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Article

Comparison of local structure of amorphous tobermorite based on empirical and non-empirical molecular dynamics simulations

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Abstract

The local structures of amorphous tobermorite are studied using both classical and *ab initio* molecular dynamics (MD) simulations. The density obtained from the classical MD simulations is lower than that from the *ab initio* MD simulations. In the *ab initio* MD simulations, a higher number of SiO_4 tetrahedra is observed compared to the amorphous structure obtained from classical MD. Additionally, network structures consisting of SiO_4 tetrahedra are observed. Furthermore, the Ca-O correlations resemble those found in the crystalline state. These features imply that the layered structure of crystalline tobermorite is partially retained in amorphous tobermorite.

Key Words: tobermorite, amorphous, molecular dynamics simulation

1. Introduction

Concrete is widely used as a construction materials, which consists of water, cement, fine aggregate, and core aggregate. When cement reacts with water, Calcium Silicate Hydrate (C-S-H) is formed, and the concrete cures due to formation of the C-S-H.

It is thought that, although crystalline tobermorite is partially formed, the main part of C-S-H is amorphous phase with a composition similar to that of tobermorite. Therefore, in addition to research of crystalline tobermorite[1-7], it is necessary to investigate the physical properties of amorphous tobermorite to understand the mechanical properties of C-S-H.

To study the local structure of amorphous systems, molecular dynamics (MD) simulations are often used. One commonly used method to construct the amorphous state in the MD simulations is the melt-quenching method. We previously used classical MD to construct amorphous tobermorite and investigate its mechanical properties[7]. However, in the melt-quenching method, bond breaking and recombination occur as the crystals melt and solidify. Therefore, the resulting amorphous structure is expected to be significantly affected by the choice of interatomic potentials. For this reason, in this paper, we investigate the local structures of amorphous tobermorite constructed by classical MD based on an empirical interatomic potential and *ab initio* MD based on density-functional theory(DFT) .

2. Calculation Methods

In the classical MD simulation, CLAYFF[8] was used for interatomic potential which is often used in the study of clay minerals. For *ab initio* MD, the atomic forces were obtained from the electronic states calculated by the projector-augmented plane-wave (PAW)[9,10] method within the framework of

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DFT. In the calculation, the generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof (GGA-PBE)[11] was used for the exchange-correlation potential. The plane-wave cutoff energies for the pseudo-wavefunctions and pseudo-charge density were 30 and 200 Ry, respectively.

3. Construction of amorphous tobermorite

To obtain a melting state, we begin by carrying out classical MD simulations at a temperature 2000 K. Then, we decrease the temperature of the system gradually (2000 K, 1500 K, 1000 K, 500 K, 300 K) to target temperature 300 K using two different methods: classical and *ab initio* MD simulations under the NVT ensemble. Finally, the system was relaxed by MD simulation under the NPT ensemble. In applying this method, we refer to a previous research[12].

4. Results and discussion

4. 1 Differences in the structure of amorphous tobermorite

The density obtained from classical MD (1.42 g/cm^3) is smaller than that from *ab initio* MD simulation (2.02 g/cm^3). However, density of C-S-H depends on CaO/SiO_2 molar ratio and amount of water contained.

Figure 1 shows the structure of amorphous tobermorite obtained from (a) classical MD, and (b) *ab initio* MD methods. Where the yellow, red, white, and blue ball show the silicon, oxygen, hydrogen, and calcium, respectively. The yellow networks show that SiO_4 tetrahedra. As presented in Fig. 1, there are a large number of SiO_4 tetrahedra in *ab initio* MD compared to that in classical MD. Furthermore, the network structures consist of SiO_4 tetrahedra are found in *ab initio* MD.

Focusing on H_2O molecules, H_2O in the classical MD simulation shows uniform distribution, but those in the *ab initio* MD simulation are partially distributed in the gaps between Si-O chains.

4. 2 Radial distribution function (RDF)

Figure 2 shows the radial distribution function g(*r*) for (a)Si-Si, (b)Si-O, and (c)O-Ca. The red line shows g(*r*) obtained from classical MD, and the blue line shows g(*r*) obtained from *ab initio* MD.

