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Synchrotron radiation studies on pressure-induced structural changes in liquids and glasses

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Abstract

Combination of synchrotron radiation sources and large-volume presses enables us to carry out *in situ* observations of structural change in liquids and glasses at high pressures up to several gigaPascals and high temperatures above 1200 °C. In this report, we present two examples: liquid Sn and SiO₂ glass. X-ray diffraction measurements were carried out on liquid Sn at 2.0 and 5.3 GPa. With increasing pressure, a shoulder of the first peak in the structure factor became less prominent and the ratio of the position of the second peak to that of the first peak decreased. These changes are attributed to a diminishing of the covalent structures remaining in the liquid state. Data on the temperature dependence of the x-ray diffraction by SiO₂ glass were measured up to 560 °C at 17 GPa. The sample crystallized to stishovite above 560 °C. While no drastic change was observed in the short-range order, a shift of the position of the first sharp diffraction peak to higher wavenumber and a sharpening of it were observed with increasing temperature. The shift and the sharpening suggest some relaxation in the intermediate-range order.

1. Introduction

Although the structure of crystalline solids under high pressure has been extensively studied for decades, less attention has been paid to pressure-induced structural changes in liquids and glasses [1–3]. Studies on crystalline solids have shown that many materials that have open structure evolve toward dense-packed structure by pressure-induced structural transitions. These transitions are often accompanied by a change of electronic structure such as metallization. Since the local atomic arrangement in the liquid state resembles that in the crystalline counterpart to some degree, it is natural to think that the structure of liquid also changes under high pressure in a similar manner. Molecular or network liquid may eventually transform to monatomic metallic liquid under strong compression. One can expect such a structural change in the glassy state if the material does not crystallize under high pressure. However, experimental and theoretical studies on pressure-induced structural

changes in liquids and glasses are limited and their details are still unclear. Among other features, the sharpness of the structural changes is under discussion. The discovery of a first-order transition between low-density and high-density ices was the first indication of a sharp transition in disordered materials [3, 4]. Temperature must be an important factor for structural change of glasses; there is a prediction that a pressure-induced continuous structural change of SiO₂ glass observed at room temperature becomes sharp at high temperature [5]. In the liquid state of the pure substance, it may be hard to imagine several distinct structures existing, because the rapid thermal motion of atoms probably smears or averages these structures. Thus the structural changes in liquids are supposed to be smooth and continuous. However, we have observed a sharp structural change in liquid phosphorus [6]. Experimental results supported the view that it is a first-order liquid–liquid transition [6, 7].

To study structural changes of liquids and glasses experimentally, *in situ* methods are essential. In the late 1980s, Tsuji *et al* [8] developed an energy-dispersive x-ray diffraction technique to study the structure of liquid under high-pressure and high-temperature conditions using a synchrotron radiation source and a large-volume press. Since then, the structures of several elements have been studied under pressure [9, 10]. We have also applied other methods to high-pressure studies: measurements of x-ray absorption fine structure [11], angle-dispersive x-ray diffraction [12] and density by means of x-ray absorption [13]. In addition, a new double-stage multi-anvil press in the SPring-8 synchrotron radiation facility extended the pressure range to over 20 GPa [14].

In this paper, we present two recently proposed examples: liquid Sn and SiO₂ glass. It is well known that crystalline Sn has a diamond structure at low temperature and a β -Sn structure at high temperature. It melts at 232 °C. The liquid is metallic but its structure is not fully described by a model of dense random packing of hard spheres [15]. There is a shoulder in the right-hand side of the first peak in the structure factor and the ratio of the position of the second peak to that of the first peak is larger than the normal value. These deviations are attributed to covalent structures that remain in the liquid state. Larger deviations are observed in the lighter group 14 elements: liquid Si and liquid Ge [15]. Because covalent bonds usually become unfavourable under compression, it is expected that these features will disappear under pressure. To investigate the change, we carried out x-ray diffraction experiments at 2.0 and 5.3 GPa.

