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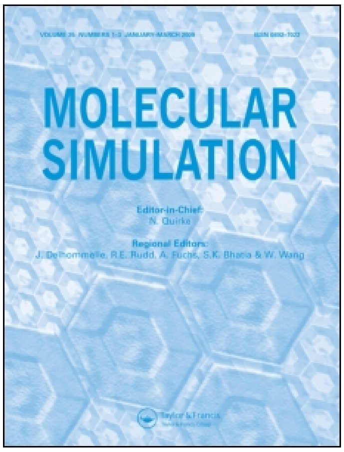

Molecular Simulation

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A MOLECULAR DYNAMICS SIMULATION OF $Na_2O{\cdot}2SiO_2$ - $K_2O{\cdot}2SiO_2$ MELTS - EFFECT OF BASIC CELL SIZE

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A pseudo-binary alkali disilicate liquid system, $Na_2O{\cdot}2SiO_2$ - $K_2O{\cdot}2SiO_2$, was investigated by means of molecular dynamics (MD) simulations. Enthalpy of mixing, diffusion coefficient of component ions, etc. revealed their non-linear mixing properties. The negative deviation of enthalpy of mixing was observed by the present MD calculations as well as by the experimental results.

The behaviour of the systems with different number of atoms (450:small and 900:large) in a MD basic cell was investigated, and it was concluded that the small system is insufficient to investigate both static and dynamic properties with the present interatomic potential model.

KEY WORDS: Molecular dynamics simulation, alkali silicate, oxide melt, mixing property

1. INTRODUCTION

Investigations of multi-component oxide liquid systems by means of molecular dynamics (MD) simulations are desired in the fields of earth sciences, glass technologies, metal refinements, inorganic material developments, etc. Since most of the liquids exist only at very high temperature, the experimental investigations of the materials have not presented the detailed information sufficiently. Furthermore, silicate liquid is one of the most complex systems in terms of the atomistic structures.

Kieffer and Angell [1] calculated the enthalpy of mixing of binary silicates, MO–SiO_2 and M_2 O–SiO_2, using systems containing relatively small number of ions (250 to 300 ions in an MD basic cell) with a rigid ion model. They claimed that the system (except those with high SiO_2 content) remained "ergodic" to below 2000 K in terms of diffusivity of ions. It is considered that the effectiveness of sampling in MD is difficult to test properly especially for silicate systems because of the strong Si–O bond and of the large complex Si–O anion clusters. The small systems might have poorer behaviour than expected due to the periodic boundary conditions.

Table 1 Potential energy parameters

ION	*z*	*a/Å*	*b/Å*
O	−2	1.629	0.085
Si	4	1.012	0.080
Na	1	1.260	0.080
K	1	1.595	0.080

