Glass Transition Temperatures Studied by MD Simulation of Some Alkali Metasilicates

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GLASS TRANSITION TEMPERATURES STUDIED BY MD SIMULATION OF SOME ALKALI METASILICATES

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Molecular dynamics simulation of some alkali metasilicates (M_2SiO_3, M = Li, Na, K) was performed to compare glass transition temperatures, T_g, defined in various ways. The potential parameters derived from *ab initio* MO calculations were used and found to reproduce the inflection of *V-T* relation on cooling the system. The T_g defined by the inflection point corresponds well to that defined by geometrical changes of coordination polyhedra found in previous work. The self-diffusion coefficients of the alkali ions in higher temperature regions were shown to be related to the amount of free volume in these systems.

KEY WORDS: MD simulation, alkali metasilicates, glass transition temperature, diffusion coefficients

INTRODUCTION

Molecular dynamics simulation (MD) was performed for alkali metasilicate systems (M_2SiO_3, M = Li, Na and K). The potential parameters derived from the *ab initio* MO calculations [1] were used in the present work. These reproduce the crystal structures of Li_2SiO_3 and Na_2SiO_3 at constant pressure while those for the potassium salt have been chosen to reproduce the density and structure of a K_2SiO_3 melt and used to predict the crystal structure of K_2SiO_3.

In previous MD studies using empirical potential parameters [2, 3], a definition of glass transition temperature in terms of a structural change (geometrical change in the coordination polyhedra) was proposed and its relation with dynamical properties were examined. From a thermodynamical point of view, the glass transition temperature, T_g is usually defined as an inflection point of volume-temperature (*V-T*) relation and/or of enthalpy-temperature (*H-T*) relation, while, other definitions of T_g based on the changes in dynamical properties have also been proposed.

In the present study the inflection point for the molar volume has been derived for the alkali metasilicates. The temperature at the inflection point corresponds well to the geometrical change in the coordination polyhedra previously obtained. It has

further been found that the self-diffusion coefficients of the alkali ions in the melts depend on the molar volume at the inflection points in a similar manner to those of dense hard sphare liquids.

Since the present potential parameter sets can reproduce the densities of liquids, glasses and crystals within an error of 10%, these are expected to be good enough to reproduce the properties near the glass transition region, including the inflection of the V-T plot.

METHOD

A Gilbert-Ida type potential function with an r^{-6} term was used for the simulation. Each system was equilibrated at 4000 K starting from a random configuration. Then the system was sequentially cooled down to 0 K under constant pressure (0.1 MPa). The chosen temperatures were 3000, 2000, 1673, 1173, 973, 700, 500, 300 and 0 K. A run of more than 4000 steps (1 step = 2-4 fs) was performed at each temperature (except 0 K). The density was obtained in the last 2000 step run.

Dynamic properties were examined at constant energy at the volume obtained in the NPT condition. The self-diffusion coefficients and self-parts of the van Hove function in the molten lithium metasilicate system were calculated from the subsequent 6000–10 000 steps run in a region between 1173 and 2000 K. Those in the molten sodium metasilicate system were also calculated from the subsequent 6000–10 000 steps run in a region between 973 and 1673 K. Those in the molten potassium metasilicate system were also calculated from the subsequent 6000–10 000 steps run in a region between 973 and 2000 K. The self-parts of the van Hove functions at 700 K were calculated from 100 000 steps run for the lithium salt and 50 000 steps run for the potassium salts.

RESULTS AND DISCUSSION

Molar volume $vs.$ temperature relations obtained by the simulation at constant pressure for the lithium, sodium and potassium salts are shown in Figure 1. Clear inflection points are observed at 830, 820 and 680 K, for the lithium, sodium, and potassium salts, respectively. These values are in satisfactory agreement with the experimental T_g values. (687 K for Li_2SiO_3 [4] and 693 K – extrapolated value – for Na_2SiO_3 [5].)