SiO₂ forms a typical network glass. It consists of SiO₄ tetrahedral units at atmospheric pressure. A previous *in situ* x-ray diffraction study on SiO₂ provided evidence for pressure-induced changes in the medium-range order [16]. A local structural change from tetrahedral to octahedral coordination followed under strong compression to 42 GPa [16]. Although the observed changes in the medium-range order at room temperature are gradual and continuous, a molecular dynamics simulation study on SiO₂ glass has proposed the possibility of a sharp amorphous–amorphous transition at high temperature [5]. A recent report of a sharp change of volume at 3.6 GPa and 680 °C may be evidence for this transition [17]. Another study on the pressure and temperature dependence of the volume of SiO₂ glass has shown complexity of the structural change [18]. To elucidate the temperature effect on the structural change of SiO₂ glass under high pressure, we have started *in situ* x-ray diffraction experiments over wide pressure and temperature ranges. Here, we present a result at 17 GPa, the highest pressure in the present study.

2. Experiment

X-ray diffraction experiments on liquid Sn were carried out using a cubic-type multi-anvil apparatus (SMAP180) installed on JAERI Materials Science Beamline I (BL14B1) at the

SPring-8, Japan [14]. Tungsten carbide anvils with a square flat of $6 \times 6 \text{ mm}^2$ were used. A pressure-transmitting medium was made of a mixture of boron and epoxy resin. Sn powder was put into a sample capsule made of NaCl with an inner diameter of 1 mm. A tube-type graphite heater inside the sample assembly was used to raise temperature. The temperature was monitored by a thermocouple. The pressure was determined using a NaCl internal pressure marker [19].

An experiment on SiO_2 glass was performed using a double-stage large-volume press (SPEED1500) installed at BL04B1 beamline at Spring-8 [13]. Anvils with a truncation size of 5 mm were used. A rod of SiO_2 glass, 1.5 mm in diameter and 1.0 mm in length, was used as a sample. It was inserted in a tube-type graphite heater. The temperature was monitored by a thermocouple and the pressure was determined using a NaCl internal pressure marker. The sample and the NaCl pressure marker were separated by a disc of boron nitride. Data on the temperature dependence of the diffraction were obtained up to 560°C at 17 GPa. The sample crystallized to stishovite above 560°C .

In both experiments, x-ray diffraction profiles were measured by an energy-dispersive method using a white synchrotron radiation beam from a bending magnet. To cover a wide scattering vector range, diffraction data were collected at several diffraction angles. The structure factor, $S(Q)$, was obtained using a program developed by Funakoshi [20] based on an empirical method proposed by Tsuji [7].

3. Results and discussion

3.1. Liquid Sn

Figure 1 shows structure factors, $S(Q)$, of liquid Sn at atmospheric pressure, 2.0 and 5.3 GPa. The curve at atmospheric pressure was drawn using values reported by Waseda [15]. The temperatures, 310°C at 2.0 GPa and 500°C at 5.3 GPa, are near the melting temperature at each pressure. There is a shoulder on the right-hand side of the first peak. Since no such shoulder is observed for simple metallic liquids, it is attributed to residual covalent structure in the liquid state. In fact, a reverse Monte Carlo modelling [21] and an EXAFS study [22] have extracted a signature of local tetrahedral order for liquid Sn. It seems that the shoulder at 5.3 GPa is smaller than that at 2.0 GPa. To evaluate its size, a reference curve is constructed using a hard-sphere model [15]. The parameters are the hard-core diameter σ and packing fraction η . The dashed curves in the figure indicate the results of the curve fit. The hard-core diameters are 3.006, 2.960 and 2.888 and the packing fractions are 0.428, 0.450 and 0.436 for 1 bar, 2.0 and 5.3 GPa, respectively. While the fit does not reproduce the shoulder at all well, it reproduces the main structure moderately well. The deviation between the fit and the main structure may be attributed to the residual covalent structures. The densities calculated from the results of the fit are smaller than those estimated from the equations of states for crystalline solids [23] by about 10%. This discrepancy is an indication that the fit does not fully describe the structure of liquid Sn. The area between the solid and dashed curves around the shoulder decreases by 15% from 2.0 to 5.3 GPa. The decrease indicates that the covalent structures in the liquid Sn gradually vanish with increasing pressure. A recent molecular dynamics simulation study predicts complete disappearance of the shoulder at 20 GPa [24].