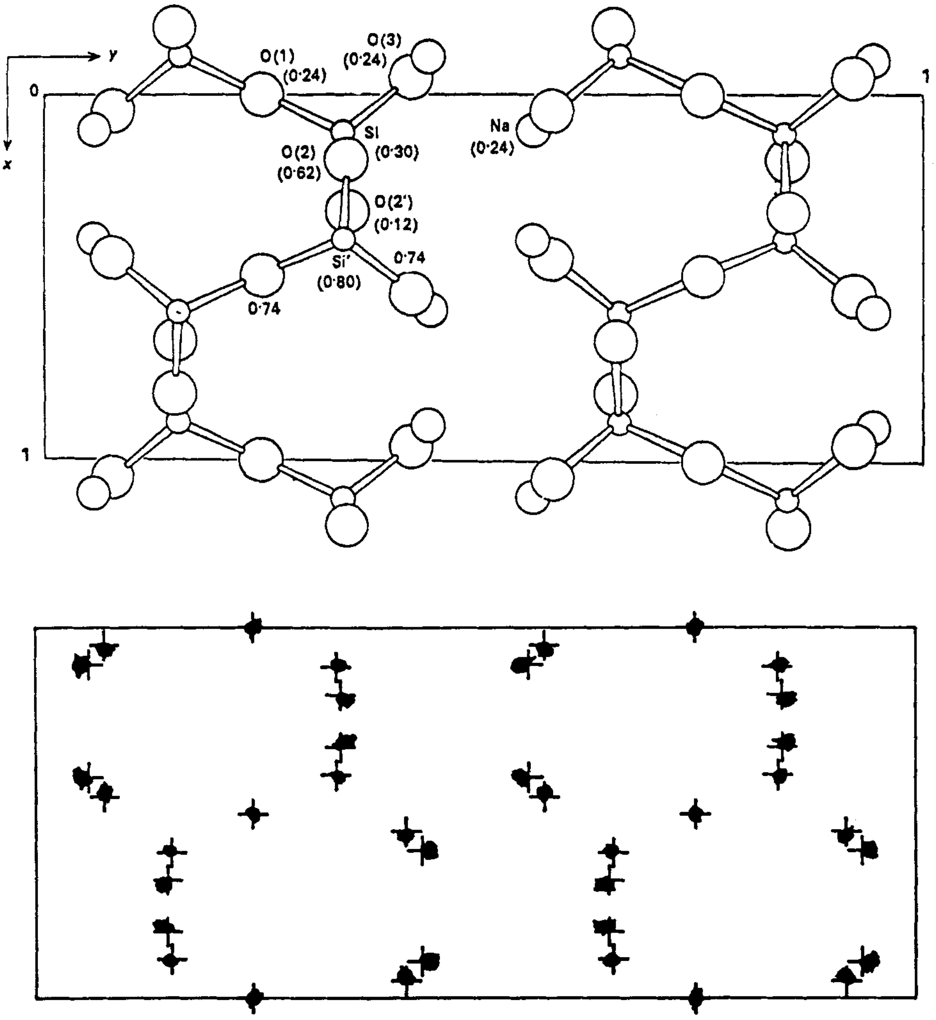

Figure 1 The trajectories of atom motion in the MD calculation of α-$Na_2Si_2O_5$ (lower). The crosses are the atomic positions determined by x-ray crystal structure analysis. The upper figure is the crystal structure from the literature [8]

Among silicate liquid systems, the properties of the systems Na_2 O·$2SiO_2$-K_2 O·$2SiO_2$ are relatively well known because of the low melting temperature and of the chemical simplicity. The thermodynamic properties of mixing were reported in several papers [2,3,4]. All of these presented the negative excess enthalpy of mixing.

In the present paper, we investigate the reproducibility of the thermodynamic properties using a simple rigid ion model, and obtain structural details of multicomponent silicate liquids. Effects of the MD basic cell size on mixing properties are also examined.

2. INTERIONIC POTENTIALS

The two-body central force interionic potential model of the Born-Mayer-Huggins type was adopted in this study. The function is composed of two terms, i.e. electrostatic and short range repulsion terms:

$$u(r_{ij}) = z_i z_j e^2/4\pi\varepsilon_0 r_{ij} - f_0 \cdot (b_i + b_j) \exp((a_i + a_i - r_{ij})/(b_i + b_j)),$$

where r_{ij} is the separation between ions i and j, ε_0 the permittivity of vaccum, e the elementary electric charge (C), z_i the effective valence of ion i and $f_0 = 6.9472 \times 10^{-11}$ N for unit adaptation. The parameters a_i and b_i used in this study are the part of the parameter set of the previously determined model [5] which is composed of the parameters for B, O, F, Na, Mg, Al, Si, K, Ca, Cl ions, etc., and was determined so as to maintain many crystal structures properly, such as SiO_2 (low-quartz, stishovite), Mg_2SiO_4 (forsterite, spinel), $MgSiO_3$ (orthopyroxene, perovskite, ilmenite), Al_2O_3 (corundom), Al_2SiO_5 (sillimanite), etc. using molecular dynamics calculations. This model was applied to Na_2O–B_2O_3 melt/glass systems successfully [6], and also used to investigate the viscosity of $Na_2O{\cdot}2SiO_2$ melt [7]. The parameters are listed in Table 1.

