Thermal Conductivity of Silica Glass at High Temperature by Molecular Dynamics Simulation

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We have evaluated the thermal conductivity in SiO₂ glass at elevated temperature by Molecular Dynamics (MD) calculation and the Green-Kubo formula in an equilibrium state using the purely ionic pair interaction potential functions. The estimated uncertainty for the thermal conductivity was $\pm 25\%$ at 981 K and $\pm 8\%$ at 1978 K. Our results were in agreement with those of the experiment by Wray and Connolly within 20–35% at 981–1978 K. The calculated thermal conductivity showed a positive temperature dependence, which also agreed with the experimental results. It was found that the calculated values did not depend on total ion number in the system. We have concluded that semi-quantitatively reliable results were given by the present MD calculation with the potential functions.

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I. Introduction

Information on thermal properties such as thermal conductivity for SiO₂ at elevated temperature is useful for many metallurgical processes since SiO₂ is one of the fundamental components in slags and fluxes as well as glasses. It is said, however, that an experimental determination of thermal conductivity of an ionic system is not an easy task at high temperature above 1000 K mainly because of large thermal radiation from the sample. Furthermore, the high ionic conductivity and corrosiveness of ionic systems limit the measurement methods with serious errors. In many cases of molten salts, the obtained results differ considerably among several reports, *e.g.* *ca.* 200% in molten KCl⁽¹⁾. Since few experimental results⁽²⁾⁽³⁾ are reported for the thermal conductivity measurement of SiO₂ glass at high temperature, it remains to be further studied in detail.

The evaluation of thermal conductivity by molecular dynamics (MD) calculation is free from above stated difficulties in the experimental methods. In the MD method, the thermal conductivity can be calculated through the integral of the time correlation function of the energy current: this is based on the Green-Kubo formula given for thermal conductivity of plasma⁽⁴⁾. The energy current originates from relaxation of very small microscopic fluctuations of temperature in an equilibrium state. The microscopic information such as the energy current within the system is also significant for elucidating the mechanism of thermal conduction. Only a few papers⁽⁵⁾⁽⁶⁾ reported, however, the thermal conductivity of molten alkali metal halides by MD calculation. Moreover, a considerable difference was found

between their results. Recently, we examined the optimum calculation condition for precise and efficient evaluations of the thermal conductivity of ionic liquids in detail⁽⁷⁾: the statistical and systematic errors were also estimated. The calculated results for the thermal conductivity agreed with the relatively reliable experimental ones within 10–20% at 1200–1300 K for molten NaCl⁽⁷⁾. Under the optimized condition, the MD calculation was applied to a series of molten alkali metal halides so that the negative temperature dependence and the cation dependence of their thermal conductivity were clarified⁽⁸⁾.

In the present work, we have attempted the evaluation of thermal conductivity of SiO₂ glass from 300 to 2250 K and examined the dependence of total ion number used in the simulated system on the calculated value. We discuss the temperature dependence of the thermal conductivity. Although SiO₂ glass forms networking structure by partially covalent bond, which is different from purely ionic alkali metal halides, the purely ionic pair interaction potential functions were adopted for the present calculations of SiO₂ glass because of its simplicity. The calculation results using partially ionic models will be published elsewhere.

II. Calculation Method

All the MD calculations were performed under the constant *NVE*, microcanonical ensemble, in equilibrium states. The total ion number *N* was 300 in the cell volume *V* determined from the density⁽⁹⁾ which was 2.20×10^3 kgm⁻³ at 300 K and was calculated from the thermal expansion coefficient at elevated temperature. The interionic pair interaction potentials of the Busing approximation of Born-Mayer-Huggins' form with the dispersion terms were used⁽¹⁰⁾:

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$$\phi_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6}. \quad (1)$$

The function parameters for SiO₂ are given in **Table 1**. The coulombic interactions were treated using the conventional Ewald method⁽¹¹⁾ with periodic boundary condition. The equations of motion were integrated using the velocity Verlet algorithm. The initial configuration of the ions had a fcc structure. In the beginning, the system was heated up to 20000 K and kept in the molten state for 100000 time steps with a time step of 1 fs in order to obtain fully disordered configuration. Subsequently, it was cooled from 20000 through 15000, 10000, 5000, 3000, 2250, 2000, 1750, 1500, 1200, 1000 and 500 to 300 K successively while the density was kept under control: experimentally, the melting point of the cristobalite is 2003 K while the glass transition temperature 1446 K⁽¹²⁾. The cooling rate was $1.0\text{--}5.0 \times 10^{14} \text{ K s}^{-1}$ above 2250 K and $1.0\text{--}2.5 \times 10^{13} \text{ K s}^{-1}$ below 2250 K. The temperature control, such as heating and cooling, was done by scaling the velocities of all ions. The fluctuation of the temperature was about 3% in the present *NVE* ensemble; the averaged temperature resulted in 1978 K without the temperature control after the system had been kept at 2000 K with the control. The time step was 1 fs above 2250 K and 2 fs at 2250 K and below. The system was equilibrated for 30 ps at each given temperature above 2250 K and for 20 ps at 2250 K and below in the course of cooling. Before MD calculations for thermal conductivity, the system was equilibrated for further 200 ps at each intended temperature, 2250, 2000, 1750, 1500, 1200, 1000, 500 and 300 K. The obtained pair correlation functions at 1978 K agreed very well with the previous MD results using the purely ionic potential functions at 2000 K⁽¹³⁾ where the X-ray weighted interference function well agreed with experimental one. The coordinates and velocities obtained for the subsequent 800 ps were used for the calculation of the thermal conductivity at each temperature. In order to keep the sum of momentum over all ions negligible, the velocities of all ions were corrected every 5000 time steps. The other MD calculations were also performed for $N=600$ and 900 at 2000 K under the same condition as above stated.

