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Structures of Melts and Glasses in The System NaF-BeF₂ from Molecular Dynamics Simulation†

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KEY WORDS : (NaF-BeF₂) (Sodium Fluoroberyllate) (Melt) (Glass) (Structural Analysis) (Molecular Dynamics Simulation)

Structures of BeF₂ melt and glasses are analogous to those of SiO₂ melt and glass consisting of BeF₄ 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 BeF₂, they enter the open network structure at interstitial sites and introduce various polymeric units of BeF₄ tetrahedra with nonbridging anions. The various physical properties such as viscosity^{1,2}, self-diffusion³, and electrical conductance⁴ of molten NaF-BeF₂ depend on the three-dimensional BeF₄ tetrahedral network characteristic of BeF₂. One of the most striking changes occurs in the viscosity resulting from the rupturing of -F- bridging in the three-dimensional BeF₄ tetrahedral network structure by the addition of modifier ions.

An X-ray study of melts of the LiF-BeF₂ system was performed by Vaslow and Narten⁵. We have also analyzed the structures of NaF-BeF₂ melts by X-ray diffraction method, including melts of compositions Na₂BeF₄⁶ (923K), NaBeF₃⁶ (743K) and NaBe₂F₅⁷ (743K). Our results show that BeF₄ tetrahedral units exist as the fundamental structural unit in these melts. Molten Na₂BeF₄ contains mainly monomeric (BeF₄)²⁻ with four unshared fluorine corners. Two Na⁺ ions are situated in the following configurations around a BeF₄ tetrahedron: one of the two Na⁺ ions occupies the corner-site position and the other occupies the edge-site. Dimeric (Be₂F₇)³⁻ with one shared fluorine corner common to two BeF₄ tetrahedra appears in molten NaBeF₃. 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 NaBe₂F₅.

Thanks to the development in high-speed computer technology, we can now calculate 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 is now a well established approach to the study of ionic salts⁸. During the past few years, an MD simulation of molten BeF₂, LiBeF₃ 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 NaBeF₃ and Na₂BeF₄ in some detail. In order to understand the melts and glasses in the system NaF-BeF₂, 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 BeF₂ and NaBe₂F₅ by molecular dynamic simulation. In addition, the obtained MD results are compared with the X-ray data of Vaslow et al.⁵ and us⁷ in both real and reciprocal space.

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

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

where, z_i : the formal charge numbers of ion i (e.g., +2 for Be²⁺ ion),
 e : the unit charge,
 r_{ij} : the distance between ions i and j ,
 f_0 : a force constant arbitrarily taken here to be 1 kcal mol⁻¹ Å⁻¹ (= 6.948 × 10⁻⁶ 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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BeF₂ glass
 Temp. = 300K
 Number of ions = 900
 Be: 300
 F: 600
 Basic cell:
 22.7447Å
 22.4582Å
 22.2707Å
 Density =
 1.9680g/cm³
 $\Delta t = 2.5 \times 10^{-15}$ sec

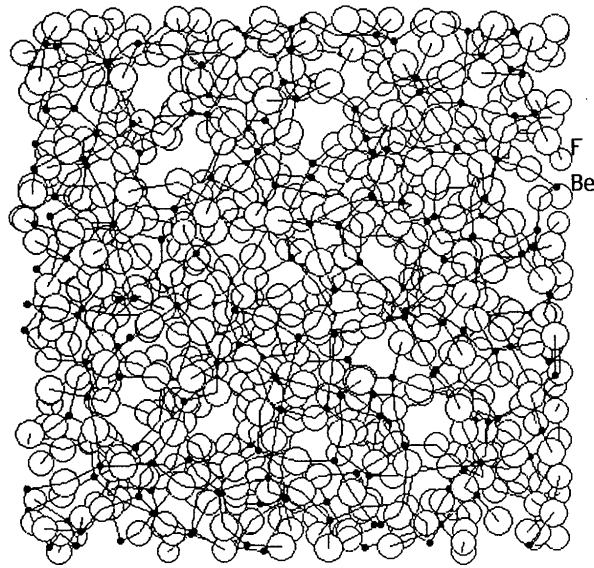


Fig. 1 Structural view of a typical instantaneous configuration of MD-simulated BeF₂ glass at 300K.

