Structural change of Na₂O-doped SiO₂ glasses by melting

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The structural change of Na₂O·5SiO₂ and Na₂O·3SiO₂ glasses by melting were analyzed. From their droplet specimens that were levitated by N₂ gas flow and melted by CO₂ laser irradiation, the X-ray diffraction spectra were successfully obtained, using 61.41 keV high energy X-ray from synchrotron radiation. The obtained spectra were corrected, normalized, and then Fourier-transformed to radial distribution functions (RDFs). It was found that the Si–O, Na–O, O–O, and Si–Si peaks in the RDFs got broadened and shifted to longer distance compared with the solid glasses, while no significant difference was found between the RDFs of the melts at 900 and 1200°C. In the classical molecular dynamics simulations using Born–Mayer–Huggins type two-body potential with optimized parameters, the trends of RDF change by melting described above were well reproduced. The simulated structural models indicated that the distortion of SiO₄ tetrahedra, increase of Na–O distance, and cleavage of Si–O and Na–O bonds are occurring in the melts.

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Sodium (Na) is one of the most popular elements that are doped in silica (SiO₂) glass. It is well known that pure SiO₂ glass is composed of a continuous random network of SiO₄ tetrahedra and that one doped Na ion generates one non-bridging oxygen (NBO) in the glass.^{1),2)} The generation of NBO lowers the glass melting point and makes it easy to form structures by the melt quenching method.

Though the glass melting process is of importance in both science and technology, there were only a few reports about the analysis of the intermediate-range order structure in the melts, mainly due to the difficulties of the diffraction measurements. However, the advance of the levitation technique combined with synchrotron radiation has enabled us to measure X-ray diffraction spectra from melting glasses. For example, Mei et al. performed diffraction measurements for pure SiO₂ melt.³⁾ As a result, they have found very little difference between the radial distribution functions (RDFs) of SiO₂ melt and that of the solid glass. From this study, the cleavage of the network chains, which should increase NBO, are hardly expected to occur in the SiO₂ melt. On the other hand, Benmore et al. reported a significant change in the RDFs of calcium silicate (CaSiO₃) melts from 1033 to 1900°C.^{4),5)} They insist that the structure of CaO polyhedra in the melts should change depending on the temperature.

In this study, we investigated the structure of Na₂O–SiO₂ melts. We performed X-ray diffraction measurements for several Na₂O–SiO₂ melts and glasses and obtained their RDFs. We also attempted classical molecular dynamics (MD) simulations in order to build structural models of the melts and glasses. Using the simulated models, we collected statistics of the distributions of Si–O, Na–O, O–O, and Si–Si distances and that of O–Si–O angles. We also checked the cleavage of the network chains and the resultant formation of NBOs. From these results, we discussed how the structure of the Na₂O–SiO₂ glasses changes by melting.

Fig. 1. Configuration of X-ray diffraction measurements.

The specimens for the diffraction measurements were fabricated as follows: First, weighed powders of Na₂CO₃ and SiO₂ were mixed and sintered at 650°C. We prepared specimens of three different compositions: Na₂O·10SiO₂, Na₂O·5SiO₂, and Na₂O·3SiO₂. Then, the sintered mass was broken into small pieces. The ones whose diameter was approximately 1 mm were picked up to be melted into droplets by the levitation technique.

Figure 1 shows the configuration of the X-ray diffraction measurements that were carried out at BL04B2 of SPring-8, where the levitator can be installed in a two-axis diffractometer. We used N₂ gas flow for levitation and a 200 W CO₂ laser for melting. The temperature of the levitated melts was monitored using a pyrometer. At the beginning of the melting process, we stayed at 1600°C for a few seconds, in order to rid the melt of bubbles. Then, we lowered the temperature and maintained at 900 or 1200°C for the diffraction measurements.

The incident X-ray from synchrotron radiation was monochromated at 61.41 keV and the diffracted X-ray was detected by horizontal step scanning of a germanium detector. Regarding the measurement step and time, we divided the diffraction angle into three regions, using the smaller step in the smaller angle region, as shown in **Table 1**. The total measurement time for one specimen was approximately 36 min.