For an insulating binary ionic solid, the thermal conductivity is given by the equilibrium Green-Kubo formulas⁽¹⁴⁾⁽¹⁵⁾ as

$$\lambda = \frac{L_{ee}}{k_B T^2}, \quad (2)$$

$$L_{ee} = \frac{1}{V} \int_0^\infty C_{ee}(t) dt, \quad (3)$$

Table 1 Parameters of the pair potential functions used in the present MD calculation for SiO₂.

	<i>Z</i>	<i>a</i> /pm	<i>b</i> /pm	<i>c</i> /(kJ/mol) ^{1/2} m ³
Si	4.0	101.2	8.0	0.0
O	-2.0	162.9	8.5	4.09×10^{-29}

$$f_0 = 4.18 \times 10^{10} \text{ kJ}/(\text{mol} \cdot \text{m}).$$

and

$$C_{ee}(t) = \frac{1}{3} \langle J^e(t) J^e(0) \rangle \quad (4)$$

where T is the temperature, V the volume of the system, k_B the Boltzmann constant, and J^e the energy current. This equation is expected to hold good even above 2000 K because of its high viscosity. The expressions for the energy current can be written as

$$J^{ex} = \sum_{i=1}^N v_{ix} \left\{ \frac{1}{2} m v_i^2 + \frac{1}{2} \sum_{j=1, j \neq i}^N \phi_{ij}(r_{ij}) \right\} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N v_i \cdot r_{ij} F_{ijx} + J_{\text{Coulomb}}^{ex}. \quad (5)$$

The coulombic interaction term J_{Coulomb}^{ex} is expressed as follows⁽⁴⁾:

$$J_{\text{Coulomb}}^{ex} = \sum_i \sum_{j \neq i} z_i z_j e^2 \left\{ \sum_{\lambda} \frac{1}{2} \left[v_{ix} + \frac{r_{ijx} + \lambda_x}{\|r_{ij} + \lambda\|} \frac{v_i \cdot (r_{ij} + \lambda)}{\|r_{ij} + \lambda\|} \right] \times \left(\frac{\text{erfc}(\alpha \|r_{ij} + \lambda\|)}{\|r_{ij} + \lambda\|} + \frac{2\alpha}{\sqrt{\pi}} \exp(-\alpha^2 \|r_{ij} + \lambda\|^2) \right) - \frac{2\pi}{\alpha^2} v_{ix} + \sum_{h \neq 0} \frac{\exp(-\pi^2 h^2 / \alpha^2 - 2i\pi h \cdot r_{ij})}{\pi h^2} \times \left[\left(1 - \frac{\pi^2 h^2}{\alpha^2} \right) v_{ix} - \left(1 + \frac{\pi^2 h^2}{\alpha^2} \right) h_x v_i \cdot h \right] \right\} \quad (6)$$

where h is the reciprocal lattice vector, λ the direct lattice vector and α the arbitrary parameter. The three terms in the braces on the right hand correspond to the real space, divergent and reciprocal space terms, respectively, in the conventional Ewald sum. The calculation method above described is similar to that in our previous work on molten NaCl. In the case of molten NaCl, the MD calculation was performed for $N=216$ and with the time step of 4 fs. On the other hand, the thermal conductivity was calculated from the coordinates and velocities obtained for the 1200 ps. Moreover, the charge current must be considered for melts. The detailed descriptions for the optimized calculation condition for the evaluation of the thermal conductivity of ionic system were given in our previous paper⁽⁷⁾.

III. Results and Discussion

Figure 1 shows the representative autocorrelation functions of the energy current and their time integral L_{ee} for SiO₂ glass at 1978 K with those for molten NaCl at 1300 K⁽⁷⁾. Although the autocorrelation function and its time integral for SiO₂ glass have some small noises with high frequency compared with those for molten NaCl, the integral can practically be regarded as converged up to 2.0 fs. The similar behavior was also observed in the case of solid KCl at 500 K by Sindzingre and Gillan⁽⁵⁾ who pointed out that such oscillation did not affect the evaluation of thermal conductivity. On the other hand, in SiO₂ glass at 297 and 498 K it was found that the evaluated values of L_{ee} were comparable to the statistical

Fig. 1 Autocorrelation functions, $\langle J^e(t)J^e(0) \rangle$, of the energy current and their time integral for (a) SiO_2 glass at 1978 K and (b) molten NaCl at 1300 K.

