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Molecular Dynamics Simulations for Melting Temperatures of SrF₂ and BaF₂

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The shell-model molecular dynamics method was applied to simulate the melting temperatures of SrF₂ and BaF₂ at elevated temperatures and high pressures. The same method was used to calculate the equations of state for SrF₂ and BaF₂ over the pressure range of 0.1 MPa-3 GPa and 0.1 MPa-7 GPa. Compared with previous results for equations of state, the maximum errors are 0.3% and 2.2%, respectively. Considering the pre-melting in the fluorite-type crystals, we made the necessary corrections for the simulated melting temperatures of SrF₂ and BaF₂. Consequently, the melting temperatures of SrF₂ and BaF₂ were obtained for high pressures. The melting temperatures of SrF₂ and BaF₂ that were obtained by the simulation are in good agreement with available experimental data.

Key words: Molecular dynamics simulation, Melting temperature, Equation of state, High pressure

I. INTRODUCTION

High-pressure melting is of general interest for our understanding of solid-liquid phase transition due to its importance in high-pressure physics and material science. Of the known first-order phase transitions, melting covers the widest range of pressures and temperatures [1]. The physics of melting, particularly the relationship between melting and intrinsic instabilities of crystals and liquids, has remained a subject of great interest since as early as Lindemann's report [2,3]. In particular, with recent advances of high-pressure techniques, melting is of considerable importance in applied physics and geophysics as well as experimental designs, so high-pressure melting experiments are motivated by the current lack of a complete or reliable theory of melting [4,5]. Typically, the experimental data for high-pressure melting is determined by means of laser heating with the diamond-anvil cell (DAC) technique. Thus, because of the very high melting temperature for materials and the difficulties both in running and in distinguishing the exact melting, only very limited investigations for a few materials have been performed to date [6,7]. At present, it is still difficult to measure results at the extreme conditions of high pressure and elevated temperature for all kinds of materials, such as SrF₂ and BaF₂. Therefore, computer simulations based on interionic interactions have been applied extensively to inves-

tigate the microscopic structures and the macroscopic thermodynamics of a wide variety of chemical and physical properties. In addition, numerical computations are particularly useful and powerful for problems that may be inaccessible to direct experimental studies. A theoretical approach can provide independent information to support experimental determinations [8].

In view of the complexity, various techniques have been applied to judge the melting: two-phase, bulk transition, radial distribution functions (RDF), snapshot and so on. One-phase models suggest that melting can be predicted from the behavior of one phase alone, without regard to the other. They do not necessarily imply that two phases do not coexist at the transition, or that the transition is not strongly first order. Arguments that melting can only be understood in terms of free-energy differences between solid and liquid (*i.e.*, two-phase theories) ignore the success of soft-mode and order-disorder phase transition in solids, which are also first-order phase transitions [2], and two-phase models cannot explain the apparently intrinsic instabilities in the solid and liquid phases on approach to melting. The two-phase method [9,10] allows for melting at the interface of an ideal lattice. However, it does not allow for defects to be generated within the ideal lattice. The method for calculating the thermal instability is straightforward. One takes a crystal configuration of a certain number of atoms.

In this work, to calculate the thermal instability temperature T at some given pressure, each subsequent molecular dynamics (MD) run is carried out at this pressure and at higher T than the previous one. The new runs at increasing T are carried out until one ob-

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serves a sudden change of volume, and the corresponding temperature is the T for the volume instability. Then we use the instability criterion for volume and consider the pre-melting to obtain the melting point at some given pressure. Under the so-called one phase model, besides the volume *vs.* temperature changes studied in this work, researchers also monitor internal energy *vs.* temperature, diffusion coefficient *vs.* temperature, etc. in order to deduce the phase transition temperature, but adopted different value correction methods [11,12]. MD simulation is a well-established technique in mineralogy, especially for studying the effects of high pressure and elevated temperature on the properties of solids and their melts. A detailed description of the molecular dynamics method has been reported elsewhere [13,14].