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Among the specimens, Na₂O·10SiO₂ was found to be very unstable during the diffraction measurement at the elevated temperatures. Its droplet specimens exploded so easily by the laser irradiation that we could not obtain any diffraction spectrum. In contrast, Na₂O·5SiO₂ and Na₂O·3SiO₂ were found to be sufficiently stable from 900 to 1200°C. They were also found to evaporate very slightly at those temperatures and we did not need to replace the specimens with new ones to obtain one spectrum. The diffraction spectra of solid glasses with the same compositions were also measured at room temperature. The obtained diffraction spectra were corrected and normalized to obtain structure factor, $S(Q)$, and then Fourier-transformed to RDFs.

Figure 2 shows the obtained $S(Q)$ curves. The maximum wavenumber ($Q_{\max}$) was 220 nm⁻¹. We found that the first peak in the Na₂O·5SiO₂ glass became fairly broadened by melting. In the case of Na₂O·3SiO₂, the first peak of its glass was not as sharp as that of the Na₂O·5SiO₂. However, a similar peak broadening by melting was also confirmed.

Figure 3 shows the obtained RDFs. It is well known that the RDF of pure SiO₂ glass has three major peaks at 0.165, 0.260, and 0.310 nm, which correspond to Si–O, O–O, and Si–Si pairs, respectively.¹⁾ In this study, another small peak assigned to the Na–O pair appeared at around 0.22 nm. In the case of Na₂O·5SiO₂ melts, it was found that the Si–O, Na–O, O–O, and Si–Si peaks became broadened and shifted slightly to longer distance compared with its solid glass. On the other hand, no significant difference was found between the RDFs of 900 and 1200°C. A similar trend was also confirmed in the case of Na₂O·3SiO₂.

In the classical MD simulation, we used the simulation software “Materials Explorer”, released by Fujitsu. Each model contained approximately 1,500 atoms in total in a cubic cell. **Table 2** shows the densities that we calculated by interpolating the measurement data reported in the past.⁶⁾ It had been experimentally confirmed that the densities of melts are lower than those of the solid glasses.

The simulation started at 3727°C for 20,000 steps. One step

corresponded to 1 fs. Then, the cooling steps at the rate of 7.4×10^{10} °C/s followed. Finally, the system was maintained at 900 or 25°C for 20,000 steps. We omitted the simulation for 1200°C, since we found no significant difference between the experimentally obtained RDFs at 900 and 1200°C.

As for the interatomic potential, we employed Born–Mayer–Huggins type, $\Phi = Z_i Z_j e^2 / r + A_{ij} \cdot \exp(-B_{ij} \cdot r) - C_{ij} / r^6$, where Z_i , e , and r are the partial atomic charge, elementary electric charge, and interatomic distance, respectively. A_{ij} , B_{ij} , C_{ij} are the empirical parameters. We used two types of parameter sets for Z_i , A_{ij} , B_{ij} , C_{ij} , which were referred as CIM⁷⁾ and CMAS⁸⁾ in the simulator (see **Table 3**). Note that we needed to optimize the

Fig. 3. Experimental RDFs obtained from Na₂O–SiO₂ melts and glasses.

Table 1. X-ray diffraction measurement conditions

Region	Step Scanning		Accumulation Time (s/step)
	range (°)	step width (°)	
(1)	0.3–10	0.10	5
(2)	9–20	0.15	7
(3)	19–42	0.20	10

Table 2. Densities of Na₂O–SiO₂ glasses and melts: (g/cm³)

Temp.	Na ₂ O·10SiO ₂	Na ₂ O·5SiO ₂	Na ₂ O·3SiO ₂
25°C	2.275	2.350	2.425
900°C	—	2.282	2.284

Fig. 2. $S(Q)$ curves obtained from Na₂O–SiO₂ melts and glasses.

parameter B_{ij} for the Na–O pair in CMAS to obtain good agreement with the experimental data. **Figure 4** shows the potential energies of Si–O and Na–O as a function of interatomic distance.

Fig. 4. Potential energies of Si–O and Na–O.

CIM gave tighter bonding than CMAS to both Si–O and Na–O pairs.

Figure 5 shows the RDFs that were calculated from the final structures in the simulation models. In the case of CIM potential, the O–O and Si–Si peaks are fairly sharp, which makes the RDFs fairly different from the experimental ones, especially at 900°C. On the other hand, when using CMAS potential, we see much better agreement with the experimental data including the O–O and Si–Si peaks even at 900°C than CIM potential. These results demonstrate that CMAS potential is appropriate to investigate the structure of the Na₂O–SiO₂ melts.