Table 2 The calculated thermal conductivity for SiO_2 glass. σ_λ denotes the estimated uncertainty.

N	T/K	$\lambda/\text{W m}^{-1} \text{K}^{-1}$	$\sigma_\lambda(\%)$
300	981	2.36	± 25
300	1167	2.92	± 10
300	1509	2.67	± 10
300	1800	3.00	± 8
300	1978	2.88	± 8
300	2239	3.06	± 8
600	2060	3.03	± 5
900	1962	3.14	± 4

fluctuations so that the calculated thermal conductivity has large uncertainty. Hereafter, therefore, we limit our discussions on the results at high temperature.

Table 2 shows the calculated thermal conductivity with its estimated uncertainty for SiO_2 glass at 981, 1167, 1509, 1800, 1978 and 2239 K for $N=300$, at 2060 K for $N=600$ and at 1962 K for $N=900$. The uncertainty was estimated from the variation of L_{ee} , which arises from the statistical fluctuations. The relatively large uncertainty at lower temperature is due to the smaller value of L_{ee} compared with that at higher temperature. The uncertainty at 1167 K was comparable to the statistical error of the calculated thermal conductivity in molten NaCl at 1300 K⁽⁷⁾. It was revealed that the calculated thermal conductivity did not depend on the total ion number in the system. No dependence on the number was also observed for molten NaCl at 1300 K as shown in our

Fig. 2 Temperature dependence of the thermal conductivity in SiO_2 glass.

previous work⁽⁷⁾. The calculated thermal conductivity of SiO_2 glass suggests a weak positive temperature dependence, which is in agreement with the experimental results as shown in Fig. 2. This dependence is common behavior for oxide glasses, which is different from the case of molten alkali metal halides, and may be traceable to the strong interaction in the SiO_2 glass. The calculated thermal conductivity at temperature range from 981 K to 1978 K was 20–35% higher than that obtained by the experiment⁽³⁾. Therefore, we have concluded that the present purely ionic pair interaction potential functions produced the semi-quantitatively reliable results. In order to quantitatively discuss the obtained values, however, more investigations have to be performed regarding the dependence on the potential functions and so on. Moreover, more experimental attempts are also requested.

IV. Conclusion

We have examined the thermal conductivity of SiO_2 glass at high temperature by MD calculation based on the purely ionic pair potential functions and the Green-Kubo formula. The estimated uncertainty for the thermal conductivity was $\pm 25\%$ at 981 K and $\pm 8\%$ at 1978 K. Our results were in agreement with those of the experiment by Wray and Connolly within 20–35% at 981–1978 K. The weak positive temperature dependence of the thermal conductivity was observed by the present MD calculation, which also agreed with the experimental result. It was shown that the calculated thermal conductivity did not depend on the total ion number in the system. We have concluded that the present MD calculation with the purely ionic pair interaction potential functions gave the semi-quantitatively reliable results.

REFERENCES

- (1) Y. Nagasaka, N. Nakazawa and A. Nagashima: *Int. J. Thermophys.*, **13** (1992), 555–574.
- (2) Y. S. Touloukian, R. W. Powell, C. Y. Ho and P. G. Klemens: *Thermophys. Properties of Matter*, 2, Thermal conductivity, Nonmetallic Solids, Plenum (1970), 183–193.
- (3) K. L. Wray and T. J. Connolly: *J. Appl. Physics*, **30** (1959), 1702–1705.

- (4) B. Bernu and P. Vieillefosse: *Phys. Rev. A*, **18** (1978), 2345–2355.
- (5) P. Sindzingre and M. J. Gillan: *J. Phys.: Condens. Matter*, **2** (1990), 7033–7042.
- (6) T. Fuchiwaki and Y. Nagasaka: *Proceedings of the 3rd KSME-JSME Thermal Engineering Conference*, (1996), III-255-III-260.
- (7) K. Takase and N. Ohtori: *Electrochemistry*, **67** (1999), 581–586.
- (8) K. Takase, I. Akiyama and N. Ohtori: to be published.
- (9) R. L. Mozzi and B. E. Warren: *J. Appl. Cryst.*, **2** (1969), 164–171.
- (10) M. Okuno and K. Kawamura: *J. Non-Cryst. Solids*, **191** (1995), 249–259.
- (11) P. P. Ewald: *Ann. Phys.*, **64** (1921), 253–287.
- (12) C. A. Angell: *J. Chem. Phys. Solids*, **49** (1988), 863–871.
- (13) I. Okada, Y. Matsui and K. Kawamura: *Nippon Kagaku Kaishi*, **6** (1982), 910–919.
- (14) G. V. Paolini, P. J. D. Lindan and J. H. Harding: *J. Chem. Phys.*, **106** (1997), 3681–3687.
- (15) P. J. D. Lindan and M. J. Gillan: *J. Phys.: Condens. Matter*, **3** (1991), 3929–3939.