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Structure and properties of MgO melt at high pressure: A first-principles study

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MgO is one of the most abundant minerals in the Earth's interior, and its structure and properties at high temperature and pressure are important for us to understand the composition and behavior in the deep Earth. In the present work, first-principles molecular dynamics calculations were performed to investigate the pressure-induced structural evolution of the MgO melts at 4000 K and 5000 K. The results predicted the liquid–solid phase boundaries, and the calculated viscosities of the melts may help us to understand the transport behavior under the corresponding Earth conditions.

Keywords: first-principles, molecular dynamics, MgO melt, high temperature and high pressure

PACS: 63.20.dk, 31.15.xv, 61.20.Ja, 64.70.dj, 64.70.fm

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1. Introduction

The study of minerals at extreme conditions such as those found in Earth's deep interior is crucial for understanding the planet's internal dynamics and composition.[1,2] Among these minerals, magnesium oxide (MgO) stands out due to its abundant presence and significant role in Earth's mantle. To unravel the structure and properties of MgO under extreme environments with high temperature and high pressure, various methodologies including advanced high-pressure experiments using a diamond anvil cell (DAC)[3] and density functional theory-based first-principles simulations[4–7] were employed, allowing scientists to investigate the various properties of MgO including the equation of state (EOS), melting curve, thermal conductivity, wave velocities, etc. The previous reports have shown that the understanding of the behavior of MgO under extreme conditions helps us gain deep insights into the processes in Earth's interior.[8] For instance, the pressure-induced anisotropy of MgO and its comparable wave velocities to seismic velocities observed in the lower mantle indicate that MgO may play a substantial role in seismic wave propagation and mantle anisotropy. Furthermore, investigations into the thermal conductivity of MgO at lower mantle conditions have provided insights into the heat flow within the Earth's interior, which is crucial for understanding mantle dynamics and the convective regime of the liquid outer core.[9,10] However, despite these significant discoveries, there are still discrepancies in previous reports arising from different technologies in both experiment and theory. McWilliams *et al.*[11] studied the phase transformations and metallization of magnesium oxide using laser-shock experiments under high pressure and temperature, reaching pressures up to 1.4 TPa. Ronchi *et al.*[12] measured the melting point of MgO to be around 3250 ± 20 K by employing controlled laser pulse heating. Alfè[13] calculated the melting curve of MgO by first-principles simulations, indicating a melting slope of $\mathrm{d}T/\mathrm{d}p \sim 100$ K/GPa, with the melting point of MgO at 135 GPa being 8140 ± 150 K. Musella *et al.*[8] calculated the EOS and the melting curve of MgO at deep planetary conditions by utilizing *ab initio* molecular dynamics simulations. Kimura *et al.*[3] used micro-texture analyses to study the melting curve of MgO under pressure, and suggested a much higher viscosity of MgO melts than the previous experiments done by earlier laser-heated DAC study.

Besides the remaining discrepancies from the previous studies, the pressure-induced structural evolution of MgO melt has been much less investigated. In the present study, the pressure-induced structural evolution of the MgO melts was calculated by first-principles molecular dynamics (FPMD) simulations. The diffusion and viscosity of the MgO melts are also discussed.

2. Computational method

All the density functional theory-based FPMD calculations were performed by using the Vienna *ab initio* simulation package (VASP).[6,14–16] The effects of the core electrons were replaced by the atomic projected augmented wave (PAW) method in the atomic potentials.[17] For the Mg and O atoms, the valence electron configurations were $3s^2$ and $2s^22p^4$, respectively. The Perdew–Burke–Ernzerhof (PBE) exchange–

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correlation functional was employed.[18] An energy cutoff of 400 eV was used to expand the wave functions. The MgO supercell contains 32 Mg atoms and 32 O atoms, and was heated to 4000 K when it melted. The canonical ensemble (NVT) was used for the MD simulation. The pressure was applied by isotropically reducing the size of the supercell. At each pressure, the FPMD run lasted for at least 60 ps with a timestep of 1 fs.[19,20] For the calculation at 5000 K, initially the structure at 4000 K and ambient pressure was heated to 5000 K, and then subjected to similar compression processes step by step.[21] The temperature was controlled by using the Nosé–Hoover thermostat.[22] A single Gamma point was employed for Brillouin zone sampling.[23]