Figure 2 shows the ratio, Q_2/Q_1 , of the peak position of the second peak, Q_2 , to that of the first peak, Q_1 . Due to the difficulty in determination of the peak positions, the errors are large. For most simple metallic liquids, this value is about 1.86. For liquid Sn, this value is 1.96 at atmospheric pressure [15]. The values at high pressures are smaller than the value at atmospheric pressure. It approaches the value for the simple metallic liquid under pressure.

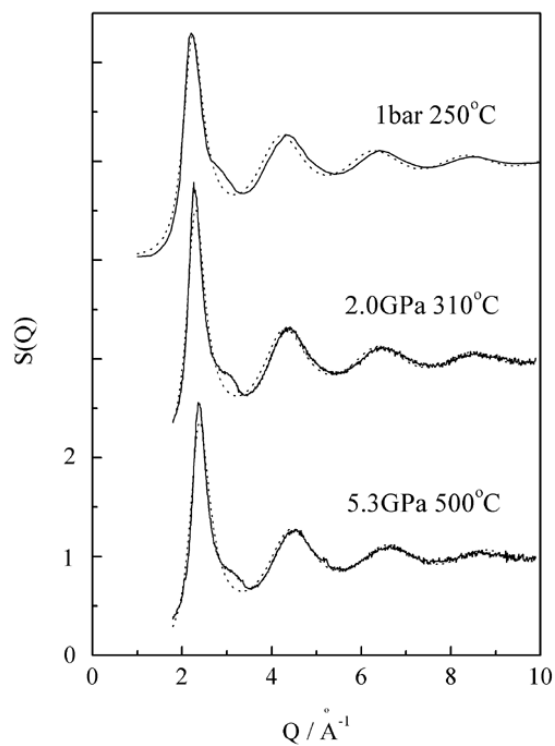


Figure 1. The structure factor, $S(Q)$, of liquid Sn under pressure. The data at 1 bar are reported in [15]. The dashed curves indicate the results of fits using a hard-sphere model.

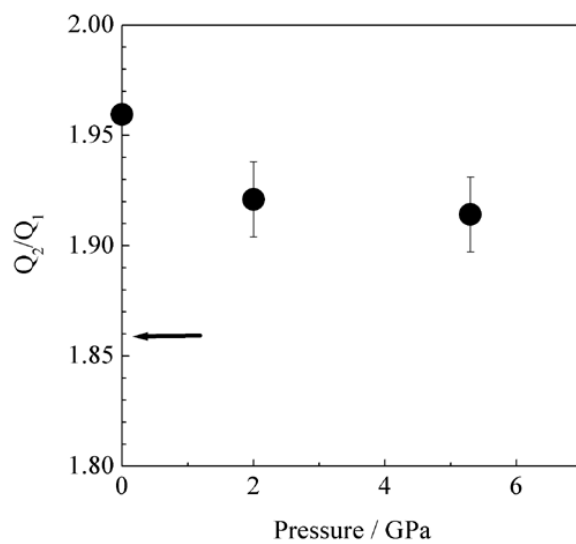


Figure 2. The pressure dependence of the ratio Q_2/Q_1 of the peak position of the second peak Q_2 , to that of the first peak Q_1 in the structure factor of liquid Sn. The arrow indicates the value for simple metallic liquids.