To test this parameters, the MD calculation with a fixed basic cell was carried out for α-$Na_2Si_2O_5$ crystal. The mean squared displacements (m.s.d, averaged for 2.5 fs) of ions from the positions determined by the x-ray crystal structure analysis [8] are 0.033 Å^2, 0.025 Å^2, and 0.039 Å^2 for oxygen, silicon, and sodium ions, respectively.

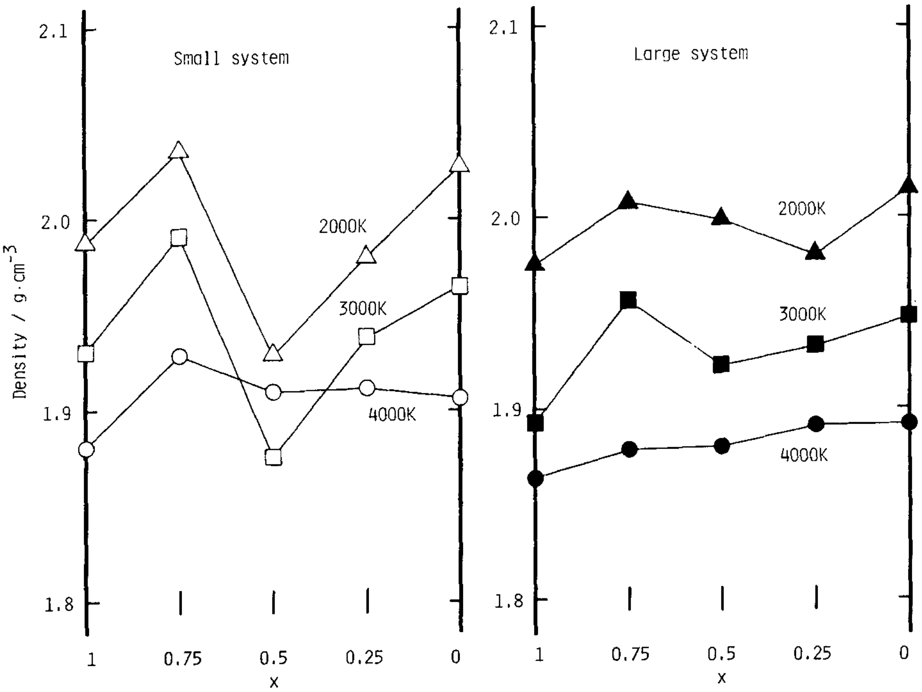

Figure 2 The density-compositon relations of $xNa_2O{\cdot}(1-x)K_2O{\cdot}2SiO_2$ melt in MD calculation. The data of the small (left) and large (right) systems at 4000 K, 3000 K and 2000 K are plotted.

The trajectories of ion motions in the MD-derived crystal structure are displayed in Figure 1. This figure and the m.s.d. values show that the parameters of the interatomic potential model are satisfactory to reproduce atomistic structures of the crystal and suggest that structures and some properties of melts/glasses with similar compositions are also reproduced.

3. COMPUTATIONAL PROCEDURES

The MD program (MDORTHO) developed by the author was used throughout this study. The Verlet alorithm for ion motion and the Ewald method for the summation of electrostatic interactions were used in the programs. The optimal gaussian parameter in the Ewald method was calculated in the MD programs at each step automatically. Temperature and pressure are controlled by means of scaling of ion velocities and basic cell parameters. The shape of a basic cell was restricted in a form of rectangular parallelepiped for the fast computation. The results by this program was confirmed to be much the same with ones by the constant temperature and pressure MD procedures [9,10].

