to investigate detailed structural features of liquids and amorphous materials under **in situ** high-pressure and high-temperature conditions, as well as ambient pressure study.

**I. INTRODUCTION**

Investigation of the structural behaviors of liquids and amorphous materials under **in situ** high-pressure conditions is vital to understand the pressure-induced phenomena, such as liquid–liquid transition,$^{1,2}$ polymorphism,$^{3,4}$ and occurrence of unique properties at high pressures.$^{5,6}$ Pair distribution function analysis by using the high-energy x-ray diffraction measurement is one of the most powerful tools to investigate structures of liquids and amorphous materials, and it has been widely used in the structural studies of liquids and amorphous materials at ambient pressure.$^{8,9}$ Combination of high-quality x-ray diffraction measurement with structural modeling using computational methods, such as molecular dynamics simulation, first principles simulation, and reverse Monte Carlo modeling, enables us to investigate atomistic arrangement of liquids and amorphous materials beyond the nearest neighbor distances.$^{11,12}$ However, such detailed structural analysis has been limited only under ambient pressure conditions due to experimental difficulties in obtaining high-quality structure factor [S(Q)] data in high-pressure experiments.

Efforts have been made to conduct x-ray pair distribution function measurements of liquids and amorphous materials under **in situ** high-pressure conditions by the angle-dispersive x-ray diffraction measurement using monochromatic x-ray$^{13,14}$ and by the energy-dispersive x-ray diffraction measurement using white x-ray.$^{15,16}$ One of the most serious issues in the high-pressure pair distribution...
function measurement is background noise signals from surrounding high-pressure cell components, such as crystalline peaks from capsule and pressure medium materials in the large volume press experiment. The influence of such crystalline peaks may be minimized in the diamond anvil cell experiment, while scattering from diamond anvils, such as Compton scattering and thermal diffuse scattering, becomes a major source of background in the diamond anvil cell experiment.\textsuperscript{15,17} In order to avoid or minimize such background signals and to obtain signals from weak scattering liquid and amorphous material, a collimation technique in front of the detector has been developed. A simple method is the use of a double-slit collimation setup with a point detector, which has been adopted in high-pressure energy-dispersive x-ray diffraction measurements.\textsuperscript{15–17} On the other hand, the multichannel collimator has been developed for angle-dispersive x-ray diffraction measurements.\textsuperscript{13,14}

In addition to the background noise issue, there is another experimental difficulty in measuring high-quality S(Q) data to a high Q range in high-pressure experiments. Available Q range in the high-pressure angle-dispersive x-ray diffraction measurements is limited to less than $\sim 10$–$12 \text{ Å}^{-1}$ because of the limitation in the $2\theta$ angle of up to $\sim 30^\circ$ with the energy of the monochromatic x-ray of less than 40–50 keV (Refs. 14 and 20) (Fig. 1). On the other hand, high-pressure multi-angle energy dispersive x-ray diffraction measurements reported S(Q) data at a relatively higher Q range typically to $\sim 12$–$15 \text{ Å}^{-1}$ by utilizing high-energy x-rays (Refs. 21 and 22). Some recent studies reported S(Q) measurements at a higher Q range of $\sim 15$–$17 \text{ Å}^{-1}$ (Refs. 23 and 24). However, the energy-dispersive x-ray diffraction measurement using white x-ray inevitably contains uncertainty in the x-ray intensity profile as a function of energy and resultantly Q. Therefore, it is difficult to conduct detailed structural analysis using the S(Q) data obtained by the energy-dispersive x-ray diffraction measurement. In addition, recently, the combined angle-dispersive and energy-dispersive x-ray diffraction measurement was developed at the PSICHE beamline of the SOLEIL synchrotron for measuring S(Q) at relatively wide Q range similar to the energy-dispersive x-ray diffraction measurement by short acquisition time comparable to the angle-dispersive x-ray diffraction measurement.\textsuperscript{1^1,23}

Here, we show the high-pressure pair distribution function measurement by using the 100 keV pink beam at the BL05XU beamline in SPring-8. The use of high-energy x-ray is beneficial for measuring S(Q) data to a wide range of Q (Fig. 1). We used Paris–Edinburgh (PE) press as the high-pressure device. The PE press can compress a millimeter-size large volume sample and has a wide angle opening in the horizontal plane, which enables us to obtain signals from weak scattering liquids and amorphous materials at a wide range of Q. Our developed high-pressure pair distribution function measurement enables us to measure S(Q) of GeO$_2$ and SiO$_2$ glasses and liquid Ge at a wide range of Q up to 20–29 Å$^{-1}$ under \textit{in situ} high-pressure and high-temperature conditions.

