Simulation of Melting Behavior of the MgSiO$_3$ Perovskite Under Lower Mantle Conditions

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The melting curve of MgSiO$_3$ perovskite was simulated using molecular dynamics method combining with the effective pair potentials under the lower mantle conditions. It was shown that the state equation simulated for MgSiO$_3$ perovskite is very successful in reproducing accurately the experimental data over a wide range of pressure. The pressure dependence of the simulated melting temperature of MgSiO$_3$ perovskite is in agreement with the recent experimental data. The melting curve simulated for MgSiO$_3$ is very steep at pressures below 60 GPa first, then it becomes smooth with increasing pressure. At the core mantle boundary pressure 135 GPa, MgSiO$_3$ perovskite melts at 6500 K, which is significantly lower than that of the extrapolations of the experimental data from Zerr and Boehler.

Key words: Melting curve, Molecular dynamics, High pressure, MgSiO$_3$

I. INTRODUCTION

MgSiO$_3$ perovskite is an important material for Earth sciences and solid-state physics because it is one of the most abundant minerals in the Earth (especially in the lower mantle). Its melting properties in the wide temperature range at high pressure are of great interest to the geophysicist [1-3].

At the early stage of Earth’s evolution, a significant part of MgSiO$_3$ was in the molten state [4,5]. The melting temperature as a function of pressure in the pressure range of the lower mantle is needed to describe the Earth’s evolution. The melting temperatures of MgSiO$_3$ perovskite also play a fundamental role in the chemical differentiation, rheology and geodynamics of the Earth’s lower mantle. However, it is difficult to obtain directly through laboratory experiments at high temperature and high pressure [6-8]. Numerical computations are particularly useful and powerful for the problem that may be inaccessible to direct experimental studies, such as the problem at high temperature and pressure. We have taken the advantage of the recent advances in computer technology to perform molecular dynamics simulations of the physical properties of MgSiO$_3$ perovskite, the major mineral of the lower mantle, at the relevant thermodynamic conditions. Furthermore, the molecular dynamics simulations are used because it allows the substantial metastable overheating of perfect crystals without suffering from surface/interfaces as heterogeneous nucleation sites for melting [9]. Molecular dynamics simulation further allows tracking the physical properties of the atoms not only in a global average state but also in a local state. This capability is indispensable for the exploration of a correction between the theories and the atomic-level mechanisms at the onset of melting. In this work, we simulated the melting curve of MgSiO$_3$ perovskite by using the molecular dynamics simulation method at constant pressure, and compared the results with the previous ones.

II. METHOD

The condition for the successful molecular dynamics calculations is the availability of the reliable interatomic potentials describing the interaction between atoms in the crystalline lattice [10]. Following our previous studies [11,12], the crystal lattice energy is taken to be the sum of the interaction energies between atoms:

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

where $Z_i$ or $Z_j$ is the effective charge of the $i$th atom, $e$ the unit of the electronic charge, $A_{ij}$ and $B_{ij}$ are the parameters for the repulsive interactions, and $C_{ij}$ is the van der Waals constants. The first term represents the Coulomb interaction, the second one is due to the overlap repulsion. Here $r_{ij}$ is the interatomic distance between atoms $i$ and $j$. Because the interparticle interaction is the most important factor in molecular dynamics simulations, a proper choice of interaction potential is necessary for better results. The values of the parameters [13] of potential of MgSiO$_3$ perovskite used in the simulations are listed in Table I.

All of the simulations are performed by using the interaction potential in Eq.(1). The simulations in NTP
(constant $N$ is the number of particles, $T$ is the temperature, and $P$ is the pressure) ensemble [14] are performed with 360 particles (72 Mg atoms, 72 Si atoms and 216 O atoms). The cut-off radius is chosen to be $(L/2,$ where $L$ is the length of the short edges of the computational box. The time steps are varied from $2$ femtoseconds ($1$ fs=$10^{-15}$ s) at low temperature to $1$ fs at high temperature. The run durations are varied from 6000 steps to 4000 steps, depending on time step. The Coulombic interaction is calculated using Ewald method [15].

### III. RESULTS AND DISCUSSION

The simulated molar volume $V_0$ (=24.414 cm$^3$/mol) agrees well with the results of Yeganeh-Haeri [16] (within 0.1%) under $300$ K at zero pressure. In a recent study, Belonoshko used the MAM0K potential to perform the molecular dynamics simulations on MgSiO$_3$ perovskite concerning the equation of state, structure and melting transition at high pressure. Our simulations are in very good agreement with those of Belonoshko ($\alpha_0=2.37 \times 10^{-8}$ K$^{-1}$ and $K''_0=4.92$) at the atmosphere pressure [17]. Knittle and Jeanloz carried out the X-ray diffraction experiments of (Mg$_{0.88}$Fe$_{0.12}$)SiO$_3$ perovskite at pressures up to $112$ GPa and $300$ K based on the diamond-anvil cell [18]. Mao et al. performed the static compression experiments of MgSiO$_3$, (Mg$_{0.9}$Fe$_{0.1}$)SiO$_3$, and (Mg$_{0.8}$Fe$_{0.2}$)SiO$_3$ perovskite at pressures up to $28.4$ GPa and $300$ K, using neon as a pressure-transmitting medium [19]. The results showed that the volume-compression data under the normalized volume conditions for these three perovskite at $300$ K are indistinguishable. Fiquet et al. also reported the volume-compression data of MgSiO$_3$ perovskite at $300$ K and in the pressure range from $28$ to $51$ GPa [20]. As shown in Fig.1, simulated pressure-volume relation of perovskite at $300$ K is in excellent agreement with that of the experimental data over a wide pressure range larger than $100$ GPa. Thereby, we can further study the melting curve of MgSiO$_3$ perovskite at high pressure and high temperature by using the same potentials.

