

# Pressure-induced structural changes in hemimorphite and dehydrated hemimorphite: first-principles calculation

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Mineral hemimorphite ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ ) contains both OH and molecular  $\text{H}_2\text{O}$  in the structure. Dehydrated form ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2$ ) can be obtained by heating hemimorphite at around 600 °C, but still keeping original structure. Thus, these phases provide us good opportunity to explore hydrogen bondings in minerals. In this study, pressure-induced structural changes for those two phases were studied using first-principles calculations. For hemimorphite, a pressure-induced phase transition to "hemimorphite II" has been reported (Seryotkin & Bakakin, 2011), and the transition is characterized by rotation of a rigid block made of  $\text{Zn}_4\text{Si}_2\text{O}_{13}(\text{OH})_2$ . Similar transition is expected for the dehydrated hemimorphite, as the structure is essentially identical except molecular  $\text{H}_2\text{O}$ . It should be noted that dehydrated hemimorphite is metastable phase at ambient condition, and it is not clear whether any stable phase exists for this composition (also see Xue's talk in this session). Hereafter, hemimorphite is abbreviated as "HEM", whereas dehydrated hemimorphite is abbreviated as "DHEM".

For the calculations for HEM, both ambient pressure phase (HEM I), and high-pressure form (HEM II) are considered. For the calculations for DHEM, its structure at ambient condition (DHEM I), and a high pressure form (DHEM II) which is modeled from HEM II by removing  $\text{H}_2\text{O}$ , are considered. Additionally, we considered bertrandite ( $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$ ) structure as a possible stable phase at high pressure. It should be noted that DHEM I has protons which is a half occupied. So we need to consider at least several possible proton distribution models for the calculation. Three models are considered with OH bonds pointing different directions. First-principles calculations were conducted using Quantum-Espresso 6.4.1 package, and in order to take into account for van der Waals interaction, we employed nonlocal correlation functional "rVV10" combined with PBE (PAW) potentials from pslibrary (ver. 1.0.0). Crystal structures were optimized at each pressure, and compressed to 10 GPa with 0.5-GPa step.

For HEM, at first we used an ideal structure obtained from X-ray diffraction study. But then we found HEM II has lower enthalpy than HEM I even at 1 bar. This is likely due to our less satisfactory model for HEM I. In realistic model, OH and  $\text{H}_2\text{O}$  is forming hydrogen bonding, and lowering their symmetry at local structure level. Our new model considered this, and now the enthalpy was lower than HEM II at 1 bar. We found a transition for HEM II at about 10 GPa, and a half of Zn becomes tetrahedral to five-fold coordination at this transition.

For DHEM, bertrandite phase has lowest volume and enthalpy than that of other phases even at 1 bar. Thus we may expect that bertrandite phase could be a candidate for stable high-pressure phase for this composition. However, our preliminary piston cylinder experiments revealed that there is no stable DHEM phase up to 1.5 GPa. We found that starting from one of three hydrogen configuration models of DHEM I, Si-O-Si angle is significantly changed, and volume of the structure becomes almost same to that of DHEM II. This suggested another possible phase transition for DHEM at low temperature, but it is not stable phase.

For DHEM II, hydrogen bond distance is geometrically related to rotation of the rigid unit, and larger rotation results stronger hydrogen bonding. The another phase (Si-O-Si kinked), the kink in Zn-O-Zn is

related to hydrogen bond distance, and more kinked angle resulted stronger hydrogen bonding. Apparently hydrogen bonding is governing structural evolution of those phases with pressure.

Keywords: hemimorphite, pressure-induced phase transition, hydrogen bonding, first-principles calculation