First-principles simulations of pyrite-type FeO_2H and its isochemical melts at high pressure

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Recent laser-heated diamond-anvil cell experiments suggest that the pyrite-structured iron peroxide with varying hydrogen concentration (FeO_2H_x) is stable up to 2,600 K and 133 GPa while exhibiting thermoelastic properties consistent with ultralow velocity zones (ULVZs). As a result, subducted FeO_2H_x has been invoked to be a plausible cause of ULVZs. However, the temperature near the core-mantle boundary is expected to reach 4000 K at 136 GPa. Under such extreme conditions, the stability of FeO_2H_x remains unkown.

Here, we perform first-principles molecular dynamics simulations on the hydrogen-rich end member of FeO_2H_x system, FeO_2H. We focus on the melting temperature of this material and also study the thermodynamic and structural properties of its corresponding melt. Our preliminary results show that FeO_2H solid is ~2% denser than the isochemical melt at 3000 K and 136 GPa. The density difference decreases gradually with pressure and a crossover is predicted to occur around 220 GPa. Our structural analysis suggests that the distribution of hydrogen atoms in the melt differs dramatically from that in the solid. In the melt, the H-bridges (linking two FeO_6 octahedral corners in the solid) become connected with each other forming longer -H-O-H-O- chains via two (even three) hydrogen coordinated oxygens and also tending to avoid Fe atoms. It is remarkable that more than one-third of the oxygen in the molten FeO_2H is not bonded with any hydrogen representing regions of hydrogen depletion. The calculated mean coordination values in most cases gradually increase with increasing pressure with abundance of various coordination species (e.g., non-octahedral Fe-O coordination polyhedra) being sensitive to both pressure and temperature.