Structures of Melts and Glasses in The System NaF-BeF_2 from Molecular Dynamics Simulation†

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Structures of BeF_2 melt and galss are analogous to those of SiO_2 melt and glass consisting of BeF_4 tetrahedra joined at corners to form a continuous random network. It is widely accepted that when modifier ions such as alkali or alkaline earth ions are added to BeF_2, they enter the open network structure at interstitial sites and introduce various polymeric units of BeF_4 tetrahedra with nonbridging anions. The various physical properties such as viscosity[1,2], self-diffusion[3], and electrical conductance[4]of molten $NaF-BeF_2$ depend on the three-dimensional BeF_4 tetrahedral network characteristic of BeF_2. One of the most striking changes occurs in the viscosity resulting from the rupturing of -F- brinding in the three-dimensional BeF_4 tetrahedral network structure by the addition of modifier ions.

An X-ray study of melts of the $LiF-BeF_2$ system was performed by Vaslow and Narten[5]. We have also analyzed the structures of $NaF-BeF_2$ melts by X-ray diffraction method, including melts of compositions Na_2BeF_4[6] (923K), $NaBeF_3$[6] (743K) and $NaBe_2F_5$[7] (743K). Our results show that BeF_4 tetrahedral units exit as the fundamental structural unit in these melts. Molten Na_2BeF_4 contains mainly monomeric $(BeF_4)^{2-}$ with four unshared fluorine corners. Two Na^+ ions are situated in the following configurations around a BeF_4 tetrahedron: one of the two Na^+ ions occupies the corner-site position and the other occupies the edge-site. Dimeric $(Be_2F_7)^{3-}$ with one shared fluorine corner common to two BeF_4 tetrahedra appears in molten $NaBeF_3$. Furthermore, the obtained X-ray result suggests that ring anions such as $(Be_nF_{3n})^{n-}$ (n = 3, 4, 5 and 6) exist mainly in molten $NaBe_2F_5$.

Thanks to the development in high-speed computer technology, we can now caluculate the three-dimensional configuration of atoms in molten and/or glassy materials by molecular dynamics (MD) simulation. The MD method which involves numerical evaluation of the Newtonian equations of motion in model systems interacting particles in now a well established approach to the study of ionic salts[8]. During the past few years, an MD simulation of molten BeF_2, $LiBeF_3$ and LiF was performed by Rahman et al.[9], though the number of particles in the basic cell was much smaller than that in our study. More recently, Furuhashi et al.[10] investigated the structures and dynamic properties of molten $NaBeF_3$ and Na_2BeF_4 in some detail. In order to understand the melts and glasses in the system $NaF-BeF_2$, it is further necessary to discuss the detailed structures of the melts and glasses with various compositions by MD simulation.

The purpose of this investigation is to study the structures and the diffusion properties of molten and glassy BeF_2 and $NaBe_2F_5$ by molecular dynamic simulation. In addition, the obtained MD results are compared with the X-ray data of Vaslow et al. [5] and us[7] in both real and reciprocal space.

In the present study, the pair potential functions are assumed to consist of a simplifed Coulombic and a repulsive term:

$$\phi_{ij}=z_iz_je^2/r_{ij}+f_0(b_i+b_j)\exp[(a_i+a_j-r_{ij})/(b_i+b_j)], \quad (1)$$

where, z_i: the formal charge numbers of ion i (e.g., + 2 for Be^{2+}ion),
e: the unit charge,
r_{ij}: the distance between ions i and j,
f_0: a force constant arbitrarily taken here to be 1kcal $mol^{-1}\mathring{A}^{-1}$(=6.948×$^{-6}$ dyn),
a_i, b_i: the crystal radius and compressibility of ion i, respectively.

