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# Structures of Melts and Glasses in The System NaF-BeF<sub>2</sub> from Molecular Dynamics Simulation†

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KEY WORDS : (NaF-BeF<sub>2</sub>) (Sodium Fluoroberyllate) (Melt) (Glass) (Structural Analysis) (Molecular Dynamics Simulation)

Structures of BeF<sub>2</sub> melt and glasses are analogous to those of SiO<sub>2</sub> melt and glass consisting of BeF<sub>4</sub> 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<sub>2</sub>, they enter the open network structure at interstitial sites and introduce various polymeric units of BeF<sub>4</sub> tetrahedra with nonbridging anions. The various physical properties such as viscosity<sup>1,2</sup>, self-diffusion<sup>3</sup>, and electrical conductance<sup>4</sup> of molten NaF-BeF<sub>2</sub> depend on the three-dimensional BeF<sub>4</sub> tetrahedral network characteristic of BeF<sub>2</sub>. One of the most striking changes occurs in the viscosity resulting from the rupturing of -F- bridging in the three-dimensional BeF<sub>4</sub> tetrahedral network structure by the addition of modifier ions.

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

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 salts<sup>8</sup>. During the past few years, an MD simulation of molten BeF<sub>2</sub>, LiBeF<sub>3</sub> and LiF was performed by Rahman et al.<sup>9</sup>, though the number of particles in the basic cell was much smaller than that in our study. More recently, Furuhashi et al.<sup>10</sup> investigated the structures and dynamic properties of molten NaBeF<sub>3</sub> and Na<sub>2</sub>BeF<sub>4</sub> in some detail. In order to understand the melts and glasses in the system NaF-BeF<sub>2</sub>, 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<sub>2</sub> and NaBe<sub>2</sub>F<sub>5</sub> by molecular dynamic simulation. In addition, the obtained MD results are compared with the X-ray data of Vaslow et al.<sup>5</sup> and us<sup>7</sup> 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 Be<sup>2+</sup> 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<sup>-1</sup> Å<sup>-1</sup> (= 6.948 × 10<sup>-6</sup> 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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BeF<sub>2</sub> glass  
 Temp. = 300K  
 Number of ions = 900  
 Be: 300  
 F: 600  
 Basic cell:  
 22.7447Å  
 22.4582Å  
 22.2707Å  
 Density =  
 1.9680g/cm<sup>3</sup>  
 $\Delta t = 2.5 \times 10^{-15}$  sec

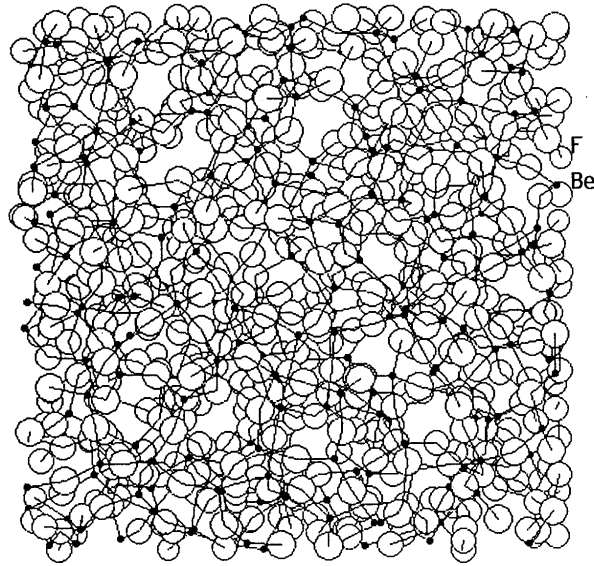


Fig. 1 Structural view of a typical instantaneous configuration of MD-simulated BeF<sub>2</sub> glass at 300K.