3. Results and discussions

3.1. Equation of states

Figure 1 illustrates the pressure-dependent EOS of MgO melts at 4000 K and 5000 K. At 0.73 GPa and 4000 K, the calculated molar volume of the MgO melt is approximately 17.1 cm^3, which is very close to the previous experimental value of 17.8 cm^3 at ambient pressure and 3800 K reported by Leu *et al.*[24] The calculated density from the present study is also consistent with the molecular dynamics simulation results from Li *et al.*'s work.[25] During the initial stage of compression, the density of the MgO melt gradually increases with pressure. With further compression ($>$ 6.58 GPa at 4000 K or $>$ 15.48 GPa at 5000 K), the densities suddenly increase, which indicates the onset of solidification.

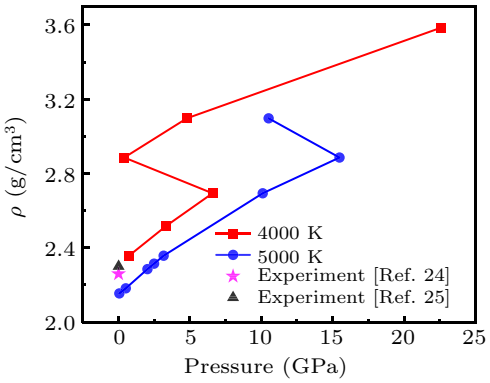


Fig. 1. Equation of state of MgO melts under compression at 4000 K and 5000 K, respectively.

3.2. The diffusion and viscosity

The mean square displacement (MSD) was used to analyze the atomic diffusion behavior of the MgO melts. The MSD was calculated from

$$\mathrm{MSD} = \langle |r(t) - r(0)|^2 \rangle, \tag{1}$$

where $r(0)$ is the position of the atom in the initial state, $r(t)$ is the position of the corresponding atom at a target time, and $\langle\ \rangle$ denotes the ensemble average. Figure 2 shows the pressure-dependent MSD results from Mg and O atoms at 4000 K and 5000 K, respectively. At low pressure, both MSD results of Mg and O atoms increase with time duration, indicating the structures remain in the molten state. When the pressure reaches 6.58 GPa at 4000 K or 15.48 GPa at 5000 K, the MSD values drop to ~ 0, which indicates the occurrence of solidification.

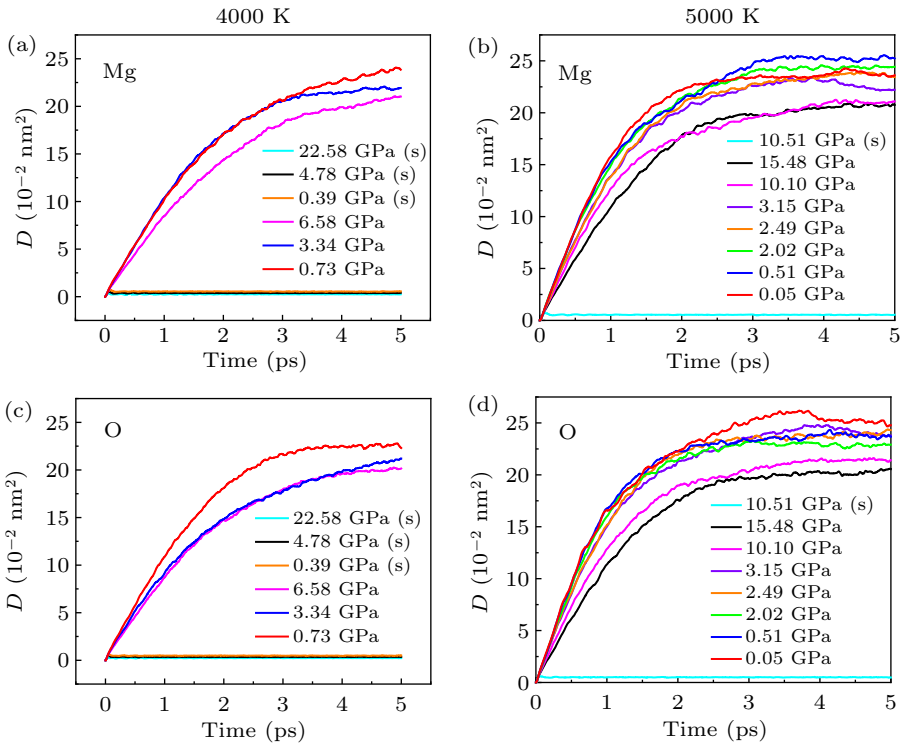


Fig. 2. Atomic MSD of MgO melts at 4000 K and 5000 K.