The total numbers of ions in MD basic cells are 450 (the small system) and 900 (the large system) where the basic cell edges are about 20 Å and 25 Å respectively. The compositions are $x = 1, 0.75, 0.5, 0.25$ and 0 in terms of $x\mathrm{Na_2O}\cdot(1-x)\mathrm{K_2O}\cdot 2\mathrm{SiO_2}$. The step time is 2 fs throughout the MD calculations. The initial structure of each system was randomly generated and the system was equilibrated at 4000 K for more than 10 ps, then the data were collected for 10 ps for the small systems and for 6.4 ps for the large systems at each 1000 K down to 2000 K. The cooling rate was −500 K

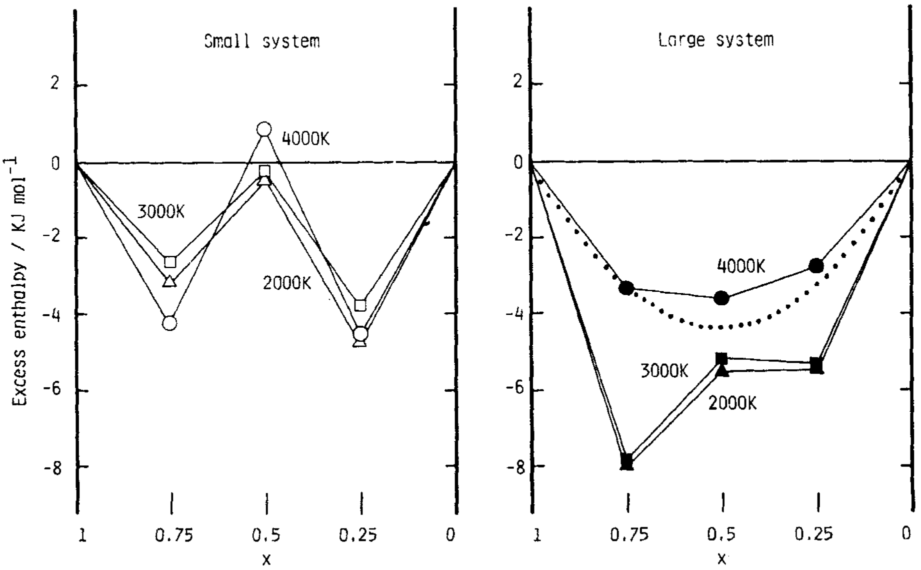

Figure 3 The enthalpy of mixing of liquids in the system $x\mathrm{Na_2O}\cdot(1-x)\mathrm{K_2O}\cdot 2\mathrm{SiO_2}$. Those of the small (left) and large (right) systems are displayed separately. The dotted line in the right figure is the experimentally determined enthalpy of mixing at 1373 K [3]

Table 2 Internal energies, E (kJ mol^{-1}) and the standard deviation (1σ) in parentheses at 2000 K. The molecule is taken as $xNa_2O \cdot (1-x)K_2O \cdot 2SiO_2$.

	Internal energy (1σ)/kJmol^{-1}	
Composition x	*Small system*	*Large system*
1	− 11932.5 (2.3)	− 11927.7 (1.8)
0.75	− 11906.3 (2.5)	− 11907.7 (1.8)
0.5	− 11874.3 (2.7)	− 11876.9 (1.5)
0.25	− 11849.1 (2.3)	− 11848.6 (1.7)
0	− 11815.3 (2.4)	− 11814.8 (1.7)