II. EXPERIMENTS

\textit{In situ} high-pressure pair distribution function measurements were conducted at the BL05XU beamline in SPring-8, Japan. Figure 2(a) shows the experimental setup of the pair distribution function measurement under \textit{in situ} high-pressure and high-temperature conditions. High-pressure experiments were conducted by using the PE press. Cup-shaped WC anvils with a cup diameter of 12 mm and a bottom diameter of 3 mm are used for generating high pressure. An example of the PE cell assembly is shown in Fig. 2(b). The cell assembly mainly consists of a boron–epoxy gasket with the polycarbonate outer ring, MgO pressure medium, ZrO$_2$ caps, graphite heater, and sample capsule. The capsule material differs depending on the sample. For example, the BN capsule is often used for room-temperature experiments for glass samples and high-temperature experiments for liquid metal samples, while the

![FIG. 1. Available range of Q as a function of 2θ angle in the high-energy x-ray diffraction measurement using monochromatic x-ray of the energy of 40 and 100 keV.](image1)

![FIG. 2. \textit{In situ} high-pressure pair distribution function measurement in Paris–Edinburgh (PE) press at the BL05XU beamline in SPring-8 (a). (b) A design of the PE cell assembly for high-pressure and high-temperature experiments.](image2)
graphite capsule is used for oxide and silicate melt samples. The large-volume sample (typically 1.2–1.5 mm in both diameter and height) is available in the PE cell. The PE cell allows high-pressure experiments up to ~7 GPa and the graphite heater generates stable high temperatures to ~2000 °C (Ref. 16). Pressures were determined by the equation of state of MgO (Ref. 26) inside the graphite heater. Temperatures were estimated based on the power–temperature curve, which were determined in a separate experiment using an identical cell configuration. The temperature estimation was consistent with the known melting curves of Fe (Ref. 27) and NaCl and KCl (Ref. 28) with a standard deviation of less than 50 °C under pressure conditions up to 7.3 GPa.

Structure measurements of GeO$_2$ and SiO$_2$ glasses and liquid Ge under *in situ* high-pressure conditions in the PE cell were conducted by the high-energy x-ray diffraction measurement using two point detectors [Fig. 2(a)]. We used a CdTe point detector (Amptek X-123) at low 2θ angles (first detector) and a Ge point detector (Canberra) at high 2θ angles (second detector). The two detectors are placed at a 15° separation angle to obtain x-ray diffraction data at the 2θ angles of 0.4°–18.0° by the first detector and of 15.4°–33.0° by the second detector. A double-slit collimation setup (a collimation slit and a detector slit) is built in front of the detectors, which is critical to obtain signals from weak scattering amorphous materials without background signals from surrounding high-pressure cell components. The collimation slit and detector slit locate at 60 and 600 mm distances from the sample position, respectively. We used collimation slits with the fixed horizontal slit width of 40 μm for the first detector and of 200 μm for the second detector, respectively. The width of the detector slit in front of the first detector is adjustable with varying 2θ angles, while the width of the detector slit for the second detector is fixed at 300 μm. In addition, the horizontal size of the incident x-ray is adjusted by an incident slit with varying 2θ angle to maximize the collimation length within the sample size. The vertical size of the incident x-ray is fixed at 300–500 μm.

Figure 3 shows the calculated collimation length at the sample position. $D_0$ is the collimation length calculated without the effect of the incident x-ray width, and $D_1$ is the total collimation length including the effect of the incident x-ray width (inset in Fig. 3). Since the collimation length becomes shorter with increasing 2θ angle in a constant slit setup, we adopted eight different slit configurations with varying 2θ angle (Fig. 3) to optimize data acquisition efficiency. Our designed collimation slit setup yields the $D_1$ collimation length of less than 1.2–1.5 mm (typical sample diameter) at 2θ angles higher than 3.8°–4.8°, implying that background noise signals from surrounding high-pressure cell components can be eliminated at higher 2θ angles. On the other hand, it is inevitable to have a larger collimation length than the sample diameter at low 2θ angles because of the geometrical constraint. Nevertheless, a few crystalline diffraction peaks from the capsule material (e.g., hexagonal BN or graphite) do not have a significant influence on the determination of S(Q).