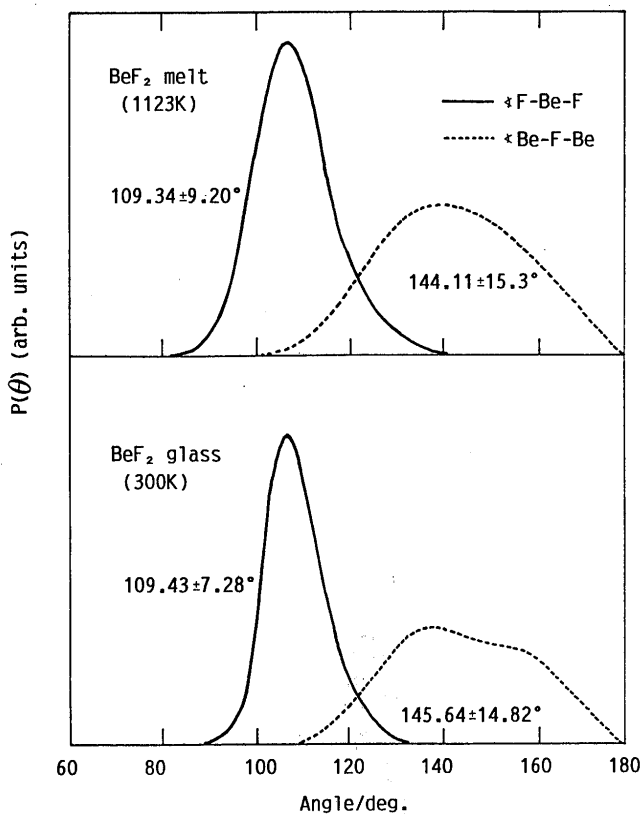


Fig. 2 Probability distribution of angles \angle F-Be-F and \angle Be-F-Be for MD-simulated BeF₂ melt at 1123K and glass at 300K.

calculated from the observed density values of molten and glassy BeF₂^{5,11} and NaBe₂F₅^{1,2}. The number of particles within a basic cell was 900 (300Be²⁺, 600F⁻) for BeF₂ and 480 (60Na⁺, 120Be²⁺, 300F⁻) for NaBe₂F₅. In evaluating the potential energy and the force, the

Coulombic 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 $\Delta t = 2.5 \times 10^{-15}$ 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 could 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 programming, 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 various properties. The average temperatures for BeF₂ and NaBe₂F₅ melts were 1123K and 743K, respectively.

Figure 1 shows the structural view of a typical instantaneous configuration of BeF₂ glass at 300K from our MD simulation. As shown in this figure, Be²⁺ ions form nearly regular BeF₄ tetrahedra with a peak around 109° in the \angle 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 BeF₄ tetrahedra are joined only at the corners. The \angle F-Be-F angle (109.43°) of the MD-simulated BeF₂ glass is almost equal to the bond angle (109.28°) of an ideal tetrahedron and to that (109.5°) from the X-ray diffraction analysis¹¹. In addition to showing the wide scatter of the intertetrahedral (\angle 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 SiO₂ glass reported by

NaBe₂F₅ melt
 Temp. = 743K
 Number of ions = 480
 Na: 60
 Be: 120
 F: 300
 Basic cell:
 18.781Å
 17.8768Å
 19.6641Å
 Density = 1.9900g/cm³.
 Δt = 2.5 × 10⁻¹⁵sec