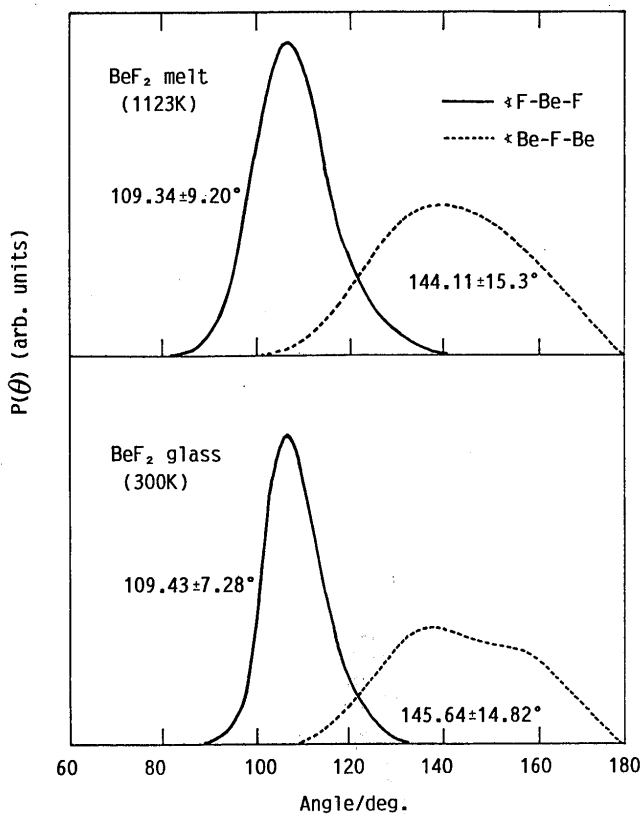


Fig. 2 Probability distribution of angles  $\angle$ F-Be-F and  $\angle$ Be-F-Be for MD-simulated BeF<sub>2</sub> melt at 1123K and glass at 300K.

calculated from the observed density values of molten and glassy BeF<sub>2</sub><sup>5,11</sup> and NaBe<sub>2</sub>F<sub>5</sub><sup>1,2</sup>. The number of particles within a basic cell was 900 (300Be<sup>2+</sup>, 600F<sup>-</sup>) for BeF<sub>2</sub> and 480 (60Na<sup>+</sup>, 120Be<sup>2+</sup>, 300F<sup>-</sup>) for NaBe<sub>2</sub>F<sub>5</sub>. In evaluating the potential energy and the force, the

Coulombic term was calculated by the Ewald method. The time increment  $\Delta t$  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 BeF<sub>2</sub> and NaBe<sub>2</sub>F<sub>5</sub> melts were 1123K and 743K, respectively.

Figure 1 shows the structural view of a typical instantaneous configuration of BeF<sub>2</sub> glass at 300K from our MD simulation. As shown in this figure, Be<sup>2+</sup> ions form nearly regular BeF<sub>4</sub> 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 BeF<sub>4</sub> tetrahedra are joined only at the corners. The  $\angle$ F-Be-F angle (109.43°) of the MD-simulated BeF<sub>2</sub> glass is almost equal to the bond angle (109.28°) of an ideal tetrahedron and to that (109.5°) from the X-ray diffraction analysis<sup>11</sup>. 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 SiO<sub>2</sub> glass reported by

NaBe<sub>2</sub>F<sub>5</sub> melt  
 Temp. = 743K  
 Number of ions = 480  
 Na: 60  
 Be: 120  
 F: 300  
 Basic cell:  
 18.781Å  
 17.8768Å  
 19.6641Å  
 Density = 1.9900g/cm<sup>3</sup>.  
 Δt = 2.5 × 10<sup>-15</sup>sec

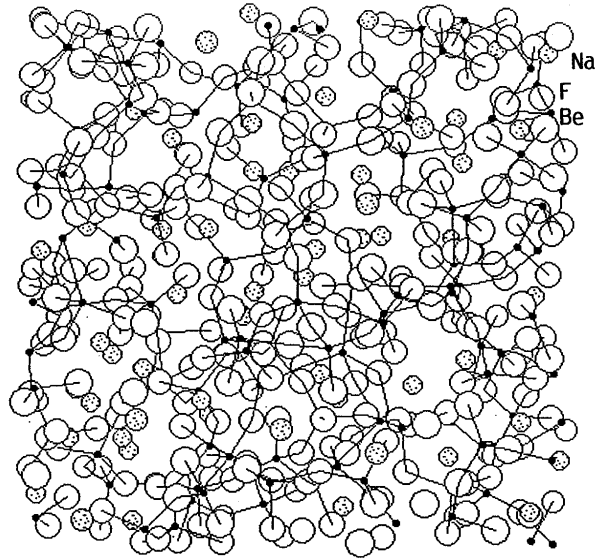


Fig. 3 Structural view of a typical instantaneous configuration of MD-simulated NaBe<sub>2</sub>F<sub>5</sub> melt at 743K.

