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Modification of medium-range order in silica glass by ball-milling: real- and reciprocal-space structural correlations for the first sharp diffraction peak

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Abstract

We have carried out high-energy x-ray diffraction measurements on mechanically milled silica glass. It has been found that the first sharp diffraction peak (FSDP) in the structure factor $S(Q)$ of silica glass appreciably decreases in intensity as a result of mechanical milling, whereas the observed features of the other peaks in $S(Q)$ almost remain unchanged. The corresponding real-space correlation function of the milled samples shows a marked decrease in intensity at $r \sim 5$ Å. This gives an experimental manifestation that the dominant real-space structural correlation pertaining to the FSDP occurs at $r \sim 5$ Å.

1. Introduction

In the network of silica glass, the SiO_4 structural units are believed to be connected together randomly, leading to the absence of periodicity of the structure on the macroscopic length scale. It is commonly accepted, however, that because of rather a regular configuration of the constituent SiO_4 units, the silica glass network cannot completely be random but shows an 'order' depending on the length scale of distance [1]. Traditionally, the structural order in silica glass has been divided into several scales of distances, for example, short-, medium-(intermediate-), and long-range orders [2, 3]. Of particular interest is the medium-range order (MRO) [4, 5], which involves the specification of relative atomic positions over several nearest-neighbor distances. Thus, in silica glass, MRO is regarded as the next highest level of structural organization or non-random structural correlations beyond that of the regular SiO_4 or the short-range order (SRO) [3, 6].

A possible experimental manifestation of MRO in glasses is the so-called 'first sharp diffraction peak' (FSDP), which is a characteristic feature of the measured structure factor $S(Q)$ observed in x-ray and neutron scattering experiments. Although several interpretations have been proposed for the origin or the real-space structural correlations of FSDP [6–9], the subject still continues to be controversial [10]. One method for gaining insight into the real-space information related to the FSDP is the structure modification of a glassy material of

interest. The intensity, position, and width of the FSDP in reciprocal space are expected to be modified by the structural rearrangements in real space, and the comparison between the observed features in reciprocal space and those in real space may clarify the structural origin of the FSDP. As for silica glass, high-pressure techniques have previously been employed to induce structure modification related to the FSDP [11–13]. According to *in situ* high-pressure x-ray diffraction measurements on silica glass [11–13], the FSDP ($Q \sim 1.52$ Å^{-1}) shifts in position to higher values of Q as a function of increasing pressure from ∼2 GPa, whereas the other peaks in $S(Q)$ shift to lower values of Q. In addition, the intensity of FSDP shows a gradual decrease with increasing pressure, accompanied by the emergence of a new peak at ∼3.2 Å^{-1} at pressures in excess of ∼10 GPa [11, 13]. It is also interesting to note that silica glass exhibits an irreversible densification after being quenched from a pressure above ∼10 GPa [14]. The pressure-quenched samples also show changes in the observed peaks in $S(Q)$ [12], including a shift in the FSDP position to a higher-Q value, reduction in its intensity, and increase in its width, such as those observed under high pressures. The above experimental results demonstrate that the characteristics of FSDP, e.g. the position, intensity and width, can indeed be changed by applying pressure, but this change also accompanies the modification and creation of the other peaks in $S(Q)$, as mentioned above. In other words, the structural changes induced by high pressure may not be confined to the length scale associated with the FSDP but may extend over a whole range of the glass structure, transforming to a pressure-densified amorphous phase often called a high-pressure amorphous polymorph [15]. Thus, the observed structural changes induced by high pressure are too intense and complicated to give a straightforward interpretation for the origin of the FSDP.

In this work, we employ an alternative method, namely a mechanical milling procedure, to induce structure modification of silica glass. Recently, mechanical milling and alloying have been widely used to prepare a large variety of nonequilibrium phases, including supersaturated solid solutions, metastable crystalline phases, and quasi-crystalline phases [16, 17]. It has also been found that mechanical milling can be used to obtain crystalline-to-amorphous and/or crystalline-to-nanocrystalline transformations for some elements and compounds [18–21]. Here we show that mechanical milling is an efficient technique for inducing the modification of the silica glass network that is relevant only to the FSDP. The milled samples show discernible structural changes especially on the medium-range length scale, revealing the real-space structural correlations pertaining to the FSDP.

2. Experimental procedures

Commercial fused silica purchased from Toshiba Ceramics was used as a starting material. Bulk silica glass was first crushed into coarse powders. The powders were then put into a ZrO_2 vial with a set of ZrO_2 balls under a dry Ar atmosphere to carry out mechanical ball milling. Ball milling was performed at room temperature using a planetary ball mill (Fritsch, P-7). We employed two values of a ball-to-sample weight ratio, 5:1 and 40:1, and the rotation rate of the vial was varied from 400 to 800 rpm. The apparent bulk density of the balled-milled samples are basically similar to that of normal silica glass (2.2 g cm^{-3}). Some of the ball-milled samples were post-annealed at 800–1000 °C in air for 1 h to partially relax the possible strained structure induced by the milling process.