Figure 6 shows the partial distribution functions of Si–O, Na–O, O–O, and Si–Si that were obtained from the simulation using CMAS potential. Each peak apparently broadened by melting.

Fig. 5. Simulated RDFs using CIM and CMAS potentials.

Fig. 6. Simulated pair distribution functions. Solid and dotted lines stand for 25 and 900°C, respectively.

Table 3. Interatomic potential parameters: A (J), B (1/nm), C (J·nm⁶)

	Partial Atomic Charge (Z)			Si–O			Na–O		
	Si	O	Na	A	B	C	A	B	C
CMAS	1.890	−0.945	0.473	8.04E-15	62.1	7.42E-24	2.33E-14	62.0	3.01E-24
CIM	4.000	−2.000	1.000	1.01E-14	60.6	0.00E-24	4.52E-14	60.6	1.39E-24

Table 4. Distributions of Si–O, Na–O, O–O, and Si–Si distances and O–Si–O bond angles

Composition	Si–O distance (nm)				Na–O distance (nm)				O–O distance (nm)			
	25°C		900°C		25°C		900°C		25°C		900°C	
	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.
Na ₂ O·10SiO ₂	0.1644	0.0035	—	—	0.2422	0.0191	—	—	0.2678	0.0102	—	—
Na ₂ O·5SiO ₂	0.1641	0.0034	0.1654	0.0064	0.2422	0.0190	0.2441	0.0214	0.2676	0.0092	0.2691	0.0137
Na ₂ O·3SiO ₂	0.1639	0.0036	0.1653	0.0067	0.2421	0.0185	0.2434	0.0211	0.2672	0.0085	0.2688	0.0133

Composition	Si–Si distance (nm)				O–Si–O angle (°)			
	25°C		900°C		25°C		900°C	
	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.	Ave.	Stdev.
Na ₂ O·10SiO ₂	0.3150	0.0114	—	—	109.34	6.55	—	—
Na ₂ O·5SiO ₂	0.3135	0.0116	0.3142	0.0146	109.37	5.65	109.25	8.21
Na ₂ O·3SiO ₂	0.3144	0.0113	0.3151	0.0135	109.36	5.26	109.22	7.97

Fig. 7. Typical structural change of Na₂O–SiO₂ glasses by melting. In the lower illustration for melt, dotted lines indicate the original SiO₄ tetrahedron.

Fig. 8. Simulated NBO ratios in glasses and melts.

Table 4 summarizes the statistical data about the distribution of distance of each pair and that of O–Si–O angles. In the calculation of average and standard deviation for Na–O, we used the cut-off distance of 0.28 nm. It was confirmed that the averages and standard deviations of Si–O, Na–O, O–O, and Si–Si pairs increased by melting. Regarding the O–Si–O angles, its standard deviation also fairly increased, though the averages decreased only slightly. These results demonstrate that the typical structural changes by melting are the distortion of SiO₄ tetrahedra and the increase of Na–O distance, as illustrated in **Fig. 7**.

Figure 8 shows the ratios of NBO, which did not increase even after the melting. This seems to be strange, since melting is generally expected to involve the cleavage of the glass network that should result in the increase of NBO. However, by checking

the coordination at every 1,000 steps or 1 ps, we found that the first neighboring O atoms to Si and Na were changing during the melting process. This means that the cleavage and recombination of Si–O and Na–O bonds occur in the melting glasses.

In summary, the structure of Na₂O·5SiO₂ and Na₂O·3SiO₂ melts was analyzed. The X-ray diffraction spectra were successfully obtained from levitated droplet specimens, melting at 900 or 1200°C. Using 61.41 keV high energy X-ray from synchrotron radiation, the $Q_{\max}$ became 220 nm^{−1}. In the RDFs, the Si–O, Na–O, O–O and Si–Si peaks broadened and shifted slightly to longer distance compared with solid glasses. The structure models by the classical MD simulations using optimized parameters of Born–Mayer–Huggins potential reproduced well the experimental RDFs. The results demonstrate that the degradation of the intermediate-range order by melting is caused by the distortion of SiO₄ tetrahedra and the increase of Na–O distance. We have also found that the cleavage and recombination of Si–O and Na–O bonds are occurring during the melting process, and hence the NBO fraction does not increase.

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