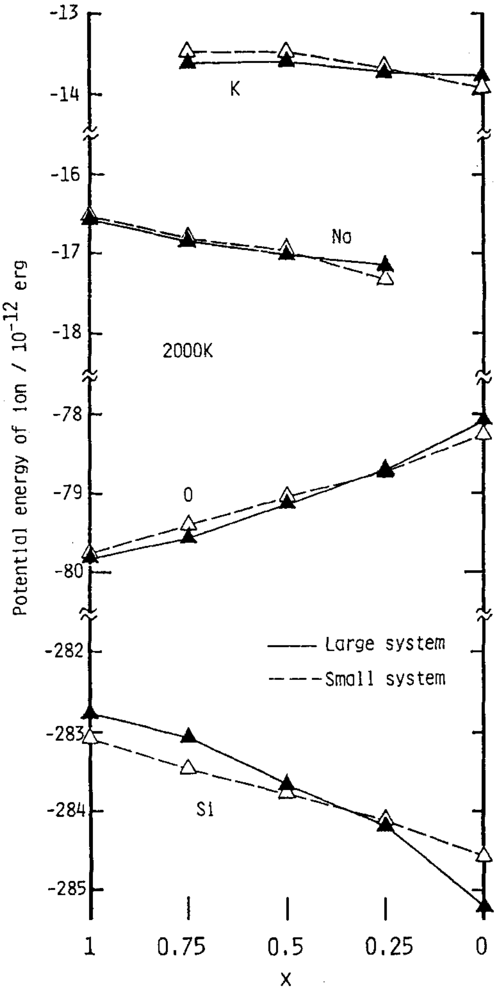

Figure 4 Variations of potential energies of component ions in $xNa_2O \cdot (1-x)\ K_2O \cdot 2SiO_2$ melt againt composition at 2000 k.

– 500 K per 1 ps for all systems. After reaching each target temperature, several pico seconds of the calculation were spent for the equilibration of the system at the temperature.

4. RESULTS AND DISCUSSION

The density-composition relations are displayed for temperatures 4000 K, 3000 K and 2000 K and for both small and large systems in Figure 2. The curves are fairly irregular for the small systems comparing with those of the large systems. For the large systems the equilibration of the structure from the initial configulation were carried out significantly better than those of the small systems.

Enthalpy of mixing also shows similar behaviour to that of the density (Figure 3).

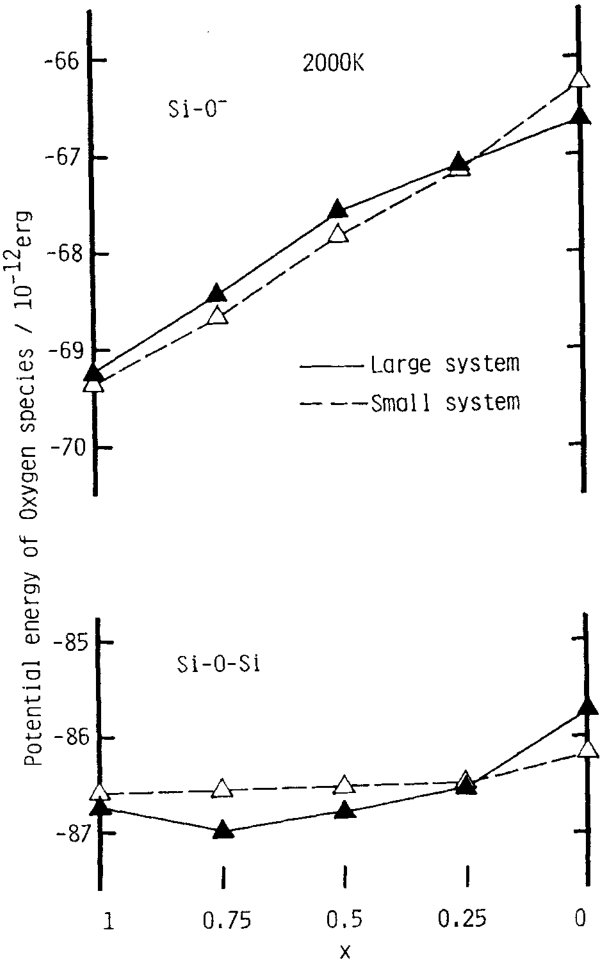

Figure 5 Variations of oxygen potential energies of two species, i.e. bridging and non-bridging ones in $xNa_2O{\cdot}(1-x)\ K_2O{\cdot}2SiO_2$ melt at 2000 K.