Up to now, there has been no accurate technique to calculate the melting of material under high temperature and elevated pressure. Aguado provided a mechanism to resolve this long-standing problem [15]. He considered the importance of pre-melting effects. Moreover he thought that pre-melting effects were associated with temperature-driven solid-solid phase transformations, which might be the true melting transition. The available results from theory and experiment indicated that the melting on the surface of materials will result in the so-called surface pre-melting [16]. The temperature of the surface pre-melting and the melting temperature of the bulk meet a certain numerical relation [16]. Considering this fact, we can make a necessary correction for the results to obtain the temperature of melting at high pressure correctly.

In this work, we studied the pressure dependence of the melting temperature, and simulated the equations of state for SrF₂ and BaF₂. The alkaline-earth fluorides SrF₂ and BaF₂ crystallize in the cubic fluorite structure and constitute an important class of relatively simple ionic crystals whose optical and lattice-dynamical properties are of much theoretical and experimental interest [17,18]. The structure of fluorite has eight fluorine atoms arranged in a cube around the Sr or Ba atom, with the cubes of fluorine edge-connected in a face-centered cubic array. Conversely, the fluorine atom is surrounded by four Sr or Ba atoms arranged in an ideal tetrahedron with the tetrahedral also edge-connected. The SrF₂ and BaF₂ have widespread applications in many aspects. SrF₂ is mainly used in the manufacture of optical glasses, and advanced electronic components. BaF₂ is relatively hard but is highly sensitive to thermal shock. Because its transmission range is 0.2-11 μm , the material is used for optical windows, lenses and prisms in UV-IR. It can also be used as a substrate for some applications. In addition, BaF₂ is usually used as a scintillator for gamma detection. It is the fastest scintillating crystal. BaF₂ crystal is also applied widely to fields concerning the study of positron annihilation, such as materials science, particle physics and nuclear medicine.

II. THEORETICAL METHOD

In molecular dynamics simulation, each ion is treated as a point particle and the motion of an ion is based on Newton's equations. The thermodynamic quantities and transport coefficients are calculated by the time average over the ensemble of particles. The interaction potential between ions i and j is given by

$$V(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

It consists of the long-range Coulomb part and the short-range repulsion part, where r is the inter-ionic distance, and where Z_i or Z_j is an effective charge of the i th or j th atom, e the electronic unit charge, A_{ij} the magnitude of repulsion force, B_{ij} the softness parameter, and C_{ij} the parameters of dipole-dipole dispersion forces. The parameters and Eq.(1) are given in Ref.[19], fitting the crystal properties of BaF₂ and SrF₂. Note that the Buckingham (BHM) term of the Ba-Ba and Sr-Sr interaction is assumed to be zero because of the predominance of the electrostatic repulsion and the large distance. The Coulombic energy between all inter-atomic core-core, core-shell and shell-shell interactions were evaluated using the Ewald summation technique for 3D periodic systems for bulk simulations. When the distance between the atoms is approximately the equilibrium distance, the BHM-like repulsive potential is a reliable representation of the interaction between the two atoms [20]. All of our simulations were performed by using the shell code which was recently devised by Fincham and Mitchell [21].

The shell code calculates analytically the dynamical free energy and its first strain derivatives within the quasiharmonic approximation, and the second derivatives of the static energy, for a periodic crystal in which the particles interact via pairwise potentials. As well as the thermodynamic properties are directly dependent on these quantities, such as the heat capacity, entropy and Grüneisen functions, the code can be used to perform efficient geometrical optimization of the structure, minimizing the dynamical free energy with respect to all internal and external geometrical coordinates, which has not previously been possible except for very simple crystals. Calculations can be carried out for crystals with unit cells containing hundreds of atoms, and the code is currently being used for a wide range of investigations including complex oxides, defective lattices, high pressure phase transitions and surfaces [21].