We empirically determined the potential parameters. A cube (the basic cell) was assumed for all MD calculations. The edge length of the basic cell was

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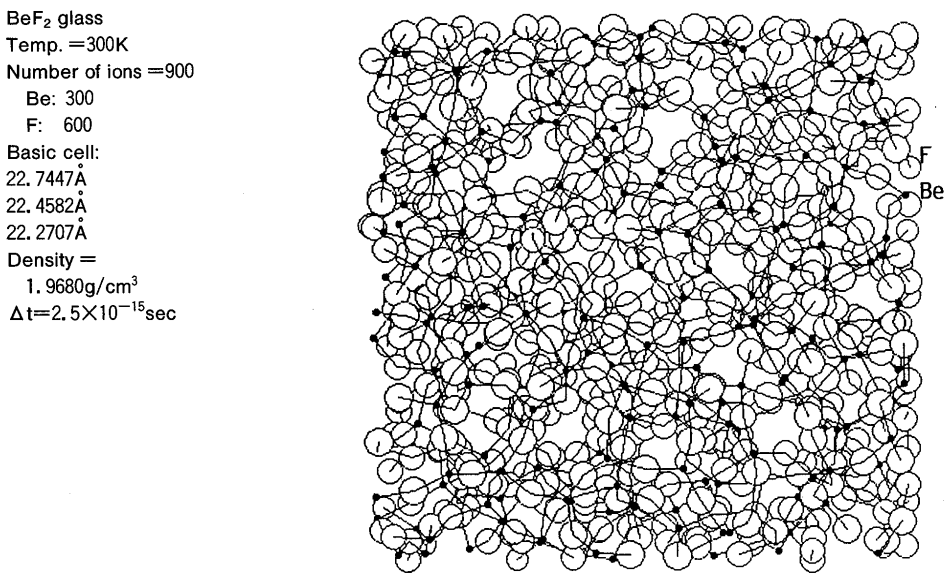

Fig. 1 Structural view of a typical instantaneous configuration of MD-simulated BeF_2 glass at 300K.

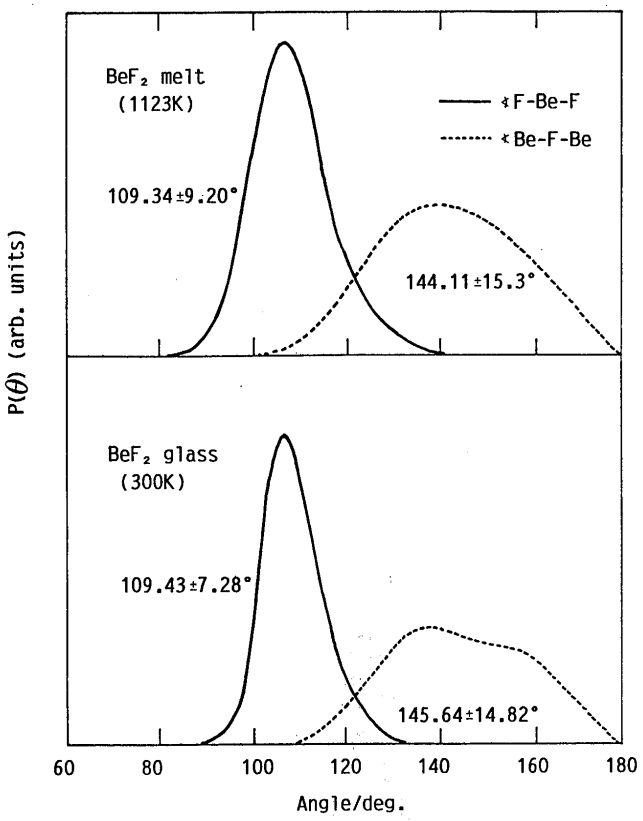

Fig. 2 Probability distribution of angles ∢F-Be-F and ∢Be-F-Be for MD-simulated BeF_2 melt at 1123K and glass at 300K.