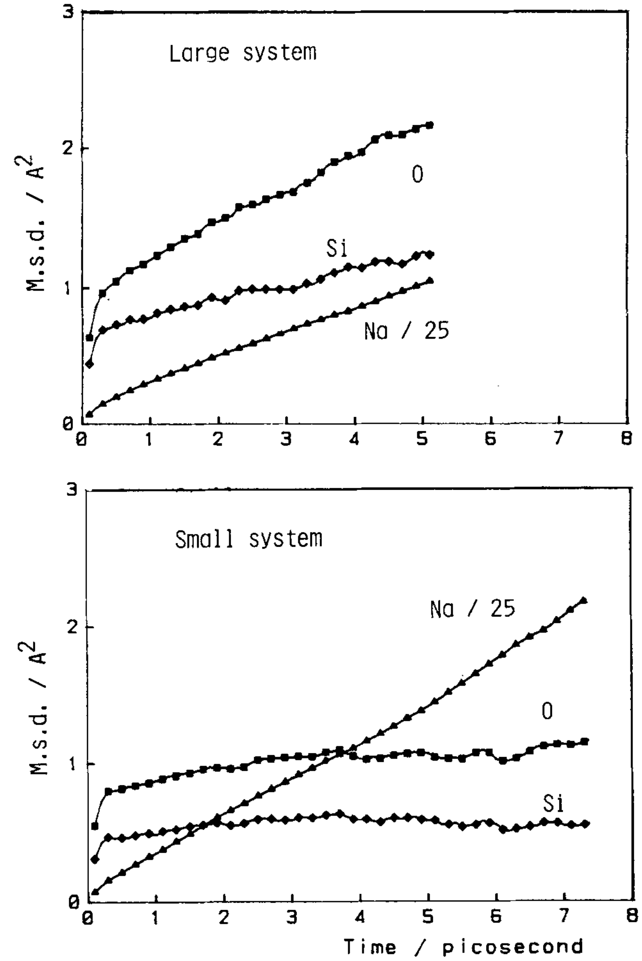

Figure 6 Plot of mean square displacements (m.s.d.) of atoms in the small and large systems of $Na_2O{\cdot}2SiO_2$ melts at 3000 K.

The large systems is considered to represent the equilibrium properties better than the small one. Figures 2 and 3 suggest that the sampling of the small system was not carried out properly even at 4000 K. It is suggested that in the small system the motion of Si–O anionic structures is restricted by the relatively small basic cell.

The values of internal energies of the small and large systems are listed in Table 2. The difference between the systems is considerable comparing with the value of the excess enthalpies of mixing (Figure 3). The negative deviation is produced by the compositional variaiton of average potential energies of oxygen ions (Figure 4). On the other hand, that of silicon has a positive deviation. There are two kinds of oxygens, bridging (O^0, involved in Si–O–Si) and non-bridging (O^-) oxygens, in the MD systems. The O^0 is responsible for the negative deviation of enthalpy of mixing (Figures 3 and 5), while there is a considerable linear change of the potential energy of O^- against the Na–K compositional change.