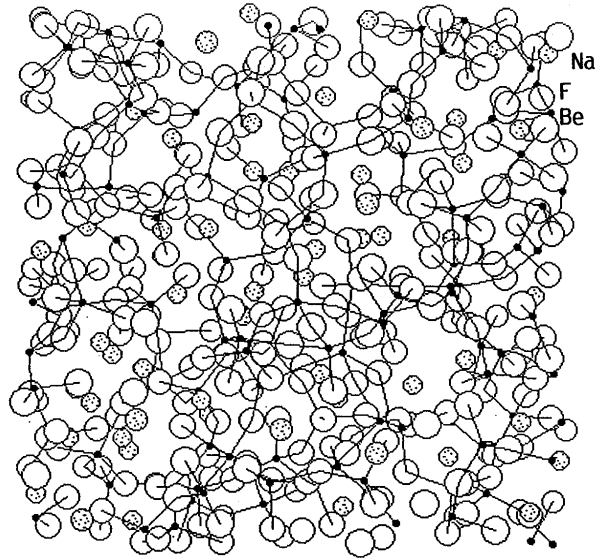


Fig. 3 Structural view of a typical instantaneous configuration of MD-simulated NaBe₂F₅ melt at 743K.

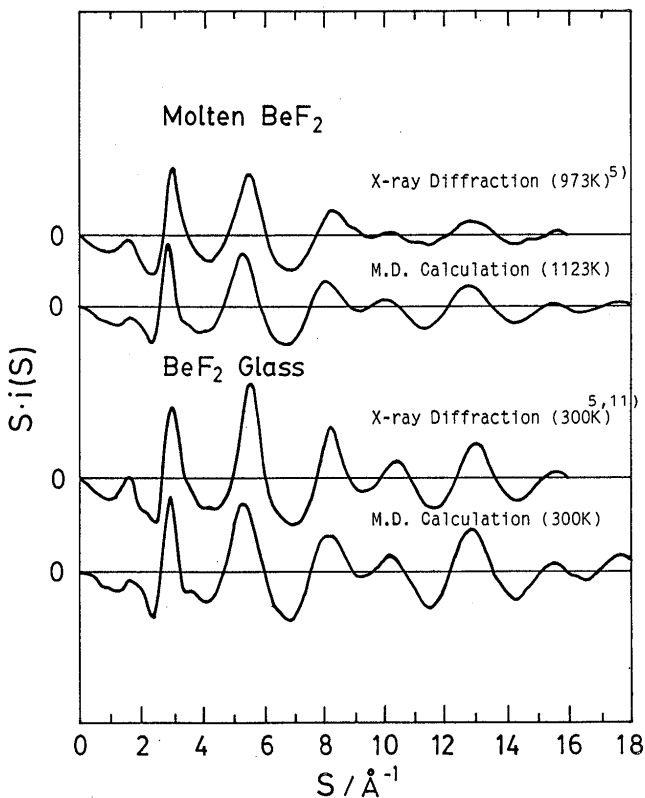


Fig. 4 Interference function curves $S \cdot i(S)$ of BeF₂ melt and glass obtained from MD simulation at 1123K and 300K and from X-ray data at 973K and 298K, respectively.

Mozzi and Warren¹³). We could not find the presence of defects¹⁴) such as fivefold-coordinated Be and threefold-coordinated F etc. in the MD-simulated BeF₂ glass.

Figure 3 shows the structural view of a typical instantaneous configuration of molten NaBe₂F₅ at 743K.

This result also indicates that BeF₄ tetrahedra persist as the fundamental structural unit in molten state, and that most of the BeF₄ tetrahedra are present as the polymerized fluoroberyllate ions such as (Be₂F₇)³⁻ dimer (= 4.84%), (BeF₃)¹⁻ chain (= 17.00%), (Be₂F₅)¹⁻ (= 47.83%) and (BeF₂)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 NaBe₂F₅ melt⁷). 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 $S \cdot i(s)$ 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.).

