Relationship between the first sharp diffraction peak and physical properties of silicon dioxide (SiO$_2$) glasses possessing different fictive temperatures

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Investigating the correlation between glass structure and physical properties is important for development of novel functional materials. It is well known that the physical and structural parameters of glass depend on the preparation condition. Fictive temperature, $T_f$, is one of the standards of glass obtained from the super-cooled liquid state. Since the $T_f$ value is defined using structural relaxation of overtone mode of Si–O–Si vibration, correlation of the $T_f$ with the structural ordering at longer range is worthy for exploring. Here, we examine structural change of SiO$_2$ glass possessing different $T_f$ values probed by the first sharp diffraction peak (FSDP) observed in X-ray diffraction data. By annealing of SiO$_2$ glass, i.e. decreasing of $T_f$, a sharpening of the FSDP is observed. Both structural periodicity and the correlation length of the FSDP decrease with increasing the $T_f$. It is suggested that increase of smaller structural units contributing to the FSDP is the origin of the increase of elastic modulus of SiO$_2$ glasses.

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1. Introduction

Oxide glass is a solidified supercooled liquid; thus, its structure and physical properties depend on the preparation process used. For example, the valence and local coordination state of the constituent cations and homogeneity of the glass melt are affected by the preparation process irrespective of whether the nominal chemical composition is fixed; therefore, along with the general glass treatment conditions, the physical properties of oxide glass depend on the treatment of the supercooled liquid above the glass transition temperature, $T_g$. Examining every local coordination state in glass is challenging because of the long-range “nonperiodic network”, as it has a significantly wider structural diversity than that of the corresponding crystal. Achieving topological homogeneity in glass is important from both scientific and industrial viewpoints.

The short-range structural ordering of SiO$_2$ glass was conventionally analyzed using IR spectroscopy. To examine the relationship between the cooling rate and the frozen state of the supercooled liquid, the concept of fictive temperature, $T_f$, has been introduced. The value of $T_f$, which is determined by the vibrational mode of Si–O–Si, indicates the fictive frozen state of glass, along with its local structural rearrangement, both standard parameters for structural relaxation. The $T_f$ value is important not only from a scientific viewpoint but also from an industrial viewpoint. For example, Rayleigh scattering reduction by reduction of the $T_f$ values was attainted for silica-based optical fiber.

Accordingly, the probe for evaluating the intermediate-range structural ordering is the first sharp diffraction peak (FSDP), which is commonly observed in the total structure factor $S(Q)$ of neutron or X-ray diffraction data. In addition to conventional static measurements, FSDP has been used for evaluating dynamic structure changes during in situ observation at higher temperatures or higher pressures (since a main advantage of diffraction measurements is the wide temperature and pressure ranges for in situ observations. Skinner et al. reported high-energy XRD data of liquid SiO$_2$ at varying temperatures combined with the
They found that the width, height, and $Q$ values of the FSDP changed depending on temperature. Furthermore, accurately measuring the $T_f$ could elucidate the relationship between the diffraction data and the physical properties of glasses. To precisely evaluate the physical-structural relationship, precise diffraction data is preferable using well-analyzed solid-state samples. The physical parameters of glasses can be thoroughly evaluated, following the successful reverse Monte Carlo reconstruction of the three-dimensional glass structure, based on experimental datasets such as X-ray diffraction and nuclear magnetic resonance. In this study, we examined the correlation between the structural and physical parameters of SiO$_2$ glasses exhibiting different $T_f$ values. As a primary structural parameter, we focused on the FSDP of high-energy XRD data, which indicated the intermediate-range modification of the glass structure. In addition, we measured various physical properties to examine their $T_f$-dependence with numerical values.

2. Experimental

2.1 Preparation of SiO$_2$ glasses with different $T_f$ values

The sample SiO$_2$ glass was commercially supplied by Tosoh Quartz Corporation (Japan). The OH concentration was less than 50 ppm. The preparation steps of SiO$_2$ glass samples with different $T_f$ values were presented in a previous paper. Afterannealing, the surfaces of the samples were mechanically polished using a lapping machine (Doctor-lap ML-182) for optical measurements.