The high-energy x-ray diffraction measurements of the ball-milled powders were performed in transmission geometry using the bending magnet beamline BL04B2 [22] at SPring-8 in Hyogo, Japan, equipped with a horizontal two-axis diffractometer [23]. Since the energy of the incident photons supplied by synchrotron radiation used in the experiments is quite high (61.6 keV), the x-ray diffraction data can be measured up to $Q_{max} = 25$ Å^{-1}, which

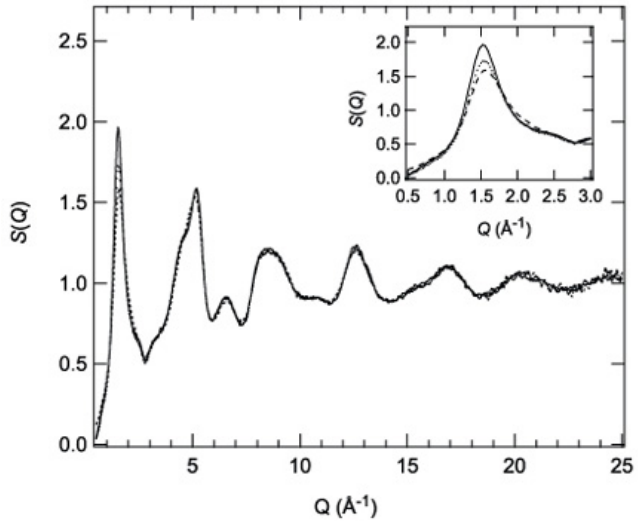

Figure 1. Examples of x-ray structure factors $S(Q)$ of silica glass before (solid line) and after (broken line) mechanical milling. The milling was performed for 3 h using a zirconia vial and balls under a dry argon atmosphere with a ball-to-sample weight ratio of 40:1. The rotation rate of the vial was 800 rpm. The dotted line shows $S(Q)$ of the above milled sample after annealing at 800 °C for 1 h. The inset shows $S(Q)$ on an expanded scale in the range 0.5–3 Å^{-1}.

allows us to obtain the real-space correlation functions with a sufficiently high resolution [24], as will be shown in the following.

3. Results

We found that the present milling procedure can successfully change the x-ray diffraction pattern of the silica glass. The observed changes in the x-ray diffraction data depend strongly on the milling conditions, e.g. the milling time, the ball-to-sample ratio, and the rotational rate of the vial. However, if we carefully choose the milling and the post-annealing conditions, we can obtain a series of $S(Q)$ data in which the intensity of the FSDP systematically varies. We found that the observed changes are quite reproducible and statistically significant.

Figure 1 shows an example of the total Faber–Ziman structure factors [25] $S(Q)$, for milled samples treated at appropriate milling and post-annealing conditions. We found the following tendency for the characteristics of the $S(Q)$ functions of the milled samples: (1) the FSDP at $\sim$1.52 Å^{-1} is decreased in intensity as a result of mechanical milling, although its position is almost unchanged or only slightly changed; (2) the decreased FSDP intensity induced by mechanical milling is partially or completely recovered, depending on the post-annealing condition—this indicates that the changes in $S(Q)$ induced by ball-milling did not result from the incorporation of grinding materials such as ZrO_2; (3) the intensity and position of the other peaks in $S(Q)$ are scarcely affected by the present mechanical milling procedure.

4. Discussion

To get information on the milled samples in real space, we next calculate the total correlation functions, $T(r)$, from the weighted interference functions $Q[S(Q) - 1]$ by Fourier

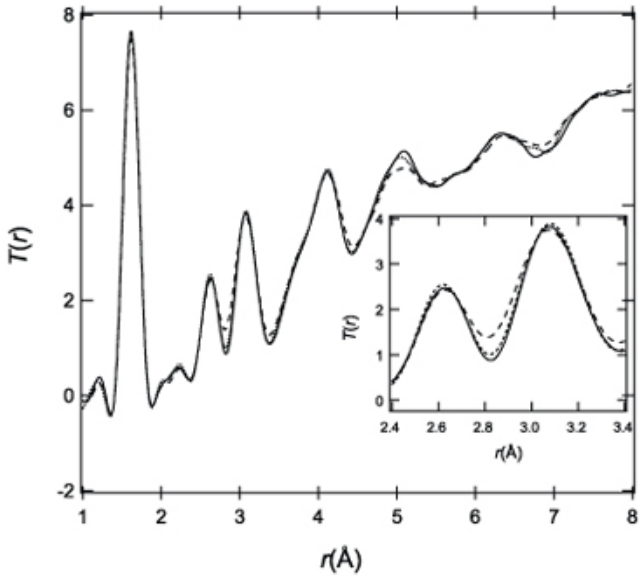

Figure 2. Examples of total correlation functions $T(r)$ of silica glass before (solid line) and after (broken line) mechanical milling. The milling condition is the same as for figure 1. The dotted line shows $T(r)$ of the above milled sample after annealing at 800 °C for 1 h. The inset shows $T(r)$ on an expanded scale in the range 2.4–3.4 Å.