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

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:

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

$$[\sum_{all} N_k f_k(S)]^2 \} \cdot \sum_{r=0}^r \sum_{ij} [r(g_{ij}(r)-1) \sin(Sr)], \quad (5)$$

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 molten NaBe_2F_5 at 743K. The self-

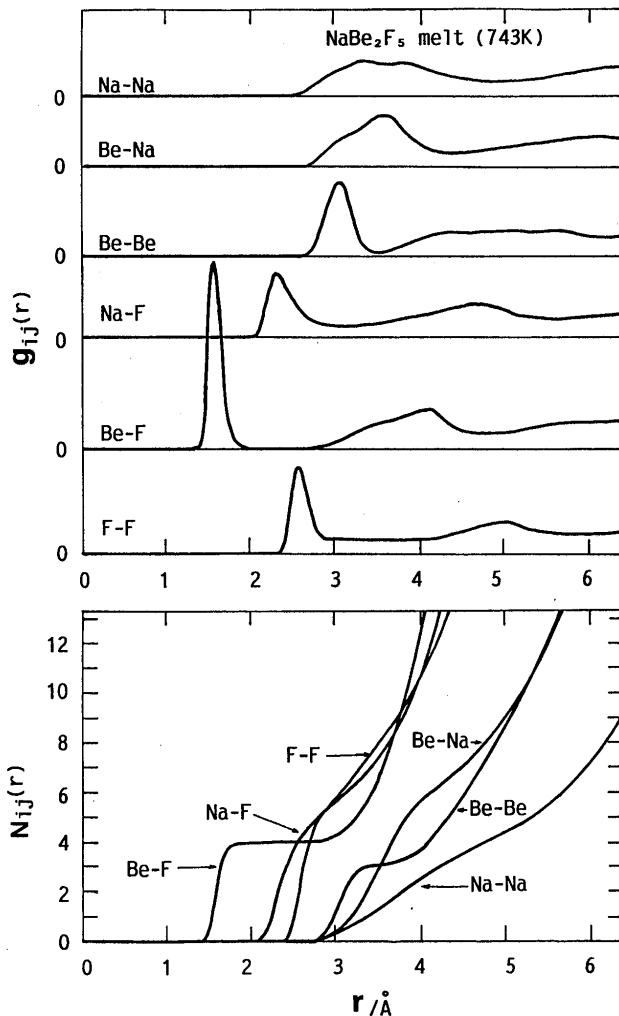


Fig. 5 Pair correlation functions $g_{ij}(r)$ and distribution of coordination number $N_{ij}(r)$ of ionic pairs F-F, Be-F, Na-F, Be-Be, Be-Na and Na-Na in MD-simulated NaBe_2F_5 melt at 743K.

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			
		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			
		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	

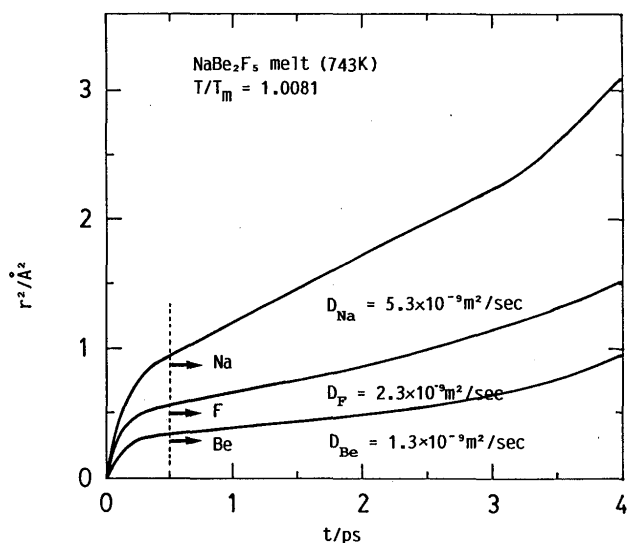


Fig. 6 Mean square displacements vs. time plots for Na⁺, F⁻ and Be²⁺ of MD-simulated NaBe₂F₅ melt at 743K.

diffusion constants are $5.3 \times 10^{-9} \text{m}^2/\text{sec}$, $2.3 \times 10^{-9} \text{m}^2/\text{sec}$ and $1.3 \times 10^{-9} \text{m}^2/\text{sec}$ for ions Na⁺, F⁻ and Be²⁺, respectively.

We conclude that important characteristics of molten and glassy BeF₂ and NaBe₂F₅ 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-BeF₂ system

can be calculated with good accuracy in our MD simulation.

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