2.2 Analysis methods

The density, $ρ$, of the samples was estimated based on a previous report. The refractive index of the samples was measured using a prism coupler with 473, 633, and 1319 nm light sources (Metricon, N.J., U.S.A.). The error of the measurement was $1 \times 10^{-4}$. The refractive indices at 532 nm were calculated by determining the fitting parameters in Cauchy’s equation $n(λ) = A + B/(λ^2) + C/(λ^4)$ at the aforementioned wavelengths, where, $A$, $B$, and $C$ are the fitting parameters. $T_f$ was estimated by Si–O–Si vibrations to be approximately 2260 cm$^{-1}$, using the Model Spectrum 2000 (Perkin Elmer Inc.) with a resolution of 1 cm$^{-1}$.

The high-energy XRD experiment was performed at the BL04B2 beamline at the SPring-8 synchrotron radiation facility, using a two-axis diffractometer dedicated to the study of disordered materials. The energy of the incident X-rays was 61.43 keV. The raw data were corrected for polarization, absorption, and background, and the contribution of Compton scattering was subtracted using standard data analysis software.

Transmittance measurements at 298 K in the vacuum ultraviolet (VUV) to ultraviolet (UV) region of 140–300 nm, and from UV to visible light region of 200–500 nm were performed using a VUV spectrometer (VU-200; Jasco Inc.) and a conventional spectrophotometer (U-4100; Hitachi Ltd.).

Brillouin shifts $ν_B$ of the glasses were measured using a high-resolution modification of a Sandercock-type tandem Fabry–Perot system. The excitation laser was a frequency-doubled diode-pumped solid state Nd: yttrium-aluminum-garnet laser oscillating in single longitudinal mode at 532 nm (Oxxius SLIM-532 300 mW). The error was approximately 0.1 % (40 MHz). The longitudinal sound velocity $V_L$ was calculated using the relation $V_L = ν_B/2n_{532}$, where $ν_B$, $λ$, and $n_{532}$ are the Brillouin shift, the wavelength of the incident light (532 nm), and the refractive index at 532 nm, respectively. The $n_{532}$ values were calculated from the Cauchy relation with the refractive indices at 473, 633, and 1319 nm. The longitudinal elastic modulus $c_{11}$ values were calculated using the relation $c_{11} = ρV_L^2$.

3. Results and discussion

SiO$_2$ glasses exhibiting different $T_f$ values were successfully obtained. The decrease in $T_f$ confirmed the structural relaxation of SiO$_2$, caused by thermal annealing. According to previous reports, the $T_f$ values of SiO$_2$ glasses were calculated from the peak energy of the overtone Si–O–Si vibrations, $ν_B$, of the IR spectra. The relationship between $ν_B$ and $T_f$ are shown in Eq. (1):

\[
T_f = \frac{1039}{1039}
\]

Fig. 1. (a) Infrared spectra of SiO$_2$ glasses possessing different $T_f$ values. (b) Peak position $ν_B$ of these SiO$_2$ glasses as a function of $T_f$ values.
\[ n_T = \frac{2221.2 + 6.1086(10^4/T_f)}{0.097385(10^4/T_f)^2} \]  

**Figure 1(a)** shows the infrared spectra of SiO2 glasses with different \( T_f \) values (\( T_f = 1300, 1403, 1493, 1610, \) and 1743 K). The absorbance in the dashed square region corresponds to the peak energy of the overtone Si-O-Si vibrations.\(^5\) By using Eq. (1), the \( T_f \) values for each sample were calculated. **Figure 1(b)** presents \( n_T \) as a function of \( T_f \). Two glass samples possessed a lower \( T_f \) than the reported \( T_f \) of SiO2 (1463 K).\(^33\)

**Figure 2(a)** shows the optical absorption spectra of SiO2 glasses with different \( T_f \) values. All SiO2 glasses exhibited an optical absorption edge at approximately 150 nm, and a broad absorption band attributed to oxygen deficiency defects, such as oxygen deficiency centers (=Si–Si=) and divalent Si (=Si\(^2\)).\(^34,35\) Since the polishing degree of the surface affected the absorption, there was no linear dependence of the absorption coefficient on \( T_f \); however, a higher coefficient was observed in higher-\( T_f \) SiO2 glass. Accordingly, the refractive index is an optical parameter for transparent glasses. As mentioned in the experimental section, the refractive index at 532 nm, \( n_{532} \), was calculated using the Cauchy dispersion equation. **Figure 2(b)** shows the relationship between the \( T_f \) values of the SiO2 glass samples, and the refractive index at 532 nm. A linear correlation between them can be observed, with a fitting curve of \( d n_{532} / d T_f = 1.83 \times 10^{-3} \) /K. These refractive indices were used to calculate the longitudinal elastic modulus \( c_{11} \).