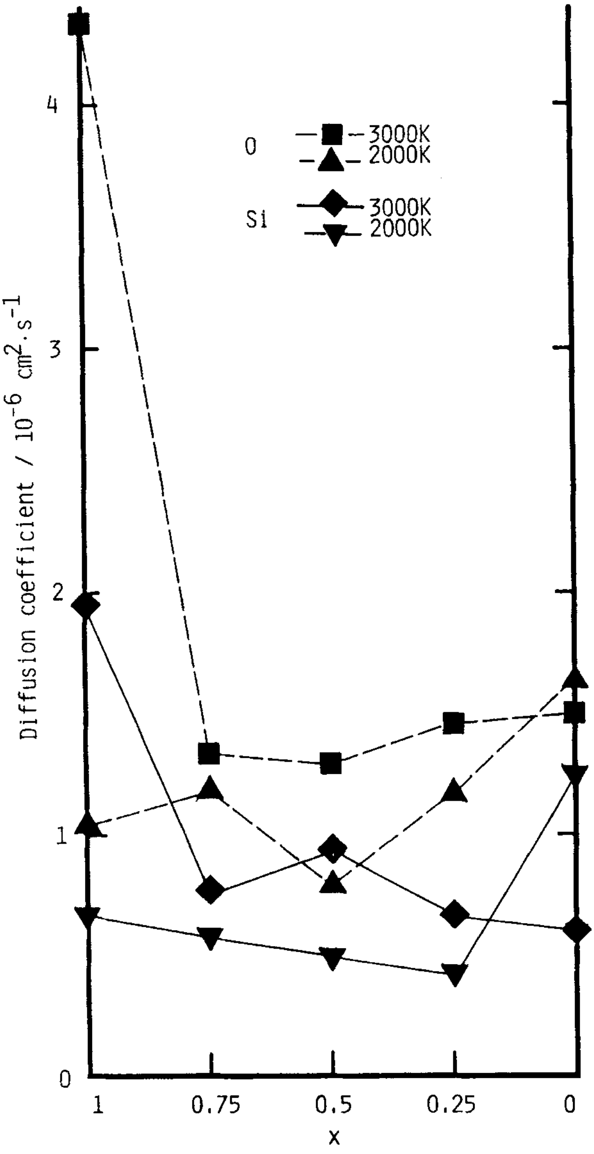

Figure 7 Diffusion coefficients of oxygen and silicon atoms for different compositions of the large system of $x\text{Na}_2\text{O}\cdot(1-x)\ \text{K}_2\text{O}\cdot 2\text{SiO}_2$ melt at 2000 K and 3000 K.

The plots of mean square displacements against time show that the diffusivities of network former ions (Si and O) in the small system are much smaller than those of the large system at the same temperature (Figure 6). Diffusion coefficients for the large systems are shown in Figure 7. The diffusivity of Si and O of various compositions at 3000 K and 2000 K suggests that the mechanism of diffusion may be different between these temperatures. The diffusion coefficients of Na and K at 2000 K (Figure

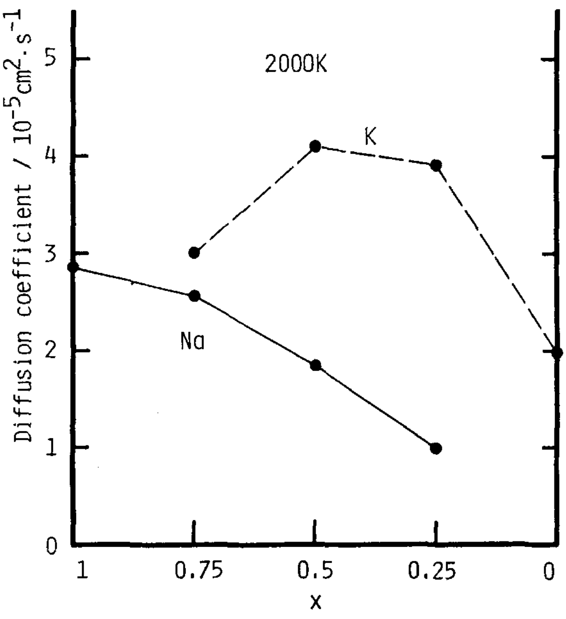

Figure 8 Diffusion coefficients of sodium and potassium atoms for different compositions of the large system of $x\mathrm{Na_2O}{\cdot}(1-x)\ \mathrm{K_2O{\cdot}2SiO_2}$ melt at 2000 K.

8) suggest the existence of the behaviour like Chemla effect [11] in the silicate liquid mixtures.