High-energy x-ray diffraction measurements were carried out by using a high-flux pink beam at a photon energy of 99.9 keV for the GeO$_2$ glass experiment and 100.1 keV for the SiO$_2$ glass and liquid Ge experiments. The 100 keV pink beam was generated with a double multilayer monochromator at the BL05XU beamline. The double multilayer monochromator with a wide energy bandwidth (ΔE/E) of 1.0% enhances the x-ray flux by orders of magnitude, compared with that of the conventional double crystal monochromator of silicon. The use of high-energy x-ray of 100 keV is critical to obtain S(Q) data to a high Q range (Fig. 1). For example, the x-ray diffraction measurement using 40 keV x-ray provides S(Q) data up to 10.5 Å$^{-1}$ at the 2θ angle of 30°. On the other hand, high-energy x-ray of 100 keV enables us to determine S(Q) at a much wider range of Q to 26.2 Å$^{-1}$ at the same range of 2θ angle of 30°. In this study, we carried out high-energy x-ray diffraction measurements of GeO$_2$ and SiO$_2$ glasses and liquid Ge by scanning the 2θ angle from 0.4° to 33.0°, which corresponds to the Q range of 0.4–28.7 Å$^{-1}$.

Since the double slit collimation setup yields different collimation volumes at the sample position with varying 2θ angles (Fig. 3), the experimentally obtained intensity data [$I_{\text{exp}}(2θ)$] is corrected by the normalized collimation volume at each 2θ angle [$V(2θ)/V_{2θ\text{max}}$].

$$I_{\text{corr}}(2θ) = \frac{I_{\text{exp}}(2θ)}{V(2θ)/V_{2θ\text{max}}} I_0(2θ) P(2θ).$$

$V(2θ)$ is calculated from the collimation length the incident x-ray width and height at each 2θ angle. $V_{2θ\text{max}}$ is the $V(2θ)$ at the highest 2θ angle. When the collimation length becomes larger than the sample diameter at low 2θ angles, the $V(2θ)$ is calculated as sample diameter × incident x-ray width × height. In addition to the correction for the collimation volume, the variation in the incident x-ray intensity during the 2θ scan measurement [$I_0(2θ)$] was corrected. Furthermore, the effect of polarization on the scattering intensity with varying 2θ angles was corrected by a polarization factor $P(2θ) = \cos^2 2θ$, assuming in-plane polarization in the horizontal direction. On the other hand, although a previous study discussed a correction for the pink beam with the ΔE/E of 3.3%, we did not...
carry out any corrections for the pink beam. In our previous study,\textsuperscript{31} we conducted S(Q) measurements of SiO\textsubscript{2} glass by using a 40.3 keV pink beam with the ΔE/E of 1.7 × 10\textsuperscript{-2} at the BL05XU beamline and 40.0 keV monochromatic beam with the ΔE/E of 1.8 × 10\textsuperscript{-5} at the BL37XU beamline in SPring-8, and we obtained consistent S(Q) results in these two measurements. Therefore, we consider that there is no significant effect of the pink beam with the ΔE/E of ∼1% on the determination of S(Q).

The analysis of S(Q) was conducted by using the method developed at the BL04B2 beamline of SPring-8 (Refs. 32 and 33). The coherent x-ray scattering intensities \([I_{\text{coh}}(Q)]\) were obtained by subtracting background scattering \([I_{\text{bg}}(Q)]\) and the Compton scattering \([I_{\text{comp}}(Q)]\) (Ref. 34) from the corrected experimental intensity data \([I_{\text{corr}}(Q)]\),

\[
I_{\text{coh}}(Q) = I_{\text{corr}}(Q) - I_{\text{bg}}(Q) - I_{\text{comp}}(Q).
\]

We measured the x-ray diffraction pattern of an empty PE cell without sample using the identical collimation slit setup, and the result is used as the background scattering data \([I_{\text{bg}}(Q)]\). Then, the Faber–Ziman S(Q) (Ref. 35) was obtained by normalizing \(I_{\text{coh}}(Q)\),

\[
S(Q) = \frac{I_{\text{coh}}(Q) - \langle f^2(Q) \rangle + \langle f(Q) \rangle^2}{\langle f(Q) \rangle^2},
\]

\[
\langle f^2(Q) \rangle = \sum c_j f_j(Q)^2,
\]

\[
\langle f(Q) \rangle = \sum c_j f_j(Q),
\]

where \(c_j\) and \(f_j(Q)\) are the mole fraction and the atomic form factor\textsuperscript{36} of the jth element in the sample, respectively.