MD simulations were performed in the NTP (N : number of particles, T : temperature, and P : pressure) ensemble [22]. The results of shell-model MD simulations in the NTP ensemble with the chosen model of the inter-atomic interaction depended on slightly, apart from the initial arrangement of particles, the size of time step Δt , number of particles N , and temperature of windows T_{win} , which allowed temperature window

for equilibration dynamics, in K. Therefore, the influence of these parameters was carefully studied and test runs were carried out at various temperatures and pressures [8]. It was found that the correct results can normally be obtained with $\Delta t=1$ fs, $T_{\text{win}}=23$ K. The results might have been affected by the choice of the above parameters, so we varied the parameters to verify that the final results were stable. The simulation system consists of 324 ions (216 F, 108 Sr and Ba ions), and the initial position of ions is chosen as BaF₂ type in a cubic box. The temperature is initially controlled to be a fixed value up to 3000 steps, and it is then reduced to the set temperature. In order to get the density at the set temperature the simulated system is taken under constant pressure (0.1 MPa) in conjunction with temperature control by using a loose-coupling method, and then the average density is calculated for constant temperature operation. It takes 30 ps for the simulation system to achieve an equilibrium state (constant temperature, volume and number of particles). In the work, there are 13 and 17 different temperatures for BaF₂ and SrF₂, respectively, and the increment of temperature for BaF₂ and SrF₂ are 30 and 20 K. In all our simulations velocities were scaled during the equilibration period. Averages were calculated without scaling velocities, allowing temperature to fluctuate around an average value. Taking into account "statistical inefficiency" [13], errors of the temperature calculations are <30 K, reaching a maximum at the highest simulated T [23].

BaF₂ and SrF₂ crystallize in the fluorite structure. Their anion sublattice is thermally less stable than the cation sublattice, and at sufficiently high temperatures becomes almost completely disordered with a large fraction of anion atoms occupying randomly regular or interstitial positions. This phenomenon is called pre-melting, from the intuitive image that the less stable chemical component is transformed into a sort of liquid somehow permeating the quasiperfect, more stable sublattice. This kind of order-disorder transition has been observed in many ionic biatomic crystals with fluorite or antifluorite structure, where one of the two ions displays higher in-solid mobility than the other. In insulators such as halides this transformation is accompanied by a sharp upswing of the ionic conductivity. Measurements of the heat capacity as a function of temperature confirm the existence of a thermodynamic transition, specified by a λ shaped $C_P=C_P(T)$ curve peaked at a defined temperature [24].

III. RESULTS AND DISCUSSION

Accurate equations of state for crystalline materials are very important in many applications involving high pressures and elevated temperatures. Such areas include geophysical studies of planetary cores, the behavior of shocked condensed matter, explosives technology,

materials processing, and studies of nuclear fuels. From the total energy calculations which were done by Kanchana, we can see that the fluorite-type structure is stable at ambient conditions for SrF₂ and BaF₂. SrF₂ undergoes a structure phase transition to the orthorhombic structure (pnam) at a pressure of about 7 GPa [25]. The high pressure phase of BaF₂ is also of orthorhombic type (pnam) and the transition pressure is found to be 3 GPa [26]. The simulated 300 K isotherms (Fig.1) in this work are in good agreement with the data from Kanchana *et al.* [25]. For SrF₂, the maximum error between our results and Kanchana's report is 0.3% [25]. For BaF₂ the maximum error is 2.2% [27]. The V_0 are the molar volumes under normal temperature and pressure (300 K, 101.3 kPa). So, we can conclude that the interatomic potentials and the parameters of the potentials that we have used are appropriate.