In a previous work using empirical potential parameters, saturation of local packing of oxygen atoms around alkali ions was observed in the lithium metasilicate system at constant energy, when the geometrical structures of coordination polyhedra of oxygen atoms around lithium ions were examined [2]. We suggested that this saturation would be a cause of the inflection of V-T relation if the system is at constant pressure. This statement is confirmed by this work, where the packing saturation occurs at nearly the same temperature as in the previous work and the inflection point is located in an expected range. At each temperature, the volume became constant within several pico-seconds at constant pressure, and this also suggests that the origin of the inflection is a change in local packing, which has short relaxation time. Thus the glass transition points defined by the inflection point of the V-T relation were confirmed to correspond to the saturation of local packing
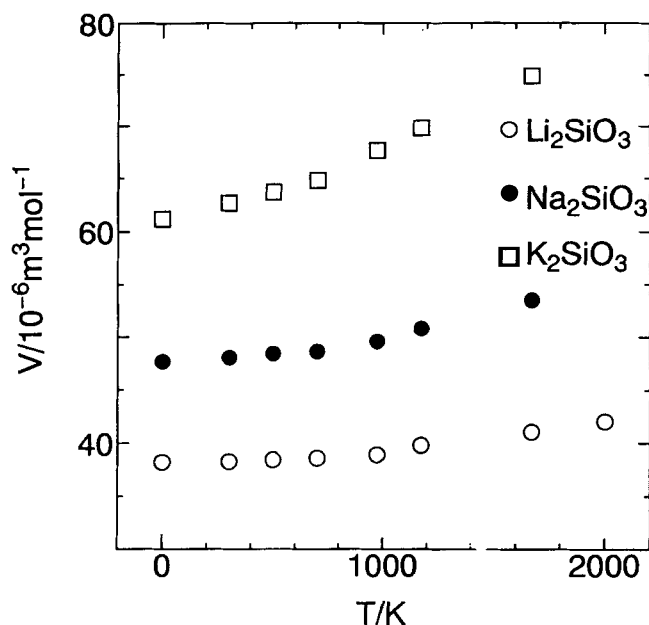
Figure 1 Temperature dependence of volumes for Li_2SiO_3, Na_2SiO_3 and K_2SiO_3.

of oxygen atoms. This explanation is also consistent with the empirical criterion for the glass transition presented by Wendt and Abraham [6]. They suggested that in a Lennard-Jones system the packing saturation of the first shell of nearest neighbour atoms occurs at the glass transition point assumed from the empirical parameter $R = g_{min}/g_{max}$. Because the rearrangement of long range structure needs much longer relaxation time, an additional volume change dependent on the cooling rate may occur on a much slower scale in an experimental glass formation.

The structure at 0 K corresponds to the local minimum energy one. Therefore, the atoms in glass vibrate around the local minima while those in liquid deviate from the minimum energy positions.

Dynamical properties for the alkali metasilicates have been examined. The self-parts of van Hove function, $4\pi r^2 G_s^\alpha(r, t)$, for the lithium and potassium ions at 1673 K and 700 K are shown in Figure 2.

$$G_s^\alpha(\mathbf{r}, t) = (1/N_\alpha) \sum_{i=1}^{N_\alpha} \langle \delta(\mathbf{r}_i(t) - \mathbf{r}_i(0) - \mathbf{r}) \rangle, \tag{1}$$

In both salts, the first peaks rapidly decay at 1673 K and attain to the hydrodynamic limits within 10 ps. The circles in Figure 2(a) represent the calculated values of $4\pi r^2 G_s^M(r, t)$ at 12.8 ps by the equation

$$G_s(r, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp(-r^2/4Dt). \tag{2}$$

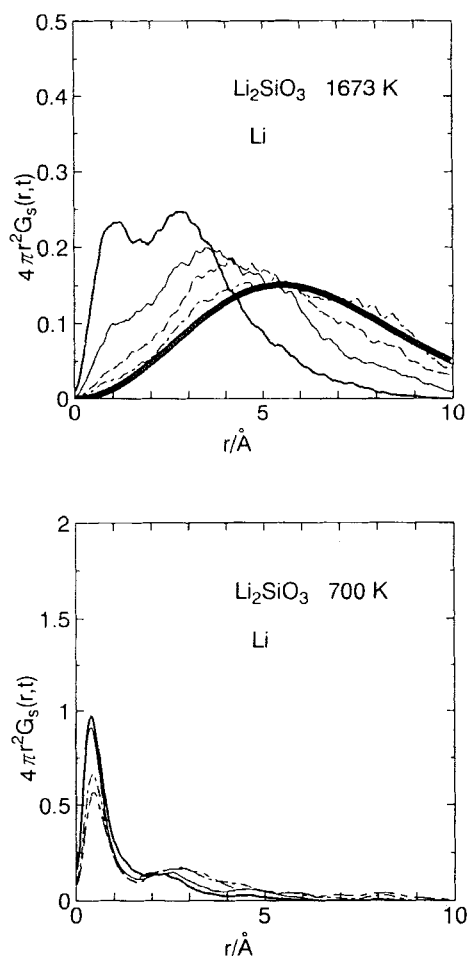The second peaks due to jump motions of alkali ions were found at 700 K. The

Figure 2(a)   Self-parts of van Hove functions, $4\pi r^2 G_s^M(r, t)$, *vs. r* for Li_2SiO_3. The curves from top to bottom for the first peak at 1673 K correspond to t = 3.2, 6.4, 9.6 and 12.8 ps, respectively. The curves from top to bottom at 700 K correspond to t = 48, 96, 192 and 288 ps, respectively.

behaviour of the lithium ion is almost the same as that in the previous simulation [3] based on the empirical potential parameters. Thus the existence of jump motion does not depend on the details of the potential surface but is a general property also for the coulombic systems. Diffusion of oxygen atoms is scarcely observed for the lithium salt at least during a 288 ps run, while jump motion of oxygen atoms occurs more frequently for the potassium salt. Such behaviour is expected for the salt having oxygen atoms more loosely packed at this temperature. Diffusion of the cations in these systems is expected to be related with the amount of free volume.