transformation up to $Q_{\max} = 25$ Å^{-1}:

$$T(r) = 4\pi\rho r + \frac{2}{\pi}\int_{Q_{\min}}^{Q_{\max}} M(Q)\,Q[S(Q) - 1]\sin(Qr)\,\mathrm{d}Q, \tag{1}$$

where ρ is the total number density and $M(Q)$ is a Lorch modification function [26] to reduce termination effects arising from the finite upper limit of Q. Figure 2 shows a series of $T(r)$ obtained from the Fourier transformation of the corresponding $S(Q)$ shown in figure 1.

It has previously been demonstrated that $T(r)$ for silica glass is characterized by first-neighbor Si–O, O–O, and Si–Si distances located at 1.61, 2.62 and 3.08 Å, respectively [3, 24]. We found that the positions and intensities of the first-neighbor Si–O, O–O and Si–Si peaks are virtually unaffected by mechanical milling, although the width of the first-neighbor O–O and Si–Si peaks tends to become broader slightly as a result of milling (see the inset of figure 2). The measured $T(r)$ is further characterized by several broad peaks in the longer distance region, which are attributed to second- and/or third-neighbor coordination shells in the silica glass network. For example, the peak at 4.1 Å is attributed to the second-neighbor Si–O shell, and the peak at 5.1 Å to the second-neighbor Si–Si and O–O shells [9, 24]. We see from figure 2 that the intensity of the peak at 5.1 Å is substantially lowered by mechanical milling, but such a drastic change in intensity cannot be seen in any of the other peaks in $T(r)$ in the whole distance region. The comparison between $S(Q)$ and $T(r)$ hence implies that the second-neighbor Si–Si and O–O correlations located at ∼5 Å is mostly responsible for the dominant real-space structural correlations related to the FSDP in silica glass. Such a real/reciprocal space relationship can further be confirmed from an almost linear correlation between the intensity of the 5.1 Å peak and that of the FSDP for a variety of milled samples (see figure 3). This result is in agreement with our recent wavelet analysis on the structure factor of silica glass, demonstrating that the FSDP in reciprocal space is highly correlated to the distance region at ∼5 Å in real space [27].

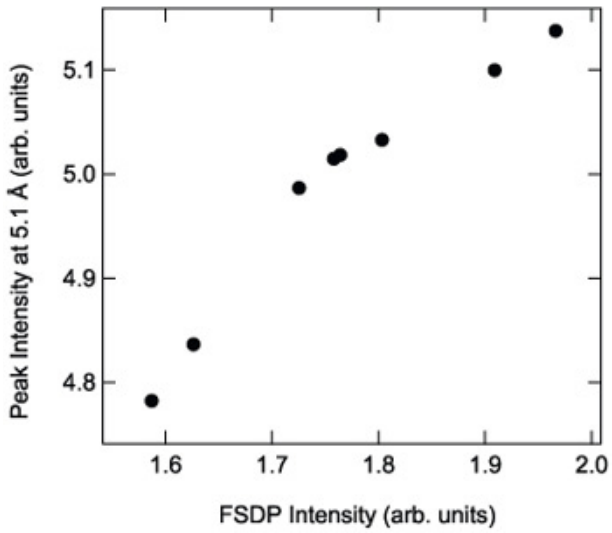

Figure 3. Correlation between the intensity of the peak at 5.1 Å in $T(r)$ and the intensity of the FSDP in $S(Q)$. The data are collected from a variety of milled and post-annealed samples under different conditions.

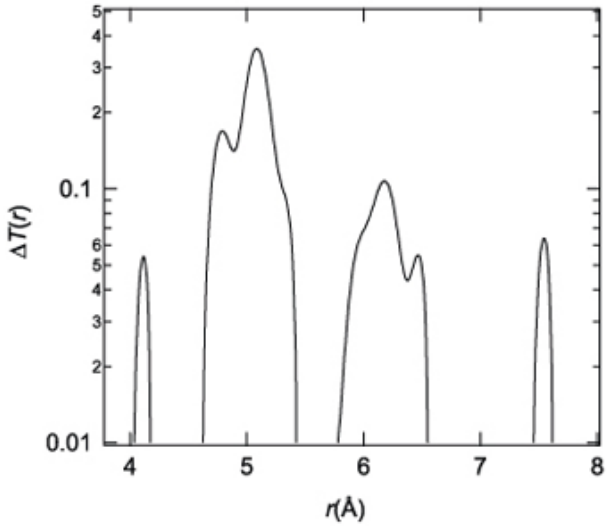

Figure 4. A difference plot $\Delta T(r)$ between $T(r)$s of silica glass before and after mechanical milling. The milling was performed for 3 h using a zirconia vial and balls under a dry argon atmosphere with a ball-to-sample weight ratio of 40:1.