To examine the elastic modulus, we employed Brillouin scattering. The Brillouin peak could be fitted using the Voigt function, as shown in the inset of **Fig. 3(a)**. Because Brillouin peaks appeared at both the Stokes and anti-Stokes sides, the average value was used for calculations. **Figure 3(a)** shows the Brillouin shifts \( v_B \) of SiO2 glass samples against different \( T_f \) values. There is a linear relationship between the Brillouin shift and the \( T_f \) value, with \( d v_B / d T_f = 527 \pm 13 \) kHz/K. According to our previous paper, a linear relationship between \( \rho \) and \( T_f \) has been confirmed, with \( d \rho / d T_f = 9.4 \times 10^{-6} \) g cm\(^{-3}\) /K. Using \( v_B \), \( n_{532} \) [Fig. 2(b)], and \( \rho \), the longitudinal sound velocity \( V_L \) could be calculated. From the values of \( V_L \), the slope of \( d V_L / d T_f = 8.73 \times 10^{-2} \) m s\(^{-1}\) /K was obtained. The \( c_{11} \) values of the glass samples are plotted as a function of \( T_f \) in **Fig. 3(b)**. An apparent linearity can be observed between the \( c_{11} \) and \( T_f \) values, with \( d c_{11} / d T_f = 2.61 \times 10^{-3} \) GPa/K. The solid linearity suggested that the \( T_f \) of SiO2 glass samples could be evaluated from the \( c_{11} \) values.

Since \( S(Q) \) represents normalized diffraction data, the obtained data enabled us to perform quantitative analysis (such as peak height and width). Here, we focused on the FSDP, also known as \( Q_c \).\(^27\) in the X-ray total structure factor, \( S(Q) \), of different-\( T_f \) SiO2 glass samples.

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**Fig. 2.** Optical properties of SiO2 glasses possessing different \( T_f \) values. (a) Optical absorption spectra of SiO2 glasses with different \( T_f \) values. (b) Refractive index at 532 nm, \( n_{532} \), of these SiO2 glasses as a function of \( T_f \) values.

**Fig. 3.** (a) Brillouin shifts (Stokes side, anti-Stokes side, and the average value) of SiO2 glasses as a function of \( T_f \). Inset shows Brillouin scattering spectrum of SiO2 glass whose \( T_f \) is 1300 K along with the fitting curve using Lorentz function. (b) Values of \( c_{11} \) of SiO2 glasses as a function of \( T_f \).
The inset shows the FSDP height of the SiO2 glass. The peak shapes slightly changed depending on the SiO2 glasses appeared at approximately 1.5 \text{Å}^{-1}. Although the FSDP of glass samples in the FSDP region. The obtained height of FSDP is positively correlated with the Si-O correlation in the silica network. Fig. 4(a) shows the X-ray total structure factor, $S(Q)$, of SiO2 glass ($T_f = 1300$ K) as a reference. Figure 4(b) shows the $S(Q)$ of different-$T_f$ SiO2 glass samples in the FSDP region. Although the FSDP of SiO2 glasses appeared at approximately $Q = 1.5 \text{Å}^{-1}$, the peak shapes slightly changed depending on the $T_f$ value. The inset shows the FSDP height of the SiO2 glass samples as a function of $T_f$. The height of the FSDP linearly increased with decreasing $T_f$ values, indicating that structures correlated with the FSDP were preferentially ordered by thermal annealing. The obtained height values were larger compared with previous data measured using the aerodynamic levitation technique. Although the origin of the differences was not clear, we speculate that the nature of glass or an error in data normalization may have affected the calculations. The FSDP in $S(Q)$ can be fitted using the Lorentz function [Eq. (2)] for evaluating the $Q$ value of the FSDP center $Q_{\text{FSDP}}$ with full width of half maximum $\Delta Q_{\text{FSDP}}$:

$$S(Q) = A_0 \times \frac{0.5B}{(Q - Q_{\text{FSDP}})^2 + (0.5B)^2}$$

where, $A_0$, $B$, and $Q_{\text{FSDP}}$ are the fitting parameters. In this study, we fitted the $S(Q)$ at the $Q$ region of 0.90–1.65 \text{Å}^{-1}. Figure 4(c) shows the $Q_{\text{FSDP}}$ and the periodicity $2\pi/Q_{\text{FSDP}}$ as a function of $T_f$. Although the $Q$ shift was small, the $Q_{\text{FSDP}}$ increased proportionally with the $T_f$ value, whereas the $2\pi/Q_{\text{FSDP}}$ decreased monotonically as $T_f$ increased with the value of $d(2\pi/Q_{\text{FSDP}})/dT_f = -3.97 \times 10^{-5}$ \text{Å}/K. Simultaneously, the diversity of the FSDP-related structure was evaluated using the $\Delta Q_{\text{FSDP}}$ values. Figure 4(d) shows the values of $\Delta Q_{\text{FSDP}}$ and the correlation length, $2\pi/\Delta Q_{\text{FSDP}}$ as a function of $T_f$. The results indicate that the peak widths were sharpened, while the correlation length was increased by annealing. All changes depending on $T_f$ are consistent with the previous in situ high-energy XRD data of SiO2 glass. The value of $d(2\pi/\Delta Q_{\text{FSDP}})/dT_f$ was measured at $-3.63 \times 10^{-3}$ \text{Å}/K. The details are discussed later, based on the partial pair correlations.

Next, we focused on the $Q_3$ peak, which is mainly contributed by the Si–O correlation in X-ray diffraction data. Figure 5(a) shows the $S(Q)$ at the $Q_3$ region of different-$T_f$ SiO2 glass samples. The height of the peak observed at approximately $Q = 4.7$ \text{Å}^{-1} decreased, and the $Q_3$ peak position slightly shifted to the lower $Q$ side after annealing. Since $S(Q)$ is obtained by normalization, spectral changes could be obtained by subtracting the reference spectrum ($T_f = 1300$ K). Figure 5(b) shows the differential $S(Q)$ spectra, $\Delta S(Q)$, of SiO2 glass samples in the $Q_3$ region, which was obtained by subtracting the $S(Q)$ of
SiO$_2$ glasses exhibiting di
dependent partial structure factors, $f_i(Q)$, and the total structure factor spectrum, $S(Q)$, is obtained by MD-RMC modeling. In XRD measurements of disordered materials containing $n$ chemical species, the total structure factor $S(Q)$ can be expressed using the X-ray weighting factors, $W_{ij}(Q)$, and partial structure factors, $S_{ij}(Q)$, for $i$-$j$ correlations,

$$S(Q) = 1 + \sum_{i=1}^{n} \sum_{j=1}^{n} W_{ij}(Q) \cdot [S_{ij}(Q) - 1]$$

$$= 1 + \frac{1}{f_i(Q)} \sum_{j=1}^{n} \sum_{i=1}^{n} c_i c_j f_i(Q) f_j(Q) [S_{ij}(Q) - 1]$$

where $c_i$ is the atomic fraction of chemical species $i$, and $f_i(Q)$ is a $Q$-dependent atomic form factor in XRD.

$$f_i(Q) = \sum_{i=1}^{n} c_i f_i(Q)$$

The X-ray-weighted partial structure factors $W_{ij}(Q)$ and $S_{ij}(Q)$ of Si–Si, Si–O, and O–O are plotted in Fig. 5(b). The differential $S(Q)$ spectra changed systematically depending on the $T_T$ values. It is notable that the directions of change at the lower and higher $Q$ sides were opposite and that a positive correlation with the $T_T$ value was observed at the lower $Q$ side. Such broadening behavior of the $Q_3$ peak is also observed in SiO$_2$ liquid. Considering the partial $S_{ij}(Q)$ and the differential $S(Q)$, apart from the Si–O partial structure, the Si–Si correlation affected the shape of $Q_3$ as well, because X-rays are sensitive to heavier atoms. It should be noted that the Si–Si correlation in $S_{11}(Q)$ is entirely different from the oxygen deficiency vacancy =Si–Si= observed in the optical absorption spectra (Fig. 2). Considering the concentration of defects in glass, the Si–Si correlations were expected due to the decrease of oxygen after annealing. Particularly, the Si–O–Si related correlation was significantly affected by the annealing process.

