Structural change of Na$_2$O-doped SiO$_2$ glasses by melting

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The structural change of Na$_2$O·5SiO$_2$ and Na$_2$O·3SiO$_2$ glasses by melting were analyzed. From their droplet specimens that were levitated by N$_2$ gas flow and melted by CO$_2$ 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 SiO$_4$ tetrahedra, increase of Na–O distance, and cleavage of Si–O and Na–O bonds are occurring in the melts.

Key-words : Na$_2$O–SiO$_2$ melt, X-ray diffraction, Levitation, RDF, Molecular dynamics

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DOI http://dx.doi.org/10.2109/jcersj2.16028

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

The specimens for the diffraction measurements were fabricated as follows: First, weighed powders of Na$_2$CO$_3$ and SiO$_2$ were mixed and sintered at 650°C. We prepared specimens of three different compositions: Na$_2$O·10SiO$_2$, Na$_2$O·5SiO$_2$, and Na$_2$O·3SiO$_2$. 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 N$_2$ gas flow for levitation and a 200 W CO$_2$ 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 a Ge detector. We used N$_2$ gas flow for levitation and a 200 W CO$_2$ 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.

In this study, we investigated the structure of Na$_2$O–SiO$_2$ melts. We performed X-ray diffraction measurements for several Na$_2$O–SiO$_2$ 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 Na$_2$O–SiO$_2$ glasses changes by melting.

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Among the specimens, \( \text{Na}_2\text{O} \cdot 10\text{SiO}_2 \) 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, \( \text{Na}_2\text{O} \cdot 5\text{SiO}_2 \) and \( \text{Na}_2\text{O} \cdot 3\text{SiO}_2 \) 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 \( (Q_{\text{max}}) \) was 220 nm\(^{-1}\). We found that the first peak in the \( \text{Na}_2\text{O} \cdot 5\text{SiO}_2 \) glass became fairly broadened by melting. In the case of \( \text{Na}_2\text{O} \cdot 3\text{SiO}_2 \), the first peak of its glass was not as sharp as that of the \( \text{Na}_2\text{O} \cdot 5\text{SiO}_2 \). 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 \( \text{SiO}_2 \) glass has three major peaks at 0.165, 0.260, and 0.310 nm, which correspond to \( \text{Si-O}, \text{O-O}, \text{and Si-Si} \) 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 \( \text{Na}_2\text{O} \cdot 5\text{SiO}_2 \) 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 \( \text{Na}_2\text{O} \cdot 3\text{SiO}_2 \).

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 \( 7.4 \times 10^{10} \)°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, \( \Phi = Z_i Z_j e^2/r + A_{ij} \exp (-B_{ij} r) - C_{ij}/r^6 \), where \( Z, e, r \) 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 CIM\(^7\) and CMAS\(^8\) in the simulator (see **Table 3**). Note that we needed to optimize the

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**Table 1.** X-ray diffraction measurement conditions

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

**Table 2.** Densities of \( \text{Na}_2\text{O} \cdot \text{SiO}_2 \) glasses and melts: \( (g/cm^3) \)

| Temp. | \( \text{Na}_2\text{O} \cdot 10\text{SiO}_2 \) | \( \text{Na}_2\text{O} \cdot 5\text{SiO}_2 \) | \( \text{Na}_2\text{O} \cdot 3\text{SiO}_2 \) |
|-------|---------------------------------|---------------------------------|---------------------------------|
| 25°C  | 2.275                           | 2.350                           | 2.425                           |
| 900°C | —                               | 2.282                           | 2.284                           |

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**Fig. 2.** \( S(Q) \) curves obtained from \( \text{Na}_2\text{O} \cdot \text{SiO}_2 \) melts and glasses.

**Fig. 3.** Experimental RDFs obtained from \( \text{Na}_2\text{O} \cdot \text{SiO}_2 \) melts and glasses.
parameter $B_i$ 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. 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 Na$_2$O–SiO$_2$ 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.

![Diagram of potential energies](image1)

![Diagram of RDFs](image2)

![Diagram of partial distribution functions](image3)

Table 3. Interatomic potential parameters: A (J), B (1/nm), C (J·nm$^6$)

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

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

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.
that should result in the increase of NBO. However, by checking
generally expected to involve the cleavage of the glass network
even after the melting. This seems to be strange, since melting is
changes by melting are the distortion of SiO\textsubscript{4} tetrahedra and the
only slightly. These results demonstrate that the typical structural
deviation also fairly increased, though the averages decreased
increased by melting. Regarding the O–Na bonds, Na
showed the ratios of NBO, which did not increase
Figure 8
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 SiO\textsubscript{4} tetrahedra and the
increase of Na–O distance, as illustrated in Fig. 7.

Figure 8 shows the ratios of NBO\textsubscript{O}, 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 Na\textsubscript{2}O·5SiO\textsubscript{2} and Na\textsubscript{2}O·3SiO\textsubscript{2}
melts was analyzed. The X-ray diffraction spectra were successfully
obtained from levitated droplet specimens, melting at 900 or
1200°C. Using 61.41 kV high energy X-ray from synchrotron
radiation, the Q\textsubscript{max} became 220 nm\textsuperscript{-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 SiO\textsubscript{4} 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.

The X-ray diffraction measurements were done at SPring-8 with the approval of Japan Synchrotron Radiation Research
Institute (JASRI) (Proposal No.: 2012B1460). The authors wish
to thank Drs. K. Yamaguchi, J. Iihara, and A. Tominaga
of Sumitomo Electric for their kind support in the X-ray
experiments.

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 Ave. | 900°C Ave. | 25°C Ave. | 900°C Ave. | 25°C Ave. | 900°C Ave. |
| Na\textsubscript{2}O·10SiO\textsubscript{2} | 0.1644 | 0.0035 | 0.2422 | 0.0191 | 0.2678 | 0.0102 |
| Na\textsubscript{2}O·5SiO\textsubscript{2} | 0.1641 | 0.0034 | 0.2422 | 0.0190 | 0.2676 | 0.0092 |
| Na\textsubscript{2}O·3SiO\textsubscript{2} | 0.1639 | 0.0036 | 0.2421 | 0.0185 | 0.2672 | 0.0085 |

Fig. 7. Typical structural change of Na\textsubscript{2}O–SiO\textsubscript{2} glasses by melting. In the lower illustration for melt, dotted lines indicate the original SiO\textsubscript{4} tetrahedron.

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

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