To highlight further the change in real space after mechanical milling, we take the difference between $T(r)$s of the milled and non-milled samples (see figure 4). We see from a difference plot $\Delta T(r)$ shown in figure 4 that the peak at ∼5 Å is the most prominent one, confirming the above-mentioned argument that this peak makes a dominant contribution to the FSDP in silica glass. We should note, however, that there exist additional peaks in the distance region from ∼4 to ∼8 Å in a periodic manner with uneven spacing; it appears that the spacing

between adjacent peaks increases with increasing r. Although the physical meaning of the uneven spacing is not yet known, the $\Delta T(r)$ plot suggests that the distance region in the range ∼4 to ∼8 Å contributes to the occurrence of the FSDP. It has been proposed from a previous molecular-dynamics study on silica glass that the peculiar features of the FSDP is closely associated with the real-space correlations in the range ∼4 to ∼8 Å [9]. Thus, the $\Delta T(r)$ plot shown in figure 4 is consistent with the previous estimation concerning the length scale associated with the FSDP. We should note again, however, that the most underlying distance region pertaining to the FSDP would be ∼5 Å, as illustrated in figure 4.

We next turn to the structural modification of the respective SiO_4 units, or the short-range order (SRO), after the milling procedure. As noted earlier, the first-neighbor O–O and Si–Si coordination shells at ∼2.6 and ∼3.1 Å, respectively, are slightly broadened by mechanical milling, whereas the first-neighbor Si–O (∼1.6 Å) shell is hardly affected. This suggests that the present milling process leads to the deformation of the basic SiO_4 structural units, as manifested by the broadening of the first-neighbor O–O and Si–Si coordination shells, without changing the Si–O bond distances. Such a deformation of the constituent SiO_4 units is likely to be related to the modification of the second-neighbor O–O and Si–Si correlations, diminishing the MRO and the corresponding FSDP intensity. These results allow us to suggest that the formation and deformation of the SRO and MRO are highly intercorrelated in the network structure of silica glass, as has been proposed previously [3, 6, 8]. Stated in another way, the structural rigidity of the constituent tetrahedral SiO_4 unit in silica glass will impose further constraints on the three-dimensional connectivity of the network, creating a secondary ordered region, or the MRO, associated mainly with the second-neighbor O–O and Si–Si correlations at ∼5 Å. In the present milled samples, however, the SRO of the SiO_4 unit is somewhat deteriorated compared with that of normal silica glass. This will result in the concomitant deterioration of the structural correlations on the medium-range length scale, as manifested by a decrease in the peak intensity at ∼5 Å in $T(r)$ and that at ∼1.52 $Å^{-1}$ (FSDP) in $S(Q)$.

Finally, we would like to comment why the second-neighbor O–O and Si–Si correlations at ∼5 Å induce a sharp feature in $S(Q)$ such as the FSDP. In our recent paper [27], we propose from the results of a continuous wavelet transform analysis and molecular-dynamics simulations that there exist a couple of local 'pseudo-Bragg' planes in the region of $r \sim 5$ Å in the silica glass network. The perpendicular distance between the parallel planes, or 'periodicity', is rather well defined even in the glassy SiO_2 network. Accordingly, these planes will result in the constructive diffraction leading to the FSDP in $S(Q)$. We should note, however, that our model for the origin of the FSDP is basically different from a previous quasi-lattice plane model [7], since our model does not necessarily require a crystalline counterpart to account for the FSDP. We do not propose that crystalline-like layered structures exist in the glassy system but that the planes of high atomic density related to the r-space ordering at ∼5 Å result from collective structural correlations among second- and third-neighbour SiO_4 structural units in the apparently 'random' SiO_2 network.

5. Conclusions

We have shown that the mechanical milling is an effective method for modifying the SRO and MRO related to the FSDP in silica glass. The method, combined with the high-energy x-ray diffraction technique, allows us to obtain the experimental evidence that the dominant distance region pertinent to the FSDP in silica glass is ∼5 Å, although smaller and longer distance correlations cannot be neglected to fully characterize the observed feature of the FSDP. Our results are consistent with a general belief that the structural stability and rigidity of SiO_4 units

account for the formation of the MRO in real space and hence for the occurrence of the FSDP in reciprocal space.

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