The self-diffusion coefficients of alkali ions in the liquid state can be well represented by Arrhenius type temperature dependence as shown in Figure 3 for the
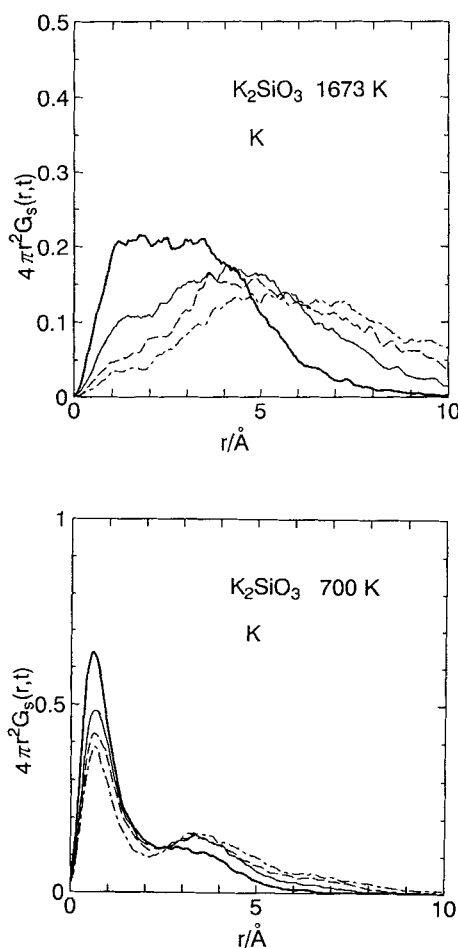
Figure 2(b) Self-parts of van Hove functions, $4\pi r^2 G_s^M(r, t)$, vs. r for K_2SiO_3. The curves from top to bottom for the first peak at 1673 K correspond to $t = 3.2$, 6.4, 9.6 and 12.8 ps, respectively. The curves from top to bottom at 700 K correspond to $t = 25.6$, 51.2, 76.8 and 102.4 ps, respectively.

Li_2SiO_3, Na_2SiO_3 and K_2SiO_3 systems. The result can be represented by the expression,

$$D = D_0 \exp(-E/RT), \qquad (3)$$

where, $D_0 = 2.05 \times 10^{-7}\,m^2\,s^{-1}$, $E = 50.63\,kJ\,mol^{-1}$ for Li_2SiO_3; $D_0 = 2.17 \times 10^{-7}\,m^2\,s^{-1}$, $E = 47.63\,kJ\,mol^{-1}$ for Na_2SiO_3, and $D_0 = 6.50 \times 10^{-8}\,m^2\,s^{-1}$, $E = 29.10\,kJ\,mol^{-1}$ for K_2SiO_3, where R is the gas constant. The expression is inapplicable for the low-temperature region and the temperature dependence may be described more accurately by a modified form of the Arrhenius equation
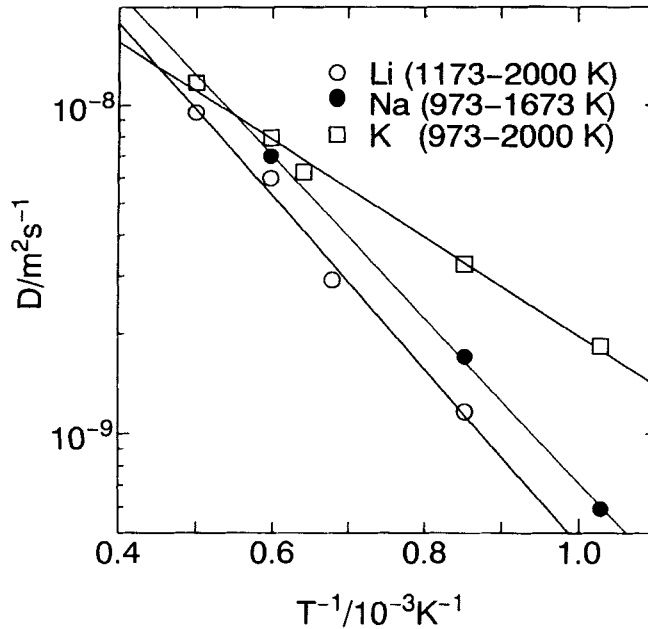
Figure 3 Temperature dependence of diffusion coefficients in Li_2SiO_3, Na_2SiO_3 and K_2SiO_3 systems.

$$D = D_0 \exp\left(\frac{k}{T - T_0}\right), \qquad (4)$$

where T_0 is a temperature where the free volume is assumed to disappear according to the free volume model [7].