Melting, a mysterious phenomenon in nature, has attracted much attention for a long time, but a general theory for this phase transformation has not been established. The current studies of the melting of MgSiO$_3$ perovskite are limited either by the technical problem or by the present state of the theory. To find the melting temperature of MgSiO$_3$ perovskite is a real challenge. A possible solution is to calculate the temperature of the thermal instability and then estimate the degree of overheating. If one simulated a bulk crystal under periodic boundary conditions, one can find that the crystal will not melt at melting temperature ($T_m$) with increasing the temperature in a certain range, instead, it will remain the metastable state of the solid state. When the temperature becomes high enough, the crystal will eventually melt. This temperature is called as the thermal instability temperature, also is known as the superheating temperature ($T$). Calculation of $T$ is a relatively simple task.

It is well known that the MgSiO$_3$ perovskite melting curve has been studied using a number of methods. Among these methods we choose the one which seems to be the most robust [21]. The first-order melting transition of MgSiO$_3$ perovskite showed that at certain temperature the mean atom volume underwent a sudden upward jump under different pressures, as marked in Fig.2. The temperature at this jump point is the superheating temperature. Instable superheating due to the melting kinetics during the rapid heating is insignificant because of the transient nature of melting at such a high degree of overheating. The superheating of a crystalline occurs when the long-range order of the crystalline structure is maintained up to certain temperatures above the equilibrium melting temperature. According to the modern theory of melting, melting temperatures of a crystal can be corrected by certainly melting mechanism [22], corresponding overheating melting of some crystalline solids at atmosphere

### TABLE I Parameters of the potential of MgSiO$_3$ perovskite used in simulations

<table>
<thead>
<tr>
<th>Source</th>
<th>$A$/eV</th>
<th>$B$/nm$^{-1}$</th>
<th>$C$/10$^{-6}$eV nm$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg–Mg</td>
<td>1309336.700</td>
<td>9.615</td>
<td></td>
</tr>
<tr>
<td>Mg–Si</td>
<td>2325826.600</td>
<td>10.869</td>
<td></td>
</tr>
<tr>
<td>Si–Si</td>
<td>5005903.500</td>
<td>12.500</td>
<td></td>
</tr>
<tr>
<td>Mg–O</td>
<td>8035.120</td>
<td>4.950</td>
<td></td>
</tr>
<tr>
<td>Si–O</td>
<td>7363.450</td>
<td>5.263</td>
<td></td>
</tr>
<tr>
<td>O–O</td>
<td>1621.680</td>
<td>3.333</td>
<td>30.222</td>
</tr>
</tbody>
</table>
pressure can be concluded as $\theta = T/T_m - 1$, where $T_m$ is the conventional melting temperature for the bulk. This melting process results from temperature increasing rate, and $T/T_m$ is not much dependent on pressure, and will be applied to correct the melting temperatures for overheating of crystal. Luo et al. investigated the nucleation energy barrier ($\beta$) for elements and compounds [23], and showed that the corresponding overheating ($\theta$) is a function of heating rate ($Q$). They pointed out that the significant superheating is achievable via ultrafast heating and the degree of superheating can be achieved in shock-wave loading and intense laser irradiation. The $Q$ value of $10^{12}$ K/s obtained by our molecular dynamics simulations agrees with the established $\theta$-$\beta$-$Q$ relation based on the undercooling experiments and the homogeneous nucleation theory. Crystalline solids can be superheated under ultrafast conditions, and the degree of superheating prior to thermal melting is in the range of (0.1-0.5)$T_m$ [23]. The superheating temperature is about 42% higher than the normal equilibrium melting point 2320 ± 100 K at 6.2 GPa. Therefore, we suggest that the superheating temperature of MgSiO$_3$ perovskite be 0.42$T_m$ at the pressure range of the core-mantle boundary. According to this value, we can conclude that the real melting curve of MgSiO$_3$ perovskite is similar to that shown in Fig. 3.

Figure 3 shows that the present melting curve of MgSiO$_3$ perovskite is in good agreement with the experimental data [7,8]. It is also found that first, the melting curve of MgSiO$_3$, is very steep at pressures below 60 GPa; then it becomes smooth with increasing pressure. The melting curves fall below the extrapolations of the diamond anvil cell data [7] at high pressures. At 135 GPa, the pressure of the core-mantle boundary, the extrapolations [7] generates the melting temperature higher than 7000 K. Therefore, first, the melting curve of MgSiO$_3$ perovskite up to lower mantle pressure, is very steep at pressures below 60 GPa; then it becomes smooth with increasing pressure. At the core mantle boundary pressure 135 GPa, the MgSiO$_3$ perovskite melts at 6500 K, which is significantly lower than that of the extrapolations of the experimental data based on the results of Zerr and Bohler.

IV. CONCLUSION

The predicted melting curve of MgSiO$_3$ is important for our understanding of the Earth’s lower mantle and the history of the Earth’s formation. The simulated melting curve of MgSiO$_3$ perovskite is in good agreement with the recent experimental data. It is found that, the melting curve of MgSiO$_3$ perovskite up to lower mantle pressure, is very steep at pressures below 60 GPa; then it becomes smooth with increasing pressure. At the core mantle boundary pressure 135 GPa, the MgSiO$_3$ perovskite melts at 6500 K, which is significantly lower than that of the extrapolations of the experimental data based on the results of Zerr and Bohler.

V. ACKNOWLEDGEMENTS

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