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Spin crossover and thermodynamic properties of ferric Fe-bearing MgSiO3 perovskite at lower mantle P-T conditions

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(Mg,Fe)SiO_3 perovskite is thought to be the most abundant phase in the Earth lower mantle. Mineral physical studies on this phase is therefore of significant importance in investigating structure and dynamics of the Earth deep mantle. Several studies suggest that Fe is primarily in the ferric oxidation state in silicate perovskite (McCammon, 1997; Frost et al., 2004). In addition, Fe^{3+} could undergo a spin transition, from high spin to low spin, and induce large changes in the thermodynamic properties of the phase, in particular, its bulk modulus (Catalli et al., 2010). However, due to some technical difficulties for the Fe-bearing phases, the high-P,T thermodynamics of ferric Fe-bearing $MgSiO_3$ perovskite are yet to be well understood both experimentally and theoretically. In particular, all the ab initio studies on Fe^{3+}-bearing $MgSiO_3$ perovskite conducted so far are limited at static condition.

Here, we present the results of a computational study on the thermodynamic properties of ferric Fe^{3+}-bearing $MgSiO_3$ perovskite up to 150GPa. We perform density functional calculations beyond conventional methods based on the internally consistent LDA+U technique (Tsuchiya et al., 2006) to describe local interactions between the d-states in Fe in more appropriately that give rise to Hubbard splitting. In this study, ferric Fe is incorporated as substitutional single-point defects in both Mg and Si sites, which can be present in different spin states (low or high) and magnetic states (ferro-, ferri-, and antiferromagnetic). The calculations are performed for several Fe-Fe interatomic distances in order to investigate the effects of the Fe configuration. We calculate the phonon dispersion relations of the Fe^{3+}-bearing phases based on the direct method, where the force constant matrices are determined by directly applying small but finite atomic displacements, similarly to our previous study in ferrous Fe^{2+}-bearing $MgSiO_3$ perovskite and post-perovskite (Metsue and Tsuchiya, 2011, 2012). Then, we determine several important thermodynamic quantities such as the vibrational entropy, free energy, heat capacities, bulk moduli and thermal expansion coefficient within the quasiharmonic approximation. These results are compared to those reported by Tsuchiya et al. (2005) for pure $MgSiO_3$ and by Metsue and Tsuchiya (2012) for ferrous Fe^{2+}-bearing $MgSiO_3$ perovskite. Our results suggest that ferric Fe undergoes a spin transition in the Si-site at pressures ˜50 GPa. The thermodynamic properties of $MgSiO_3$ perovskite are more affected by the incorporation of Fe^{3+} compared to Fe^{2+} but remain limited. Although the spin crossover pressure is consistent with experiments, it does not induce large changes on the thermodynamic properties, contradicting the previous experimental study of Catalli et al. (2010).

Keywords: MgSiO3 perovskite, spin transition, mineral physics