### III. RESULTS AND DISCUSSION

Figure 4 shows an example of x-ray diffraction patterns of GeO\textsubscript{2} glass measured in a PE cell at 1.3 GPa and room temperature (blue and red lines) and the background signals measured in an empty PE cell without sample at ambient pressure (light blue and orange lines). The data are acquired at eight segments with different collimation slit setups as shown in Fig. 3. The corrections for the collimation volume and \(I_0\) have been applied.

Figure 5 shows the comparison of S(Q) of GeO\textsubscript{2} glass measured in the PE cell at ambient pressure at the BL05XU beamline and that measured in a vacuum without PE cell at the BL04B2 beamline in SPring-8. The BL04B2 beamline is dedicated to the x-ray pair distribution function measurement, and many studies for the structures of liquids and amorphous materials have been carried out under ambient pressure conditions.\textsuperscript{33} The S(Q) of GeO\textsubscript{2} glass measured in the PE cell at the BL05XU beamline is identical to that determined at the...
BL04B2 beamline, which verifies the validity of our developed experimental setup for measuring $S(Q)$ of amorphous materials in the PE cell.

We carried out the $S(Q)$ measurements of GeO$_2$ glass at 1.3 GPa and room temperature [Fig. 6(a)], SiO$_2$ glass at 1.1 GPa and room temperature [Fig. 6(b)], and liquid Ge at 0.4 GPa and 1000 °C [Fig. 6(c)]. We conducted the $S(Q)$ measurements by different acquisition times to investigate the quality of $S(Q)$ with varying acquisition times. Figure 6 shows the results by the $Q[S(Q)-1]$ formula to show the quality of $S(Q)$ at a high $Q$ range. The $S(Q)$ of GeO$_2$ glass shows clear oscillation features to the maximum $Q$ range up to 28.7 Å$^{-1}$ even at the shortest acquisition time of 14 min [Fig. 6(a)], although the data obtained by 14 min acquisition time show relatively high noises at the $Q$ range higher than ~24 Å$^{-1}$. The noise at a high $Q$ range becomes smaller with increasing acquisition time, and we can obtain high-quality results to the maximum $Q$ of 28.7 Å$^{-1}$ at the acquisition time of more than 28 min. Similar to the results of GeO$_2$ glass, we obtained the $S(Q)$ of SiO$_2$ glass at the $Q$ range up to 26.0 Å$^{-1}$ [Fig. 6(b)]. Because of weaker scattering from SiO$_2$ glass compared to GeO$_2$ glass, the $S(Q)$ of SiO$_2$ glass measured by 16 and 33 min acquisition times show high noise level at the $Q$ range higher than ~18 Å$^{-1}$. We obtained clear oscillation features to the highest $Q$ of 26.0 Å$^{-1}$ in the data measured by the acquisition time longer than 62 min [Fig. 6(b)]. Figure 6(c) shows the $S(Q)$ results of liquid Ge at the $Q$ range up to 19.9 Å$^{-1}$. The $S(Q)$ results of liquid Ge measured by the acquisition time of 10 and 16 min show high noise level above ~14 Å$^{-1}$. Clear oscillation features up to 19.9 Å$^{-1}$ were obtained by the acquisition times of 33 and 62 min.

Figure 7 summarizes the available range of $Q$ and the data acquisition time of the high-pressure pair distribution function measurements of GeO$_2$ glass (red squares), SiO$_2$ glass (red circles), and liquid Ge (red diamonds) by using 100 keV pink beam, compared with those of previous studies. High-pressure pair distribution function measurements by angle dispersive x-ray diffraction using monochromatic x-ray and area detector have been carried out at the ID27 beamline of the European Synchrotron Radiation Facility (ESRF) and the 13IDC beamline of the Advanced Photon Source (APS). The angle-dispersive x-ray diffraction measurements use a multichannel collimator to minimize background signals from surrounding high-pressure cell components. The measurement requires oscillation of the multichannel collimator by a few degrees to obtain continuous x-ray scattering data. The typical data acquisition time is ~5–10 min, and the $Q$ range is up to ~10–12 Å$^{-1}$ by using monochromatic x-ray of the energy of ~40–50 keV (Refs. 14 and 20) (Fig. 7).