calculated from the observed density values of molten and glassy BeF_2[5,11] and $NaBe_2F_5$[1,2]. The number of particles within a basic cell was 900 ($300Be^{2+}$, $600F^-$) for BeF_2 and 480 ($60Na^+$, $120Be^{2+}$, $300F^-$) for $NaBe_2F_5$. In evaluating the potential energy and the force, the Coulomic term was calculated by the Ewald method. The time increment Δt must be sufficiently short to satisfy the conditions of energy conservation. we choose here $\Delta t = 2.5\times10^{-15}$ sec which corresponds to a mean fluctuation of the internal energy smaller than 0.1 per cent. Our MD runs were made on a personal computer system - a NEC PC-9801RA (CPU80386 + WTK3167). For 900 particles, interacting via a Coulomb potential, a single time step cloud be done in about 30 seconds. Thus, a picosecond of fluid time required 500 minutes of CPU time, whereas a nanosecond would require 347 day! With super computers and more careful progrmming, a time step could probably be performed in 0.06 sec, perhaps even less, but eight hours of CPU time still be necessary for a nanosecond simulation. In most cases, the 3000 time steps after equilibrium were used for calculations of varius properties. The average temperatures for BeF_2 and $NaBe_2F_5$ melts were 1123K and 743K, respectively.

Figure 1 shows the structural view of a typical instantaneous configuration of BeF_2 glass at 300K from our MD simulation. As shown in this figure, Be^{2+} ions form nearly regular BeF_4 tetrahedra with a peak around 109° in the ∢F-Be-F angle distribution as shown in **Fig. 2**, coordinated by four fluorine ions, and each fluorine is shared by two tetrahedra in such a way that the BeF_4 tetrahedra are joined only at the corners. The ∢F-Be-F angle (109.43°) of the MD-simulated BeF_2 glass is almost equal to the bond angle (109.28°)of an ideal tetrahedraon and to that (109.5°)from the X-ray diffraction analysis [11]. In addition to showing the wide scatter of the intertetrahedral (∢Be-F-Be) angle, the angular analysis reveals that the mean bond angle is 145.64° and is in agreement with the X-ray data of SiO_2 glass reported by

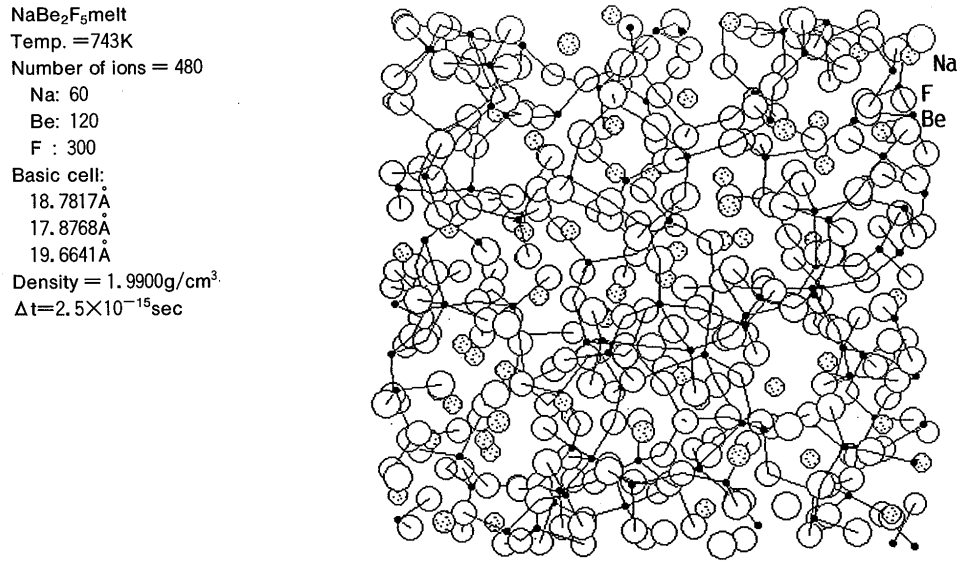

Fig. 3 Structural view of a typical instantaneous configuration of MD-simulated $NaBe_22F_5$ melt at 743K.