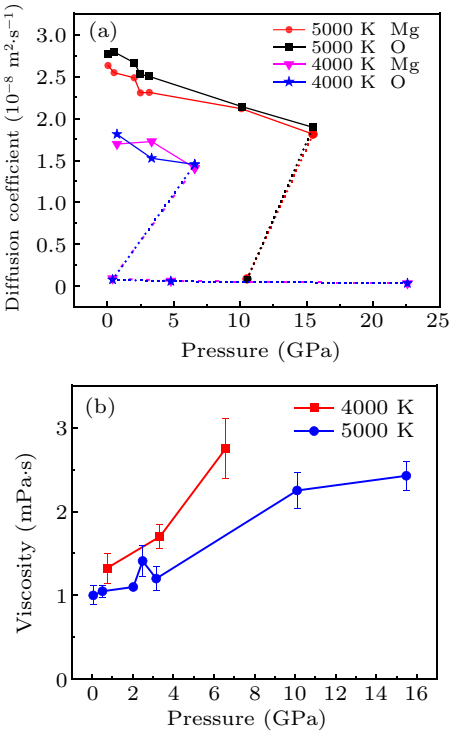


Fig. 3. (a) Self-diffusion coefficients of MgO melts at 4000 K and 5000 K. (b) Viscosity of MgO melts at 4000 K and 5000 K.

The atomic self-diffusion coefficients calculated from the MSD are shown in Fig. 3(a). Despite the large difference in atomic weight between Mg and O atoms, their diffusion rates are quite close to each other, especially at relatively lower temperature of 4000 K. This indicates there is a strong interatomic correlation between these two atoms. When the temperature increases to 5000 K, the Mg–O interaction becomes weaker and the lighter O atom shows a slightly higher diffusion rate. At high pressure, the pressure effect restores the Mg–O interaction and consequently their diffusion rates approach each other again.

The viscosity of the molten structures was calculated by the Green–Kubo relationship[26], which utilizes the stress autocorrelation function as given by

$$\eta_{\mathrm{GK}} = \frac{V}{k_{\mathrm{B}}T}\int_0^{\infty}\langle P_{xy}(t)P_{xy}(0)\rangle \mathrm{d}t, \tag{2}$$

where η_{GK} represents the Green–Kubo viscosity, V is the volume of the system, and P_{xy} refers to the off-diagonal element of the stress tensor at a target time. As shown in Fig. 3(b), all the calculated viscosities of MgO melts are less than 3 mPa·s, which is several orders of magnitude smaller than that of a silicate melt. This differs from the previous work by Kimura *et al.*,[8] in which the measured viscosity of MgO was suggested to be much higher and close to its silicate counterpart. The calculated viscosities of the MgO melts in the present work are also close to a value of 3.8 mPa·s at 4405 K and 17 GPa in the previous calculation.[13]

3.3. Structural analysis

To further understand the pressure-induced structural evolution of MgO melts, the partial radial distribution functions (RDFs) were analyzed and shown in Fig. 4. All the partial