The temperature dependence on the volume is given in Fig.2. The inflexion point T_c in Fig.2 corresponds to the T_c^* that have been studied [28] and are the pre-melting temperatures. The volume instability still exists at higher pressure. We performed constant pressure simulations and structural optimizations for SrF₂ and BaF₂. The thermodynamic potential was minimized with respect to the coordinates at the finite temperature T and pressure P_0 . During all the simulations and calculations, the SrF₂ and BaF₂ are in the cubic

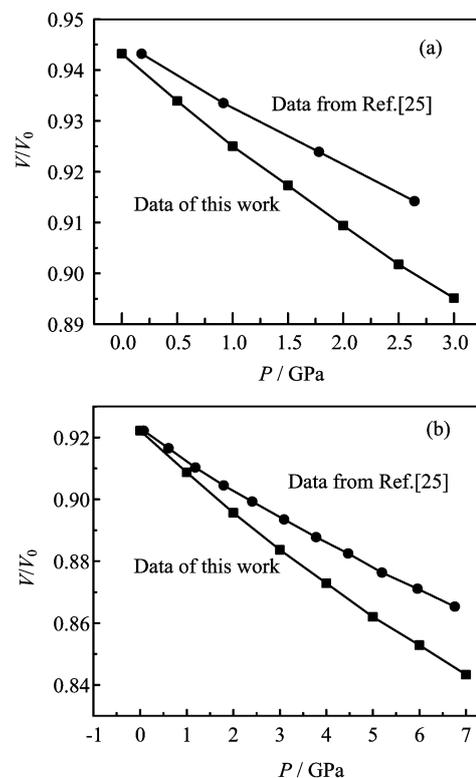


FIG. 1 Calculated pressure *vs.* volume in the fluorite, and orthorhombic phases of BaF₂ (a) and SrF₂ (b).

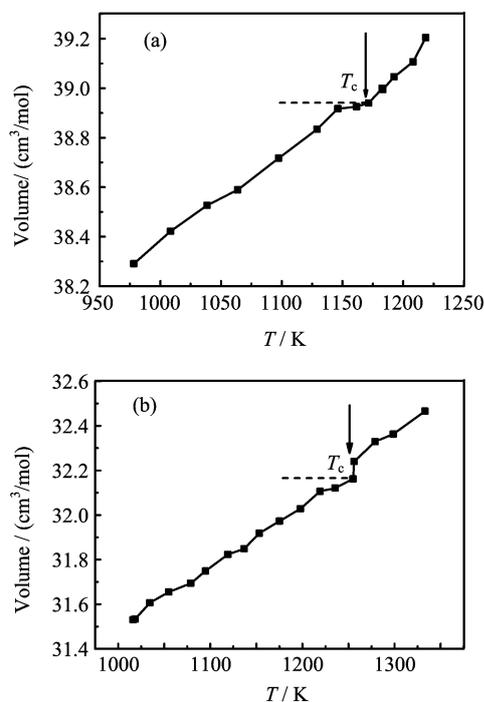


FIG. 2 The calculated volume of BaF₂ (a) and SrF₂ (b) at 0.1 kPa vs. temperature. The volume is suddenly changed at a temperature of about 1171.5 and 1254.9 K, respectively.

phases, so the instability criterion for the melting under atmospheric pressure can be extrapolated to higher pressures.

Pre-melting is the localized loss of crystalline order at surfaces and defects at temperatures below the bulk melting transition. It can be thought of as the nucleation of the melting process. Pre-melting has been observed at the surfaces of crystals but not within [29]. The heavy disorder of the fluorine sublattice gives rise to a maximum in the specific heat at the temperature of the pre-melting transition temperatures [30]. For a number of fluorite-type compounds (SrCl₂, CaF₂, SrF₂, BaF₂, etc) the presence of a broad peak in the heat capacity curve has been observed at the temperature T_c^* (specific heat maximum) essentially below the melting point T_m . Moreover in DAC (diamond-anvil cell) experiments the eye-evident surface texture change is usually used as an indicator of the melting of samples heated by laser. When a very thin melting layer exists at the sample/DAC interface, the heat balance between this thin layer and the crystal beyond this layer is built. In an experiment, large variations might occur in the eye-visible surface melting, as discussed by Chaplot *et al.* [16]. The variations are due to the sample not being under thermodynamic equilibrium at a uniform temperature and hydrostatic pressure, or due to sample history, etc. Most of the surface melting temperatures can be related to bulk ones as