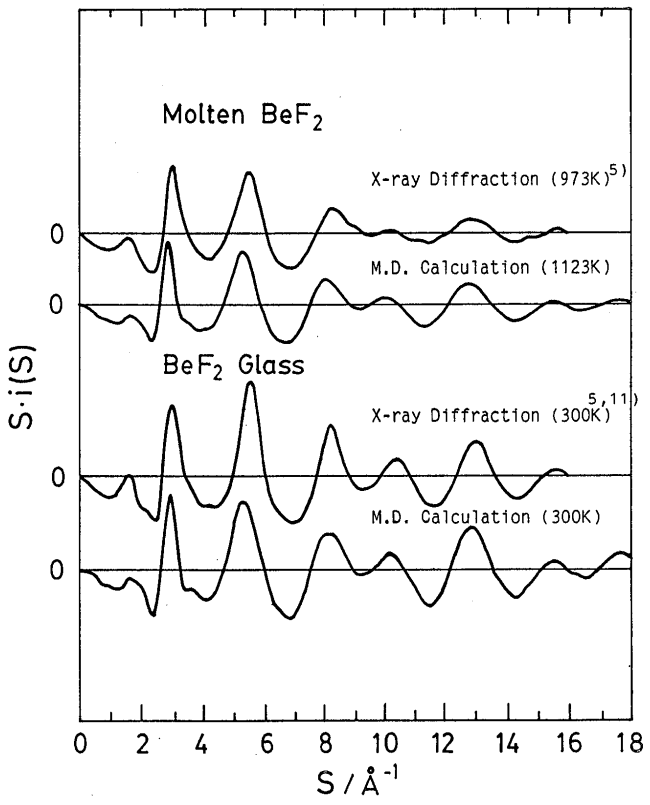

Fig. 4 Interference function curves S·i(S) of BeF_2 melt and glass obtained from MD simulation at 1123K and 300K and from X-ray data at 973K and 298K, respectively.

Mozzi and Warren[13]. We could not find the presence of defects[14] such as fivefold-coordinated Be and threefold-coordinated F etc. in the MD-simulated BeF_2 glass.

Figure 3 shows the structural view of a typical instantaneous configuration of molten $NaBe_2F_5$ at 743K. This result also indicates that BeF_4 tetrahedra persist as the fundamental structural unit in molten state, and that most of the BeF_4 tetrahedra are present as the polymerized fluoroberyllate ions such as $(Be_2F_7)^{3-}$ dimer (= 4.84%), $(BeF_3)^{1-}$ chain (= 17.00%), $(Be_2F_5)^{1-}$ (= 47.83%) and $(BeF_2)^0$ three-dimensional network unit (= 30.33%) by the addition of NaF. Our MD simulation result is in satisfactory agreement with X-ray data of the $NaBe_2F_5$ melt[7]. As shown in this figure, most of the Na^+ ions occupy various stable positions around the polymeric anions for holding electrostatic neutrality.

In order to compare the structural information obtained by our MD simulation with that obtained from X-ray diffraction data[5,7,11], we calculated the interference function S·i(s) in reciprocal space and the pair correlation function $g_{ij}(r)$ in real space from the MD results. In ordinary X-ray diffraction measurements, the scattering intensity of the X-ray beam is the primary information of the structure in reciprocal space. On the other hand, the primary information of MD simulation is the positions of ions as a function of time. Therefore, the instantaneous structure is the most straightforward way of presenting the result of MD-derived simulation. The pair correlation function for the ionic species i and j, $g_{ij}(r)$, is obtained from the positional data accumulated during the final equilibrium (in the actual computation, the distance interval, Δr, is taken to be 0.1Å.).

$$g_{ij}(r) = (V/N_iN_j)(n_{ij}(r)/4\pi r^2), \quad (2)$$

where, $n_{ij}(r)$: time-averaged number of ion pairs between i and j within a distance range from $r-\Delta r/2$ to $r+\Delta r/2$,

N_i: the number of ionic species i in the basic

cell,

v : the volume of the basic cell.

