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Cooling-rate dependence of thermal conductivity in a sodium silicate glass: A molecular dynamics study

Koki CHOJIN¹, Masahiro SHIMIZU¹, Yasuhiro SHIMOTSUMA¹ and Kiyotaka MIURA¹

¹Graduate School of Engineering, Department of Material Chemistry, Kyoto University, Japan

In glasses, the cooling-rate dependence of thermal conductivity has not been sufficiently studied and has not been microscopically interpreted. In this study, we investigate the cooling-rate dependence of thermal conductivity in 33.3Na₂O–66.7SiO₂ (mol.%) glasses with molecular dynamics (MD) simulations. We simulated the glasses by changing the cooling rate in the range of 0.01 to 10 K/ps, and then we calculated thermal conductivity using non-equilibrium MD. The calculated thermal conductivity was approximately 1.58 W/mK, which shows good agreement with the experimental value (1.02 W/mK). When the cooling rate was decreased, the thermal conductivity monotonically increased. To investigate the correlation between the thermal conductivity and the change in the glass structure, we defined the degree of relaxation using the Q⁷ distribution and checked the correlation. Consequently, a clear positive correlation with a correlation coefficient of 0.492 is obtained, suggesting that the dependence of the thermal conductivity on the cooling rate is attributable to the rearrangement of the medium-range structure.

Key-words: Glass, Molecular dynamics (MD), Thermal conductivity, Cooling-rate dependence, Q⁷ distribution

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The structure of glass depends on its thermal history, and it has been reported that various physical properties such as density,¹ thermal expansion coefficient,² Rayleigh scattering intensity,³ hardness,⁴ and refractive index⁵ significantly depend on the fictive temperature. Although thermal conductivity is also an important physical property, the effect of composition, temperature, and thermal history on thermal conductivity has not been sufficiently studied and microscopically interpreted. In this study, we focus on fictive temperature (cooling rate) and study its effect on the thermal conductivity of the sodium silicate glass, using molecular dynamics (MD) simulations.

We performed MD simulations of a sodium silicate glass of composition 33.3Na₂O–66.7SiO₂ (mol.%) and containing 18000 particles (O: 10000, Si: 4000, Na: 4000). MD simulation is a method of tracking the trajectory of particles on the basis of the interaction between atoms, and it is used in various domains to study the structural and physical properties that cannot be experimentally observed. The force field used in MD simulation is one of the most important factors to determine the particle trajectories. In this study, we used the following Coulomb-Buckingham-type potential

\[ V_{ij}(r) = \frac{1}{4\pi\varepsilon_0} \frac{z_i z_j e^2}{r} + A_{ij} \exp\left(-\frac{r}{B_{ij}}\right) - \frac{C_{ij}}{r^6} \]  

(1)

with the parameter set determined by Teter et al.⁶ (see Table 1). It is a simple pair potential with low computational cost and is in good agreement with experimental values in the sodium silicate system.⁷

The grass-forming process is showed in Fig. 1. Initially, we randomly arranged the particles and held the system at 4000 K for 15 ns to eliminate the thermal history of the initial positions. Next, to transform the system into a stable

Table 1. Interionic potential parameters used in the MD simulation of 33.3Na₂O–66.7SiO₂ glasses

|        | A_{ij} (10^{-16} J) | B_{ij} (10^{-11} m) | C_{ij} (10^{-78} J m^6) |
|--------|-------------------|-------------------|---------------------|
| O^{-12}·O^{-12} | 3.25117           | 3.43645           | 30.8067             |
| Si^{2+}·O^{-12} | 21.9545           | 1.93817           | 8.76086             |
| Na^{+}·O^{-12}  | 7.02355           | 2.43838           | 4.97868             |

Fig. 1. Relationship between temperature T and time in the heating schedule used to prepare 33.3Na₂O–66.7SiO₂ glasses. The system was cooled at 0.1 K/ps from 4000 K to 2500 K and then at one of four different cooling rates to 300 K.