Populations of $\mathrm{SiO_4}$ tetrahedral species (Q_0 – Q_4) are calculated (Table. 3). The Q_n represents a type of $\mathrm{SiO_4}$ tetrahedron where n is the number of bridging oxygens in the $\mathrm{SiO_4}$ tetrahedron. The distributions are broader than those determined by the ^{29}Si-MAS-NMR measurements for glasses with the same compositions [12,13]. Nearly 80% and more than 85% of silicons are in the Q_3 form in $\mathrm{Na_2O{\cdot}2SiO_2}$ and $\mathrm{K_2O{\cdot}2SiO_2}$ glasses respectively [13]. The difference of the states, i.e. liquid and glass, must be noted.

Ring size distributions in Si–O network which are not available by experiments, are

Table 3 Silicate species, Q_n, in $x\mathrm{Na_2O}{\cdot}(1-x)\mathrm{K_2O{\cdot}2SiO_2}$ melt at 2000 K. The figures are in percentages.

Composition	*x*	*1*	*0.25*	*0.5*	*0.75*	*0*
	Q_0	0.0	0.0	0.0	0.0	0.0
450	Q_1	2.0	2.0	3.0	3.0	3.0
system	Q_2	25.0	25.3	23.1	23.0	23.6
	Q_3	42.0	41.7	44.0	44.3	40.3
	Q_4	30.0	31.1	30.0	29.8	33.1
	Q_0	0.5	0.5	0.5	0.5	0.5
900	Q_1	4.0	4.8	4.0	4.5	3.5
system	Q_2	20.2	19.3	21.5	20.5	20.7
	Q_3	43.0	44.4	42.9	39.1	42.1
	Q_4	32.3	31.0	31.2	34.4	33.2

Table 4 Distribution of Si–O ring size forming Si–O network per 100 Si atoms. The composition x is from $x\mathrm{Na_2O}\cdot(1-x)\mathrm{K_2O}\cdot 2\mathrm{SiO_2}$.

System	*Ring size*	*Composition x*				
		1	*0.25*	*0.5*	*0.75*	*0*
Small system	3	1.0	2.0	1.0	2.3	2.1
	4	12.5	9.5	13.8	9.9	12.2
	5	12.8	14.2	15.6	16.4	18.1
	6	9.8	10.7	6.3	13.0	12.9
	7	12.5	9.8	14.5	13.0	14.0
	8	12.7	11.6	13.3	8.6	13.0
Large system	3	1.0	1.1	2.1	1.5	1.0
	4	12.3	9.7	7.5	15.8	15.7
	5	17.2	15.4	18.0	17.5	16.3
	6	12.9	12.4	12.0	9.8	15.6
	7	15.0	14.6	13.5	11.9	16.2
	8	12.8	10.8	11.0	15.6	14.9
	9	17.5	20.5	16.5	18.3	16.0

predicted for various compositions, systematically. The six membered rings are considered to be suitable for structures without network modifier cations at atmospheric pressure. It was considered that the number of both larger (larger than six membered) and smaller (smaller than six membered) rings increase when the larger cations are introduced in the network structures. There seems to be no systematic variation with composition in the present MD results in Table 4. The difference of the distribution between the small and large systems also is not significant.

5. CONCLUSIONS

The negative excess enthalpy of mixing was reproduced for the system $\mathrm{Na_2O{\cdot}2SiO_2} - \mathrm{K_2O{\cdot}2SiO_2}$ liquids by the molecular dynamics simulation.

The large and small systems behave differently in the density-composition relation, diffusion, etc. The small system is quite insufficient to investigate equilibrium properties by MD calculations. The large system could be still insufficient to calculate specially dynamic properties. Effectiveness of sampling in MD is also related to the strength of interactomic interactions. Further investigations are necessary to know the applicability of MD methods to silicate liquid/glass systems and ergodicity.

Acknowledgements

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