The Structure of Soda-Lime-Silicate Glass and Melt by X-ray Diffraction Method

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The structure of soda-lime-silicate(16Na₂O·10CaO·74SiO₂) glass and melt (~1500°C) was investigated by X-ray diffraction method in combination with molecular dynamics(MD) calculation. The short- and intermediate range structure of the glass was investigated as a function of temperature by using MD simulation. The experimental results clearly show that there is no distinct difference in structure between the present glass and melt. We also found from MD calculation that the linkage of Si-O network made of SiO₄ tetrahedra shows similarities between glass and melt. It is also found that the first sharp diffraction peak(FSDP) associated with intermediate range structure is contributed from the correlation between Na⁺(or Ca²⁺) and SiO₄ network.

Keywords: Silicate Glass / Melt/ Structure / X-ray diffraction / Molecular Dynamics Calculation

As well known, many commercial glasses are produced through melting process. Although enormous efforts have been made to investigate their physical and chemical properties in a melting state, such as viscosity, density and redox reaction etc., there are few works on the structure of oxide melts. On the other hand, MD calculation is regarded as one of the most powerful techniques to get insight into materials. By a combination of high temperature X-ray radial distribution function(RDF) analysis and MD calculation, it is expected that we can get not only information about the average structure of specific elements but also structural parameters of short and medium range orders in glasses and melts.

In the present study, the technologically important soda-lime-silicate glass is chosen to investigate the local structure of glass and melts. The difference in structure between glass and melt is discussed with the result of MD calculation in order to explain the temperature dependence of macroscopic properties.

Figure 1 shows the interference functions of glass and melt obtained from X-ray diffraction together with the MD-derived ones. It is seen that the interference functions from MD calculation are in fairly well agreement with the experimental ones indicating that the MD simulation reproduces the characteristics of the real structures. It is also seen from Figure 1 that there are two peaks in the low-Q region at 15 and 21nm⁻¹ which are hereafter referred to $Q_1$ and $Q_2$, respectively. It is clear that the $Q_1$ peak disappears at high temperature, while the $Q_2$ becomes more pronounced in a melting state. Our MD calculation also reproduced this result. By comparison between the total $Q_i(Q)$ and pair $Q_i(Q)_{ij}$, it is obvious that the peaks at ~15nm⁻¹ and ~21nm⁻¹ are assigned to Si-O(Si-Si) and Na(Ca)-Si correlations, respectively (see Figure 2).
Namely, the former corresponds to network and the latter to correlations between cation and network of glass. The previous result from MD calculation of pure SiO$_2$ also shows the FSDP at ~15nm$^{-1}$ which is a contribution of Si-Si, Si-O and O-O pairs$^{2, 3}$. In our MD calculation, the peak at ~21nm$^{-1}$ is shifted to low $Q$ side on increasing temperature. It indicates the expansion of Na(Ca)-Si correlation due to thermal motion. Now we can draw a picture that the distance between the modifier cations and the network former in glass tends to expand with increasing temperature.

It is surprising that almost no change of Si-O and Si-Si atomic distances was observed between the RDF curves of glass and melt. However, we have observed that the atomic distances of Na-Ca and Ca-Ca were increased by 0.031nm and 0.019nm, respectively, with increasing temperature (see Figure 3). This value is longer than expansion of Si-O at 1000K(0.002nm)$^4$. The distinct change of distribution of Na-O and Ca-O correlations that are difficult to be distinguished in experimental $G(r)$ with increasing temperature was also observed. This allows us to suggest that the temperature dependence of density cannot be simply explained by the change of local structure of network former and instead the thermal motion of Na$^+$ and Ca$^{2+}$ ions mainly contributes to the expansion of glass at high temperatures.

In the present study, we have investigated the structure of soda-lime-silicate(16Na$_2$O·10CaO·74SiO$_2$) glass and melt (~1500°C) by X-ray diffraction method in combination with MD calculation. The experimental results clearly show that there is no distinct difference in structure between the present glass and melt, which was also supported by MD calculation. The decrease in density with increasing temperature is due to expansion of atomic distance between Na$^+$ and Ca$^{2+}$ (Na$^+$). It is concluded that the increase of correlation length between cations and network with increasing temperature is also responsible for the decrease of density.

References

![Figure 1. The interference functions of 16Na$_2$O·10CaO·74SiO$_2$ glass and melt.](image1)

![Figure 2. MD results for partial and total interference function of 16Na$_2$O·10CaO·74SiO$_2$ glass and melt.](image2)

![Figure 3. Pair distribution functions of 16Na$_2$O·10CaO·74SiO$_2$ glass and melt derived from MD calculation.](image3)