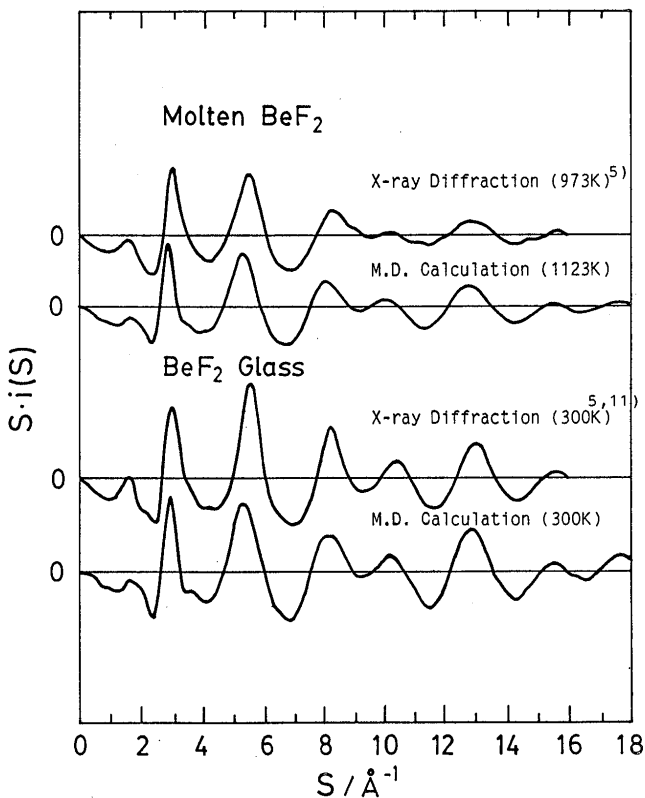


Fig. 4 Interference function curves  $S \cdot i(S)$  of BeF<sub>2</sub> melt and glass obtained from MD simulation at 1123K and 300K and from X-ray data at 973K and 298K, respectively.

Mozzi and Warren<sup>13</sup>). We could not find the presence of defects<sup>14</sup>) such as fivefold-coordinated Be and threefold-coordinated F etc. in the MD-simulated BeF<sub>2</sub> glass.

Figure 3 shows the structural view of a typical instantaneous configuration of molten NaBe<sub>2</sub>F<sub>5</sub> at 743K.

This result also indicates that BeF<sub>4</sub> tetrahedra persist as the fundamental structural unit in molten state, and that most of the BeF<sub>4</sub> tetrahedra are present as the polymerized fluoroberyllate ions such as (Be<sub>2</sub>F<sub>7</sub>)<sup>3-</sup> dimer (= 4.84%), (BeF<sub>3</sub>)<sup>1-</sup> chain (= 17.00%), (Be<sub>2</sub>F<sub>5</sub>)<sup>1-</sup> (= 47.83%) and (BeF<sub>2</sub>)<sup>0</sup> 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<sub>2</sub>F<sub>5</sub> melt<sup>7</sup>). As shown in this figure, most of the Na<sup>+</sup> 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<sup>5,7,11</sup>), 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,  $\Delta r$ , 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,  $\lambda$  : 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<sup>5,11)</sup>  $S \cdot i(S)$ . Unfortunately, it is considered that observed  $S \cdot i(S)$ <sup>5,11)</sup> 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  $\text{BeF}_2$  melt and glass, as shown in Fig. 4.