High-pressure multi-angle energy dispersive x-ray diffraction measurements using white x-ray have been carried out at the 16BMB beamline in the APS, and the BL-14C2 and AR-NE5C beamlines in the Photon Factory (PF). The multi-angle energy dispersive x-ray diffraction measurements reported $S(Q)$ data at a relatively higher $Q$ range typically to ~12–15 Å$^{-1}$ (Refs. 21 and 22), while a long acquisition time of more than 2–3 h is required (Fig. 7) because of limited x-ray flux from a bending magnet source. On the other hand, combined angle-dispersive and energy-dispersive x-ray diffraction measurements using white x-ray at the PSICHE beamline of the SOLEIL synchrotron reported $S(Q)$ measurements at the $Q$ range up to ~10–13 Å$^{-1}$ by short acquisition time of ~20 min (Fig. 7).
Recently, we conducted high-pressure pair distribution function measurements of SiO$_2$ glass by using 40 keV monochromatic and pink beams at the BL37XU and BL05XU beamlines in SPring-8, respectively. S(Q) data up to 20 Å$^{-1}$ can be obtained by scanning 2θ angles up to 70° (Fig. 7), but it was not possible to obtain higher Q data because of the limitation of available 2θ angle in the high-pressure experiment. In this study, we succeeded in measuring S(Q) at a wide Q range up to 29 Å$^{-1}$ by utilizing 100 keV pink beam at the BL05XU beamline in SPring-8 (Fig. 7). Acquisition times of more than ~30 min were required to obtain clear S(Q) data to the Q range higher than 25 Å$^{-1}$ in GeO$_2$ and SiO$_2$ glasses, while the S(Q) data to the Q range of ~20 Å$^{-1}$ can be obtained by shorter acquisition time of ~14–33 min. The available Q range of our developed high-pressure pair distribution function measurement is almost two times larger than those of conventional high-pressure angle-dispersive x-ray diffraction measurements using monochromatic x-ray.

Some previous studies have used 80 keV or 100 keV monochromatic x-ray at the 1ID beamline in the APS, while the Q range of the S(Q) measurements was limited to ~15–16 Å$^{-1}$, probably due to weak scattering from a very small sample in diamond anvil cell used as the high-pressure device in these studies. The advantage of the diamond anvil cell is a high-pressure generation, and high-pressure pair distribution function measurements of glasses at ultrahigh pressure conditions above 40 GPa have been reported. However, it is difficult to obtain high-quality S(Q) data at a wide range of Q due to weak scattering from very small amorphous samples in diamond anvil cells. The small sample issue in the ultrahigh-pressure experiment may be solved by an opposed type double-stage large-volume cell. The opposed type double-stage large volume cell uses diamond anvils as the second stage anvil in the first stage PE cell, which opened a new way to conduct ultrahigh-pressure experiments using large volume samples. For example, pressure generation of 58 GPa has been achieved with the large volume sample of 0.5 mm in diameter and 0.2 mm in height, which is more than 100 times larger than that of the conventional diamond anvil cell experiment. A combination of the opposed type double-stage large-volume cell technique with our developed high-pressure pair distribution function measurement would enable us to measure high-quality S(Q) data at a wide range of Q under ultrahigh-pressure conditions. In addition, the use of large volume multi-anvil press may be another possibility to conduct S(Q) measurement under higher pressure and high-temperature conditions, as the PSICHE beamline has utilized multi-anvil press high-pressure experiment for the S(Q) measurement of liquid.

In conclusion, the high-pressure pair distribution function measurement by using a 100 keV pink beam enabled us to measure the S(Q) of liquids and glasses at a wide range of Q to 20–29 Å$^{-1}$ under in situ high-pressure and high-temperature conditions. The high-quality S(Q) data obtained in the high-pressure experiment opens the way to investigate detailed structural features of liquids and amorphous materials, as well as ambient pressure study. For example, the combination of the S(Q) data of SiO$_2$ glass at the Q range up to 19–20 Å$^{-1}$ measured under high-pressure conditions with the molecular dynamics simulation and reverse Monte Carlo modeling enabled us to investigate detailed structural behaviors of SiO$_2$ glass, such as the translational order of the silicon’s second shell, void radius formed from silicon atoms, ring size, and cavity volume under in situ high-pressure conditions. Thus, the high-pressure pair distribution function measurement using a 100 keV pink beam opens a new way to investigate the structural behavior of liquids and amorphous materials under in situ high-pressure and high-temperature conditions and provides wide-ranging applications in scientific fields as well as engineering and industry.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yoshihiko Kono: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Funding acquisition (lead); Methodology (lead); Writing – original draft (lead). Koji Obara: Data curation (equal); Methodology (equal); Software (lead); Writing – review & editing (equal). Nozomi M. Kondo: Data curation (equal); Resources (equal). Yuji Higo: Methodology (equal); Software (equal). Sho

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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