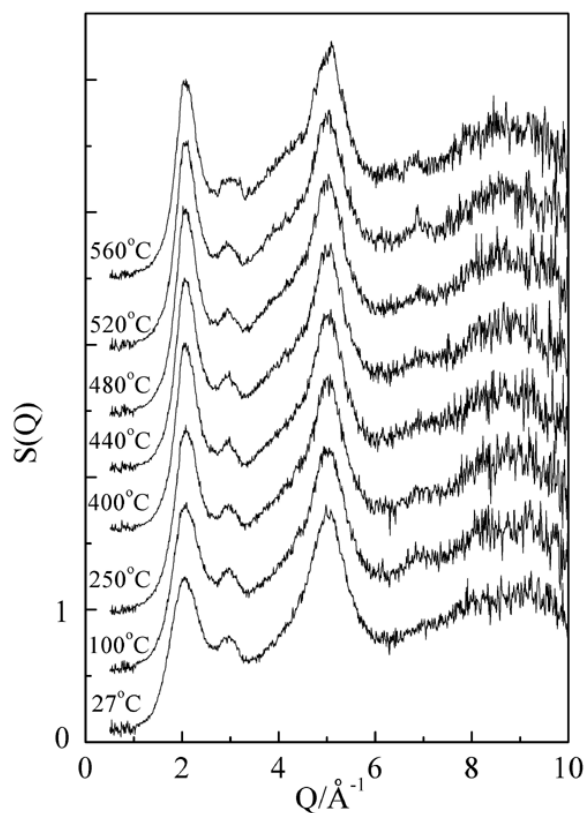


Figure 3. The structure factor, $S(Q)$, for SiO_2 glass at 17 GPa and various temperatures.

This decrease in Q_2/Q_1 also supports the view that the covalent structures gradually diminish with increasing pressure.

3.2. SiO_2 glass

Figure 3 shows the temperature dependence of the structure factor, $S(Q)$, of SiO_2 glass at 17 GPa. Above 560°C , the sample crystallized to stishovite in which Si atoms have octahedral coordination. The first sharp diffraction peak (FSDP) is seen at 2.03 \AA^{-1} at room temperature. The position of the FSDP at atmospheric pressure is 1.55 \AA^{-1} , so it shifts to higher Q by 0.5 \AA^{-1} . There is a small peak at 2.9 \AA^{-1} . The peak is not observed at atmospheric pressure. The shift of the FSDP and the appearance of the new small peak are consistent with the previous high-pressure x-ray diffraction data measured at 8 and 28 GPa at room temperature [16]. The new peak at 2.9 \AA^{-1} became bigger with increasing pressure and it was attributed to a new structure that may be related to the formation of octahedral coordination [16]. With increasing temperature, the position of the FSDP shifts to the larger- Q side and it becomes sharp, while no drastic change occurs in other regions. The small peak at 2.9 \AA^{-1} does not change with temperature. Details of the change in the FSDP will be mentioned later.

Figure 4 shows the temperature dependence of the pair correlation function, $G(r)$, for SiO_2 glass, obtained from a Fourier transform of $S(Q)$. No drastic change is observed in $G(r)$ with increasing temperature. The first peak corresponds to the Si–O correlation. The position of

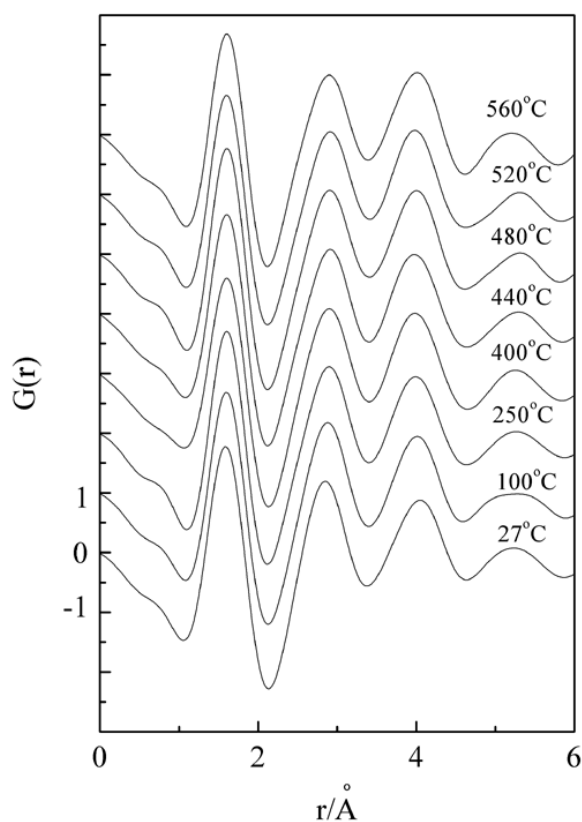


Figure 4. The temperature dependence of the pair correlation function, $G(r)$, for SiO_2 glass at 17 GPa.

the first peak is 1.6 Å. It is close to the Si–O bond length in SiO_2 glass at atmospheric pressure, 1.59 Å. If the Si atoms had octahedral coordination, the nearest-neighbour distance would be much longer. The Si–O distance for octahedral coordination at this pressure is estimated to be 1.73 Å [16]. Therefore we conclude that tetrahedral coordination is largely preserved even at 17 GPa and 560 °C, where stishovite is the most stable phase.