† Corresponding author: K. Chojin; E-mail: k.chojin@func.mcc.kyoto-u.ac.jp
liquid state, we cooled the system to 2500 K at a constant cooling rate of 0.1 K/ps. The system was then cooled to 300 K at one of four different cooling rates (0.01, 0.1, 1.0, and 10 K/ps) to obtain glass configurations with different fictive temperatures $T_f$, which is the temperature at which the structure of the stable liquid state corresponds to the glass structure. Generally, upon increasing the cooling rate, the fictive temperature increases. All glass-forming stages were performed at a pressure of 1.0 bar, and after obtaining the glass configurations, we held them at 300 K and 1.0 bar until volume and total energy relaxation were completed. We used the Gromacs package \(^9\) to perform all glass-forming process with a 1.0 fs time step and three-dimensional periodic boundary cubic box. The cut offs of both the Coulomb and Buckingham terms were 1.0 nm each, and the Coulomb interactions were calculated using the particle-mesh-Ewald method. We controlled the pressure and temperature by using the Berendsen barostat and performing stochastic velocity rescaling.

We calculated the thermal conductivity with non-equilibrium MD, using the method of Ikeshoji et al. \(^9\) In this method, we divided the simulation box into even number of slices along the x-axis, as showed in Fig. 2, and we then calculated the temperature of each slice. After removing the thermostat and barostat, we transferred a constant amount of energy $\Delta E$ from slice 1 to slice 6 in Fig. 2. By repeatedly imposing this heat transfer at a constant interval $\Delta t$, we calculated the heat flux $J_x$ as follows

$$J_x = \frac{\Delta E}{2 S \Delta t}$$

where $S$ denotes the area of the cross section. During the heat transfer, we rescaled the velocity of the particles in slices 1 and 6 as follows

$$v_i^f = v_i^G + \alpha (v_i - v_G)$$

$$\alpha = \sqrt{1 \pm \frac{\Delta E}{E_i^R}}$$

$$E_i^R = \sum_{j=1}^{1} \left( \frac{1}{2} m_i v_i^2 \right) - \sum_{j=1}^{1} \left( \frac{1}{2} m_i v_i^2 \right)$$

where $v_i^G$ denotes the velocity of the center of mass of each slice and $E_i^R$ the relative kinetic energy of each slice.

Continuing this operation for a period, the system achieved the temperature gradient $\partial T/\partial x$ and we could calculate the thermal conductivity $\kappa$ using Fourier’s law as follows

$$\kappa = - \frac{J_x}{\partial T/\partial x}$$

To improve the statistics, we performed the above calculations for eight initial configurations and quantified the uncertainty on the basis of the standard deviation.

Reportedly, when the simulation box length is not significantly greater than the phonon mean free path of the glass (0.393 nm as calculated in Ref. 10), the calculated thermal conductivity will vary with the simulation box length because of the ballistic phonon scattering near the boundaries of the heat source and sink \(^1\) (slices 6 and 1, respectively, in Fig. 2). To investigate the effect of the interval between heat source and sink ($L_{\text{interval}}$, in Fig. 2), we change the $L_{\text{interval}}$ by setting two pairs of heat source and sink with 20 slices in the 18000-atom system ($L_{\text{interval}} \equiv 15.7$ Å) or one pair with 10 slices in the rectangular simulation boxes which are prepared by connecting 2, 3, or 4 simulation boxes along the $x$-axis ($L_{\text{interval}}$ is approximately 62.9, 94.4, and 125 Å). We used the LAMMPS package \(^1\) to perform the calculation of thermal conductivity.

In Fig. 3, we show the pair distribution function between the selected pairs of the elements of the simulated glass at 300 K. Although the peak position of the pair distribution function does not change with cooling rate, the first peak becomes narrower upon decreasing the cooling rate. In Table 2, we present a comparison of the first peak position of the pair distribution function and bond length from experimental data. \(^1\) The good agreement suggests that our MD simulations can accurately reproduce the properties of silicate glasses.