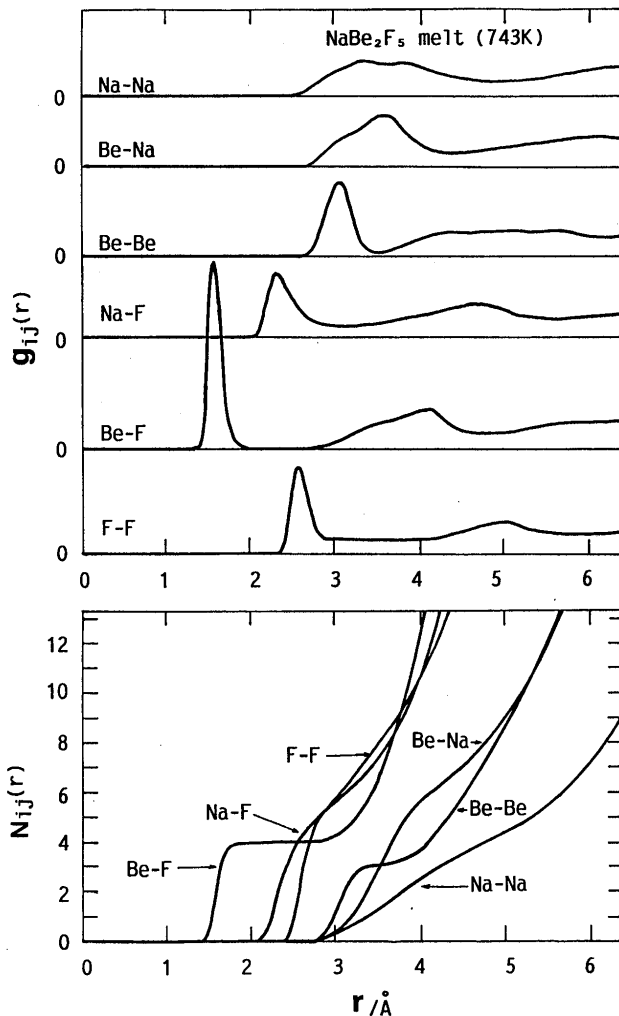
The pair correlation functions  $g_{ij}(r)$  and the distribution of the coordination number  $N_{ij}(r)$  of the ionic pairs F-F, Be-F, Na-F, Be-Be, Be-Na and Na-Na in molten  $\text{NaBe}_2\text{F}_5$  at 743K are illustrated in **Fig. 5**. The positions of the first peaks in the  $g_{ij}(r)$  curves, 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<sup>5,7,11)</sup>. These distances are in good agreement with results derived from X-ray diffraction<sup>5,7,11)</sup>.

Diffusion coefficients of ions  $\text{Na}^+$ ,  $\text{F}^-$  and  $\text{Be}^{2+}$  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,  $\tau$  : an arbitrary time interval.

**Figure 6** shows the mean square displacements plotted against time for the molten  $\text{NaBe}_2\text{F}_5$  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  $\text{NaBe}_2\text{F}_5$  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<sup>5,7,11)</sup>.

	T (K)	i	j	$r_{ij}$ (Å)				
$\text{BeF}_2$ melt	1123	Be	F	1.58	MD			
		F	F	2.58				
		Be	Be	3.04				
		Be	F	1.589(9)		X-ray <sup>5)</sup>		
		F	F	2.544(7)				
$\text{BeF}_2$ glass	300	Be	F	1.58	MD			
		F	F	2.56				
		Be	Be	3.10				
		Be	F	1.554(4)		X-ray <sup>5,11)</sup>		
		F	F	2.537(4)				
Be	Be	3.037(5)						
$\text{NaBe}_2\text{F}_5$ 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 <sup>7)</sup>
				Na		F	2.20	
				F		F	2.55	

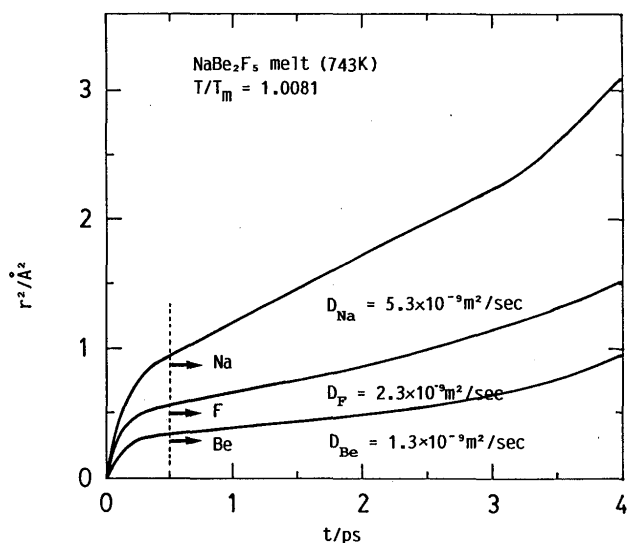


Fig. 6 Mean square displacements vs. time plots for Na<sup>+</sup>, F<sup>-</sup> and Be<sup>2+</sup> of MD-simulated NaBe<sub>2</sub>F<sub>5</sub> melt at 743K.

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<sup>+</sup>, F<sup>-</sup> and Be<sup>2+</sup>, respectively.

We conclude that important characteristics of molten and glassy BeF<sub>2</sub> and NaBe<sub>2</sub>F<sub>5</sub> 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-BeF<sub>2</sub> system

can be calculated with good accuracy in our MD simulation.

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