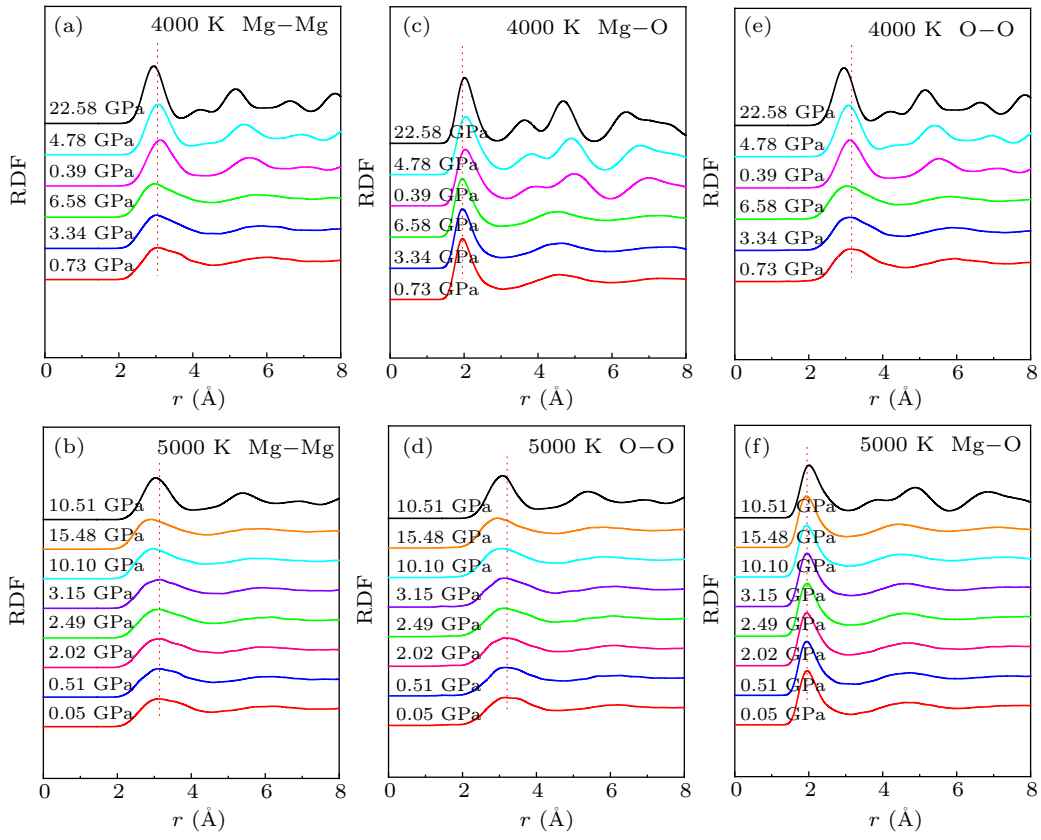


Fig. 4. Pressure-dependent partial RDF of MgO melts at 4000 K and 5000 K.

RDFs show a similar trend, that is, the first peak positions of the partial RDFs gradually shift to the left with increasing pressure as expected. When the melts were compressed further and solidified into a crystal, the first peak positions shift to the right. An increased interatomic distance under compression usually implies an increased coordination number. This is confirmed by the coordination analysis as shown in Fig. 5. At low pressures when the MgO remains in the molten states, the coordination numbers also increase with pressure, which is a normal observation as a result of compression. The compression effect is dominant and the interatomic distance decreases with pressure. When the MgO melts transform into crystalline solids, the structures turn into a denser packing with a sudden increase in coordination number. Now the effect of atomic packing is dominant; as a result, the interatomic distance increases due to a weakened interatomic interaction.

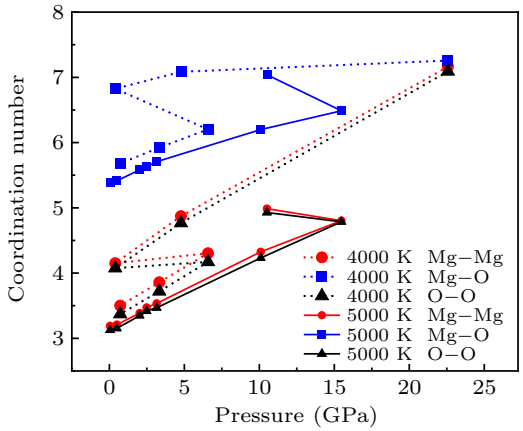


Fig. 5. The pressure-dependent coordination number of MgO melts at 4000 K and 5000 K. The cutoff radii were selected from the first peak position of the RDF.

4. Conclusion

In summary, FPMD calculations were conducted to study the structures and properties of the MgO melts at high pressure. The results show that the MgO melt solidifies into a crystalline structure at 6.58 GPa, 4000 K and 15.48 GPa, 5000 K. The diffusion rates of the Mg and O atoms in the melts are close to each other, indicating a strong interatomic correlation. All the calculated viscosities are smaller than 3 mPa·s. This is several orders of magnitude smaller than that of a silicate melt, which is similar to a previous theoretical study, but different from the results from the micro-texture analyses by Kimura *et al.*[4] Structural analyses including RDF and coordination number were conducted to understand the structural evolution of the MgO melts under compression. The present theoretical results may trigger more investigations in both experiment and theory to further explore the structures and properties of mineral melts and their consequent impact on the behavior of the Earth's interior.

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