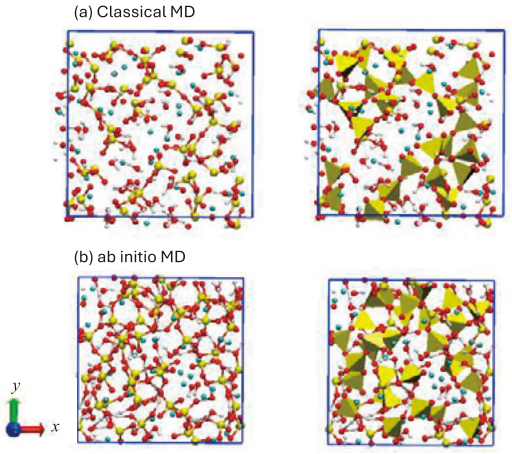

Fig.1 Structure of the amorphous tobermorite constructed by: (a)classical MD, and (b)*ab initio* MD methods. The yellow, red, white, and blue ball show the silicon, oxygen, hydrogen, and calcium, respectively. The yellow network shows that SiO_4 tetrahedra.

As shown in Fig. 2 (a), g(*r*) for Si-Si obtained from classical MD and *ab initio* MD have peak at about 3.6 Å and 3.1 Å, respectively. For the Si-O interactions, g(*r*) for classical MD and *ab initio* MD shows the peak at about 1.8 Å and 1.7 Å, respectively. In terms of Ca-O interaction, g(*r*) for classical MD and *ab initio* MD shows the peak at about 2.8 Å and 2.4

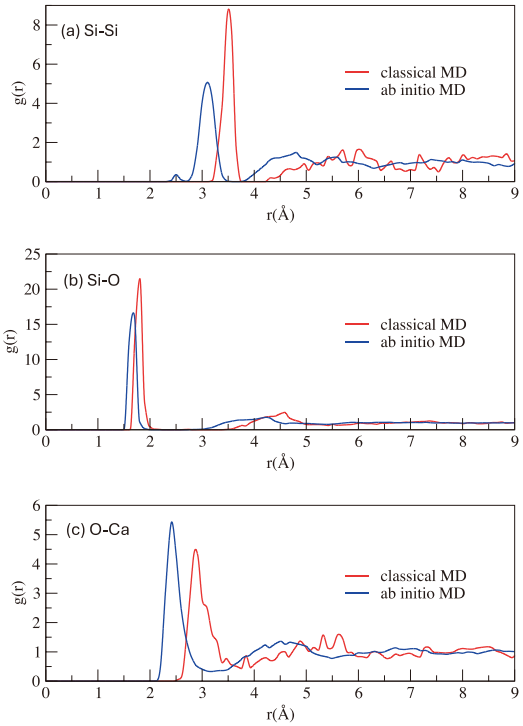

Fig.2 Radial distribution function g(r) of (a)Si-Si, (b)Si-O, and (c) O-Ca. The red line shows the g(r) obtained from classical MD, the blue line shows the the values obtained from *ab initio* MD.

Å, respectively. In crystalline 11Å tobermorite, the layer surface consists of Ca and O atoms and the distance is about 2.4-2.6 Å. Therefore, the peak position of Ca-O implies that the layered structure of crystalline tobermorite is partially retained in amorphous tobermorite obtained from *ab initio* MD simulation.

5. Summary

In this research, we investigated the local structure of amorphous tobermorite using classical and *ab initio* MD method. In the classical MD using CLAYFF[8], the density was lower than C-S-H obtained from experiment and the amount of SiO_4 tetrahedra was low. In *ab initio* MD based on DFT, the density was higher than that obtained from classical MD, and network structures consists of SiO_4 tetrahedra were observed. Additionally, the *ab initio* MD simulation results imply that the layered structure of crystalline tobermorite is partially preserved in amorphous tobermorite.

In conclusion, in the amorphous structure constructed by *ab initio* MD, the partial retention of crystalline tobermorite layered structure is observed. Since the amorphous structure depends on the construction method and the composition of the C-S-H, in addition to the interatomic potential used, more detailed and extensive studies are needed in the research on amorphous tobermorite.

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