We present the differential $S(Q)$ spectra over a wide $Q$ range in Fig. 6. The $W_{ij}(Q)$ and $S_{ij}(Q)$ of Si–Si, Si–O, and O–O are also shown to highlight their contribution. In the difference spectrum, increases were observed in both the higher and lower $Q$ sides of the FSDP ($Q_3$), whereas the FSDP center was uniformly decreasing. The intersections with zero were approximately $Q = 1.31$ Å$^{-1}$ (within the fitting region) and 1.74 Å$^{-1}$ (beyond the fitting region), for all cases. This trend indicates that both smaller and larger Si–O structures contributed to the broadening of the FSDP in high $T_T$ samples.

Based on the results, we evaluated the effect of $T_T$ that is, the annealing process, on the SiO$_2$ glass samples structure and properties. Table 1 shows the $T_T$ dependence on their physical and structural parameters. The relative difference was calculated from the values of SiO$_2$$_{2T_T=1300K}$
and SiO₂,Tₖ=1743K glass samples. Interestingly, both Vₛ and 2π/Q₁₅FSDP, which were directly related to Si–O partial structures, possessed comparable relative differences. On the other hand, the value of 2π/ΔQ₁₅FSDP exhibited a larger change compared with the rest, suggesting that the structural ordering of the FSDP was remarkably evolved by annealing. In the case of SiO₂ glass, six-membered rings consisting of six SiO₄ tetrahedra, which form the framework of a cristobalite crystal,37) comprised the main ring structure. Studies have reported rings consisting of three SiO₄ tetrahedra, that is, three-membered rings, existing in SiO₂ glass with higher Tₛ values.38) The smaller rings are estimated to induce higher refractive index, density, and elastic modulus, features that reflect the increasing of atom population per unit volume.40) Additionally, studies have reported, via positron annihilation spectroscopy,3) that larger voids are formed in SiO₂ glasses exhibiting higher Tₛ values. There is no apparent discrepancy between the structures proposed in Ref. 15), and the current differential S(Q) data, suggesting the formation of both smaller and larger units in higher-Tₛ samples. To better understand the structure, further experimental probes are needed in addition to those presented in our study. Additionally, we are confident that dₖ/d₁₅ rates constitute a categorizing parameter for other types of glasses. Such numerical categorization is important for the future research on the science of amorphous materials.

Finally, we discuss network modifications from smaller rings to stable six-membered rings, including the possibility of Si–O bonds recombination. We support two speculations regarding the explanation of Tₛ-dependent structural changes in rings. First is the network modification association with the bond recombination process, in which a combination of distorted small rings (three- or four-membered rings) can transform into more stable six- to eight-membered rings; however, to date, there is no clear evidence for the reconstruction of the ring network associated with the breakdown and recombination of covalent Si–O bonds during the annealing process. The second is network modification without bond interchange. It is well known that Si–O bonds in SiO₂ glass are covalent; however, the annealing process is expected to induce weak ionic interactions if Si cations are spatially located near the unpaired electrons of oxygen anions. Thus, we propose the possibility of ring deformation in accordance with the distortion of the rings in SiO₂ glass, which was recently analyzed via novel topological analysis by Onodera et al.28) Consequently, it is suggested that the distortion of six-membered rings in glass can generate Si–O–Si interactions via further ionic bonds. In an analogous case, the distorted structure can be modified during the relaxation process to form more symmetrical six-membered rings. Although we are not aware of any experimental techniques for the direct observation of bond recombination in the ring network of amorphous materials, precise diffraction measurements in the low Q region can potentially provide insights for understanding the structural changes during the annealing process.

4. Conclusions

We have examined the structural-physical properties of different-Tₛ SiO₂ glass samples. Following annealing, the narrowing of the FSDP and an increase in the correlation length were observed. Differential S(Q) data indicated that both smaller and larger units were preferentially generated in SiO₂ glass with higher Tₛ values. The change in the Q₁₅ peak suggested that the Si–Si correlation was also affected by the annealing process, inducing the increase in density, refractive index, and elastic modulus. The values of Vₛ and 2π/Q₁₅FSDP possessed comparable Tₛ dependence, which is proof that these data were affected by Si–O correlations.

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