We show the changes in the volume and enthalpy of the simulation box at various cooling rates in Fig. 4. The density of the system becomes higher upon decreasing the cooling rate, and this trend agrees with the trend of silicate glasses which is generally known. \(^1\) The opposite trend, i.e., the density of the glass becomes lower upon decreasing the cooling rate, is observed in the silica glass. \(^1\) The inset of Fig. 4(b) shows the heat capacity, $C_p = (\partial H/\partial T)_p$, as a function of temperature for cooling rates 0.1
and 0.01 K/ps. From the cross-over points of the different slopes (black lines), the fictive temperatures at 0.01 and 0.1 K/ps are estimated to be 1305 and 1606 K, respectively. Note that we could not accurately determine the fictive temperatures at 1.0 and 10 K/ps, as the slopes of the heat capacity plots changed in a step-like fashion.

In Fig. 5, we show the $Q^n$ distribution of the glass structure that corresponds to each cooling rate. A $Q^n$ species refers to a SiO$_4$ tetrahedron unit with $n$ bridging oxygen. In this composition, the decrease in the fictive temperature can be confirmed from the sharper $Q^n$ distribution around $Q^3$ because the $Q^n$ distribution becomes 100% $Q^3$ in the crystalline state. The $Q^n$ distribution approaches the $^{29}$Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) results upon decreasing the cooling rate, which shows that the glass network structure changes when the cooling rate is decreased. Maekawa et al. prepared glass samples by quenching the melt using water or liquid nitrogen. The cooling rate employed when using liquid nitrogen is not known, but the cooling rate when using water is at most 100 K/s.

In Fig. 6(a), we show the dependence of the calculated value of thermal conductivity on $J_x$ for the same cooling rate of 10 K/ps and $L_{interval}$ of 94.4 Å. The change in the average value of thermal conductivity due to the change in $J_x$ is within 1%, which indicates that the thermal conductivity does not depend on $J_x$. In Fig. 6(b), we show the effect of $L_{interval}$ on the calculated thermal conductivity for the same cooling rate of 10 K/ps. From this figure, it appears that the box size effect is sufficiently eliminated when $L_{interval}$ is longer than 62.9 Å. We plot the cooling-rate dependence of thermal conductivity in Fig. 6(c). From this figure, it is seen that the thermal conductivity monotonically increases upon lowering the cooling rate. The experimental value is 1.02 W/mK, and the calculated value is approximately 1.55 times greater than this.

Table 2. Comparison of peak positions from simulations and experiment

|                  | Calculated (Å) | Experiment (Å) |
|------------------|----------------|----------------|
| Si–O             | 1.61           | 1.62           |
| Na–O             | 2.37           | 2.36           |
| O–O              | 2.63           | 2.65           |
| Si–Si            | 3.18           | 3.21           |

Fig. 4. (a) Volume and (b) enthalpy of the simulation box as a function of temperature at different cooling rates. The inset of (b) shows the heat capacity $C_p$ obtained by differentiating the enthalpy with respect to the temperature.

Fig. 5. Comparison of $Q^n$ distributions of simulated glasses for each cooling rate with those of random model glass, and $^{29}$Si MAS-NMR results.

Fig. 6. Dependence of the calculated thermal conductivity of 33.3Na$_2$O–66.7SiO$_2$ glasses on (a) heat flux $J_x$, (b) interval between heat source and sink, $L_{interval}$, and (c) cooling rate. In (a) and (b), the simulation is performed at 10 K/ps. In (a) and (c), the thermal conductivity is calculated under the condition that $L_{interval}$ is approximately 94.4 Å.
It is reported in experiments and simulations that the $Q^0$ tetrahedron units in a sodium silicate system.\textsuperscript{19,20} In this reaction, the attaching $Q^0$ species change to $Q^1$.\textsuperscript{4} As the number of $Q^0$ species does not change upon lowering the cooling rate, the decrease in the number of $Q^0$ species at lower cooling rates means that they change mainly to $Q^2$. $Q^1$ species are Si–O tetrahedra with one bonding O atom at the edge of the Si–O network and are unable to transmit phonons, but the $Q^2$ species can transmit phonons because they bridge Si–O tetrahedrons. This may result in the correlation between the decrease in the number of $Q^1$ species and increase in the thermal conductivity.

The above-mentioned results suggest that the change in the thermal conductivity observed upon changing the cooling rate is attributable to the rearrangement of the glass network structure. As a future work, we would like to identify dominant factors in detail.

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