The running coordination number, $N_{ij}(r)$, which is important in characterizing the coordination state of ions, is given by

$$N_{ij}(r) = \sum_{r=0}^{r} n_{ij}(r)/N_i. \quad (3)$$

The interference function $S\cdot i(S)$ from the MD-simulated melt and glass can be calculated from the $g_{ij}(r)$ functions by Fourier transformation: S *is* the scattering vector given by

$$S = (4\pi \sin\theta)/\lambda, \quad (4)$$

where, λ : the incident X-ray wavelength.

The function $S\cdot i(S)$ can be obtained from the following equation:

$$S\cdot i(S) = (4\pi N/V)\{[\sum_i \sum_j N_i N_j f_i(S) f_i(S)]/$$

$$[\sum_{all} N_k f_k(S)]^2\}$$

$$\cdot \sum_{r=0}^{r} \sum_{ij} [r(g_{ij}(r)-1)\sin(Sr)], \quad (5)$$

where, $f_i(S)$: the atomic scattering factor of ionic species i.

Figure 4 shows a comparison between the calculated and observed[5,11] $S\cdot i(S)$. Unfortunately, it is considered that observed $S\cdot i(S)$[5,11] may contain some experimental errors, so that no quantitative discussion is possible. However, it can be concluded that the $S\cdot i(S)$ curves obtained by the MD simulation using equation (5) are in good agreement with those from X-ray diffraction both for BeF_2 melt and glass, as shown in Fig. 4.

The pair correlation functions $g_{ij}(r)$ and the distribution of the coordination number $N_{ij}(r)$ of the ionic pairs F-F, Be-F, Na-F, Be-Be, Be-Na and Na-Na in molten $NaBe_2F_5$ at 743K are illustrated in **Fig. 5.** The positions of the first peaks in the $g_{ij}(r)$ curves, that is, the distances of the nearest-neighbor i-j pairs are listed in **Table 1** in comparison with the corresponding values obtained from X-ray diffraction data[5,7,11]. These distances are in good agreement with results derived from X-ray diffraction[5,7,11].

Diffusion coefficients of ions Na^+, F^- and Be^{2+} were determined from mean square displacements of these ions by the following Einstein equation:

$$D_i = (1/6\tau N_i) \sum_i \langle[x_i(t)-x_i(t+\tau)]^2\rangle, \quad (6)$$

where, τ : an arbitrary time interval.

Figure 6 shows the mean square displacements plotted against time for the moltn $NaBe_2F_5$ at 743K. The self-