To see the temperature dependence of the FSDP in detail, we plot $S(Q)$ between 1.0 and 3.0 Å⁻¹ in figure 5. The arrows indicate directions of the change on heating. The height of the FSDP increased with increasing temperature up to 400 °C. At the same time, the width of the peak, ΔQ_{FSDP} , became narrower. The position of the FSDP shifted to higher Q by about 0.03 Å⁻¹ between room temperature and 250 °C. Above this temperature the position was almost the same. Since the FSDP is correlated with the medium-range order, there must be a change in medium-range order with increasing temperature. The increase of the height may be related to the higher degree of medium-range ordering. The sharpening of the FSDP suggests that the correlation length, $\xi = 2\pi/\Delta Q_{\text{FSDP}}$, becomes longer. Therefore these changes of the FSDP suggest a structural change toward more ordered arrangements on the medium-range scale. Because no change was observed in the temperature dependence of the x-ray diffraction intensity for silica glass at atmospheric pressure [25], this behaviour is unique. The better hydrostatic conditions in the sample assembly at high pressure may be responsible for a part of this change. It is also suggested that the thermal motions of atoms at high temperature relax frustrations induced by compression at room temperature.

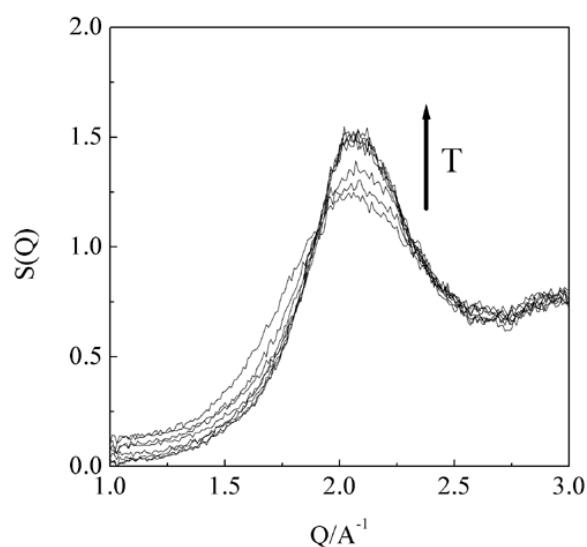


Figure 5. The temperature dependence of the FSDP of SiO₂ glass at 17 GPa. The arrows indicate the direction of the change with increasing temperature.

The shift of the peak toward higher Q suggests an increase of density, because previous diffraction studies indicated that the shift of the FSDP to higher Q is associated with densification of the glass [16, 26]. This behaviour is contrary to the normal thermal expansion of materials. However, the increase of the density at high temperature is also observed at 5.7 and 6.7 GPa [18]. The shift may be another indication of a relaxation in medium-range order. If we apply a linear relation between the density of the densified glass and the position of the FSDP reported in [25], the shift of the FSDP of 0.03 \AA^{-1} corresponds to a density increase of 0.05 g cm^{-3} . Of course, there is no additional experimental evidence of the increase of the density at this pressure available so far. Direct measurement of density is needed to confirm this hypothesis.

4. Conclusions

X-ray diffraction measurements were carried out on liquid Sn at 2.0 and 5.3 GPa. With increasing pressure, the shoulder of the first peak in the structure factor became less prominent and the ratio of the position of the second peak to that of the first peak decreased. These changes are attributed to the covalent structures that remain in the liquid state diminishing. Data on the temperature dependence of the x-ray diffraction by SiO₂ glass were measured up to 560 °C at 17 GPa. The sample crystallized to stishovite above 560 °C. While no drastic change was observed in the tetrahedral coordination, a shift of the position of the FSDP to higher wavenumber and a sharpening of it were observed with increasing temperature. The shift and the sharpening suggest some relaxation in the intermediate-range order.

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