However, an exact determination of diffusion coefficients near the glass transition temperature is fairly difficult in MD because of small number of jump motions and time dependent character of the mean square displacement [3].

Thus the results in the present work are discussed as a function of the volume with reference to the following literature [8]: Dymond used Enskog's expression for transport coefficients of dense hard spheres corrected for the correlated motions. He suggested that analytical relationship for the self-diffusion coefficient of a dense liquid was,

$$D = (2.306/V_0^{2/3})(T/M)^{1/2}(V - 1.384V_0), \qquad (5)$$

where D, T and V are in units of $10^{-9} m^2 s^{-1}$, K and $10^{-6} m^3$, respectively. M is the molar mass and $V_0 = N\sigma^3/2^{1/2}$ the molar volume of close-packed hard spheres with a diameter σ, where N is the Avogadro number.

Experimental data on the density, the diffusion coefficient and the viscosity of some molten salts were examined by van Loef [9]. The diffusive transport in some monovalent molten salts was well represented in a similar manner to the hard sphere system. Figure 4 shows the relationship between the diffusion coefficients of the alkali ion scaled by $T^{1/2}$ and volume in the present systems, where V_{T_g} defined by
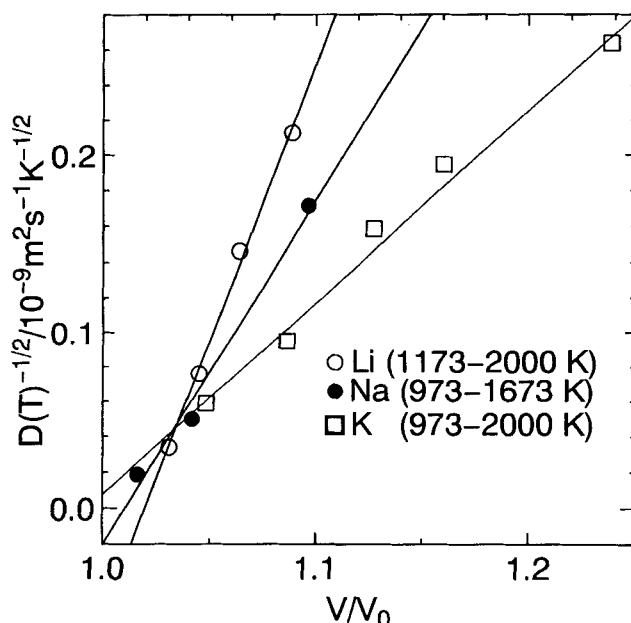
Figure 4 Scaled diffusion coefficients *vs.* V/V_0 in Li_2SiO_3, Na_2SiO_3 and K_2SiO_3.

the inflection point is taken as V_0. When the self-diffusion coefficients scaled by $T^{1/2}$ are plotted against the V/V_0, the result for each salt can be represented well by the following expression,

$$D = D_0'' / V_0 \times (T)^{1/2}(V - f \times V_0),\qquad(6)$$

where $D_0'' = 3.135 \times 10^{-9}\,m^2\,s^{-1}\,K^{-1/2}$ and $f = 1.02$ for the Li salt, $D_0'' = 1.950 \times 10^{-9}\,m^2\,s^{-1}\,K^{-1/2}$ and $f = 1.01$ for the Na salt, and $D_0'' = 1.089 \times 10^{-9}\,m^2\,s^{-1}\,K^{-1/2}$ and $f = 0.99$ for the K salt.

The self-diffusion coefficients of the alkali ions depend on the amount of free volume just like in the short range potential system. An extrapolated value of D becomes 0 when V/V_0 becomes ~ 1 in Figure 4. This point can be considered as a glass transition point defined in terms of the amount of free volume. However, it should be noted that the relation cannot be extrapolated to the glass transition region, because the jump motions of alkali ions become predominant in this region and residual diffusion of oxygen by the jump motion cannot be neglected, either.

The self-diffusion coefficients are sensitive to the volume of the system and hence to the used potentials; the potential parameters in this work are not necessarily sufficient to reproduce the self-diffusion coefficients in the real systems, as, for example, the thermal expansion coefficient for the lithium salt is considerably smaller than the experimental one [1].

The T_g defined by the inflection point well corresponds to that defined by the geometrical changes of coordination polyhedra found in the previous work. The saturation of local packing of oxygen atoms is also related to the diffusion

coefficients, although it seems that the T_g values defined by structural change and dynamical change are not necessarily equal.

Acknowledgement

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