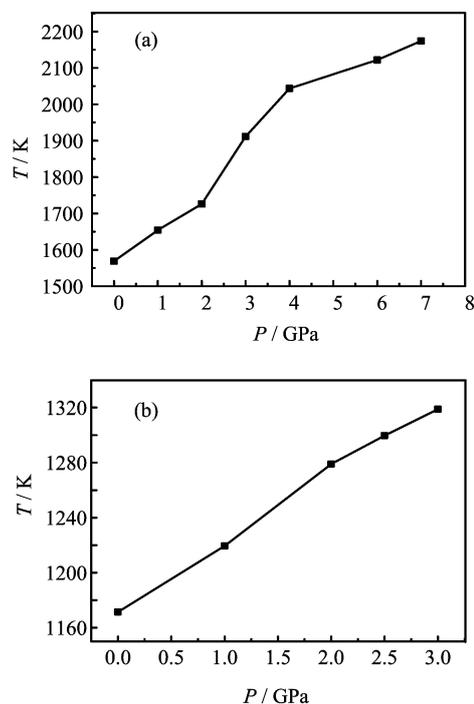


FIG. 3 Molecular dynamics simulated melting temperatures of SrF₂ (a) and BaF₂ (b).

$$0.75 < T_c^*/T_m < 0.90 \quad (2)$$

where T_m is the conventional melting temperature for the bulk. As a first approximation, Eq.(2) can be used to correct the melting temperature under static high pressures T_c to T_m . We considered the pre-melting of the SrF₂ and BaF₂, and so modified the temperature T_c ; the corrected melting temperatures of SrF₂ and BaF₂ are in good agreement with the results of experiment [28] (where $T_m = T_c/0.75$) at atmospheric pressure, as shown in Table I. The pressure dependence of the melting temperatures of SrF₂ and BaF₂ are correctly shown in Fig.3.

Molecular dynamics simulations on NaCl and MgO showed that the mean atomic volume underwent a sudden upward jump at a temperature which is higher than the melting point [31,32]. Taking into account the superheating melting of the molecular dynamic simulation, the simulated melting temperatures of NaCl and MgO were corrected. Consequently, the melting temperatures of NaCl and MgO were accurately obtained

TABLE I The pre-melting temperature and melting temperature of SrF₂ and BaF₂.

	T_c /K	T_c^* /K	Error/%	T_m /K	T_m^* /K [27]	Error/%
SrF ₂	1254.9	1380	9.1	1673.3	1740	3.8
BaF ₂	1171.5	1245	5.9	1561.9	1620	3.6

at elevated temperature and high pressure. In this work, the mean atomic volume of SrF₂ and BaF₂ did not undergo a sudden jump near the melting temperature. To give a good explanation for the differences, we performed molecular dynamics simulations for NaCl and MgO again. This time we changed the parameters in Ref.[31,32] and set the BHM potential parameters of Na-Na, Mg-Mg to zero, and the results indicated the volume did not undergo the sudden jump near the melting temperature as [31,32]. Therefore, we deduce that the volume change is determined by the interaction potential, and the interactions of cation-cation play an important role.

In summary, on account of the pre-melting, we propose to modify our MD simulation melting temperature to get the real melting temperature. Moreover, the tendency of the simulated melting temperature curve for BaF₂ and SrF₂ are consistent with Liu *et al.* for MgO [31] and Chen *et al.* for NaCl [32]. MD simulation can allow tracking the physical properties of the atoms not only as global but also local average. This capability is indispensable for exploration of a correction between the theories and the atomic level mechanisms at the onset of melting.

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