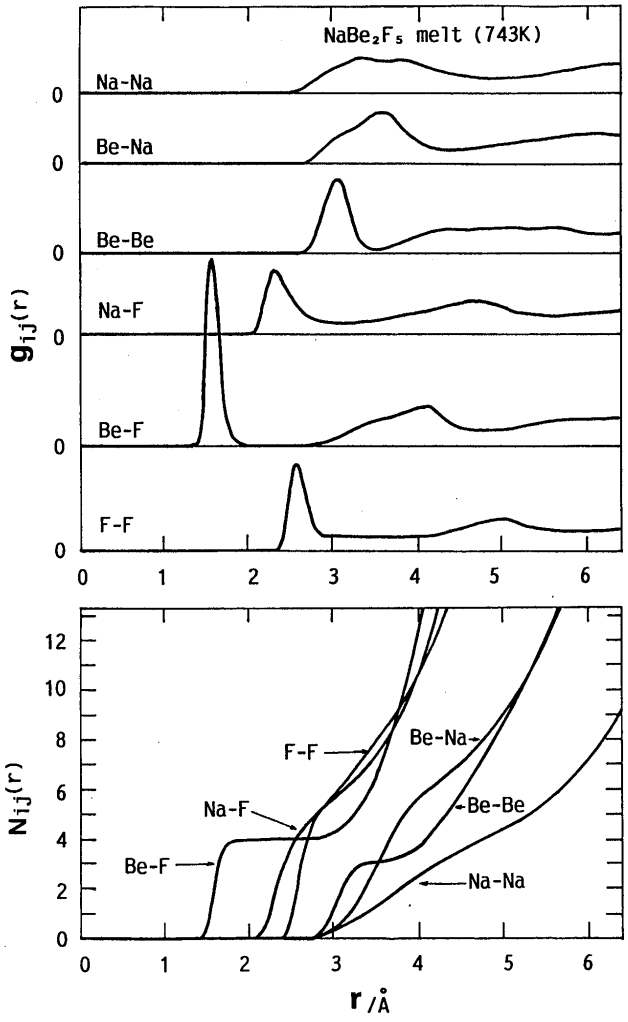

Fig. 5 Pair correlation functions $g_{ij}(r)$ and distribution of coordination number $N_{ij}(r)$ of ionic pairs F-F, Be-F, Na-F, Be-Be, Be-Na and Na-Na in MD-simulated $NaBe_2F_5$ melt at 743K.

Table 1 Average nearest-neighbor distances r_{ij} of ions j around any origin ion i from MD simulation and X-ray data[5,7,11].

	T (K)	i	j	r_{ij} (Å)	
BeF_2 melt	1123	Be	F	1.58	MD
		F	F	2.58	
		Be	Be	3.04	
	973	Be	F	1.589(9)	X-ray[5]
		F	F	2.544(7)	
BeF_2 glass	300	Be	F	1.58	MD
		F	F	2.56	
		Be	Be	3.10	
	298	Be	F	1.554(4)	X-ray[5,11]
		F	F	2.537(4)	
		Be	Be	3.037(5)	
$NaBe_2F_5$ melt	743	Be	F	1.58	MD
		Na	F	2.30	
		F	F	2.58	
		Be	Be	3.08	
		Na	Na	3.30	
	743±5	Be	F	1.55	X-ray[7]
		Na	F	2.20	
		F	F	2.55	

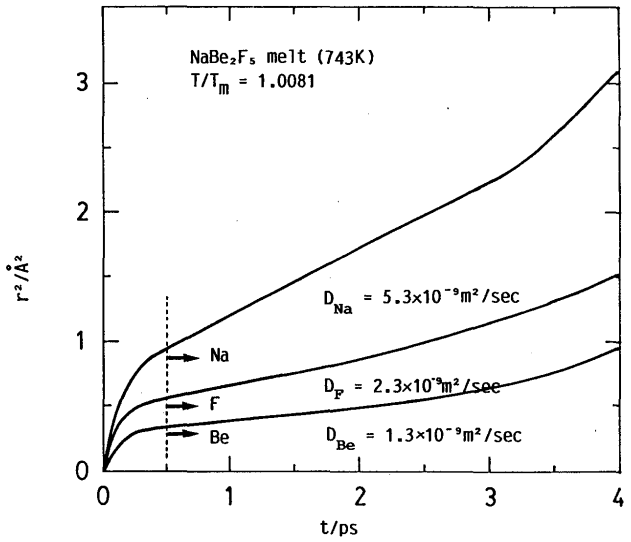

Fig. 6 Mean square displacements vs. time plots for Na^+, F^- and Be^{2+} of MD-simulated $NaBe_2F_5$ melt at 743K.

diffusion constants are $5.3 \times 10^{-9}m^2/sec$,$2.3 \times 10^{-9}m^2/sec$ and $1.3 \times 10^{-9}m^2/sec$ for ions Na^+, F^- and Be^{2+}, respectively.

We conclude that important characteristics of molten and glassy BeF_2 and $NaBe_2F_5$ are well reproduced by relatively small system of particles interacting with central ionic forces. We are confident that various physical properties of melts and glasses in the $NaF\text{-}BeF_2$ system can be calculated with good accuracy in our MD simulation.

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