A first-principles investigation of hydrous defects and IR frequencies in forsterite:
The case for Si vacancies

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ABSTRACT

We investigate charge-balanced hydrous magnesium and silicon defects [(2H)ₓMg, (4H)ₓSi] by first principles. Two new lowest-energy hydrogen configurations are proposed for (4H)ₓSi. With these new configurations, the distribution of O-H stretching phonon frequencies in Group I (>3450 cm⁻¹) are better reproduced. Substitution of silicon with four hydrogen atoms gives rise to significant elongation of distances between O atoms at the tetrahedron of the silicon vacancy. Our calculations indicate that the correlation between O-O distances and O-H stretching phonon frequencies, which has been well established for hydrous minerals, does not apply directly to nominally anhydrous minerals and should not be used to determine the identity of hydrous defects responsible for infrared absorption peaks.

Keywords: Hydrous defects, forsterite, phonon frequencies, nominally anhydrous minerals, first principles

INTRODUCTION

The physical properties of the Earth’s upper mantle, whose main component is olivine, are strongly affected by trace amounts of water (for a review, see Kepler and Smyth 2006). Water is incorporated in the olivine structure as interstitial hydrogen, in some cases associated with another minor element, such as aluminum or ferric iron. Structures of hydrous defects, therefore, offer fundamental information about the nature and energies involved in processes related to the presence of water. Several computational first-principles studies, which looked into hydrous defects at the atomic scale, have investigated the formation energies of H associated with Mg and Si vacancies and at interstitial sites (Wright and Catlow 1994; Haiber et al. 1997; Brodholt and Refson 2000; Braithwaite et al. 2003; Walker et al. 2003, 2006, 2007; Verma and Karki 2009). Experimental documentation of the atomic structures of hydrous defects is not straightforward, but infrared (IR) spectroscopy of hydrous forsterite/olivine provides helpful information about O-H stretching modes. There are several IR studies of water-bearing forsterite/olivine (e.g., Bai and Kohlstedt 1992, 1993; Libowitzky and Beran 1995; Lemaire et al. 2004; Matsyuk and Langer 2004; Berry et al. 2005; Matveev et al. 2001, 2005; Koch-Müller et al. 2006; Smyth et al. 2006; Kudoh et al. 2006; Mosenfelder et al. 2006; Verma and Karki 2009) and these show that the IR spectra depend on silica activity influenced by buffer materials (periclase and enstatite) and the presence of metallic cations (iron, titanium, and so on). Absorption bands of IR spectra have been divided into two groups: Group I (phonon frequencies > 3450 cm⁻¹) and Group II (<3450 cm⁻¹) (Bai and Kohlstedt 1992, 1993). The Group I bands consist of multiple convoluted peaks. The origin of this complex profile has not been clear, but it is not likely from a single hydrogen configuration. Some experiments attributed these peaks to hydrous Si vacancies (Matveev et al. 2001; Berry et al. 2005; Kosov et al. 2010) and hydrous Mg vacancies (Kudoh et al. 2006; Smyth et al. 2006). Others claimed that these peaks should be related to both Mg and Si vacancies (Lemaire et al. 2004; Koch-Müller et al. 2006; Gose et al. 2010). Kohlstedt (2006) also suggested, on the basis of solubility and diffusion constants, that the primary defects involved in incorporation of hydrogen in olivine should be Mg vacancies. Theoretically, the Group I bands were attributed to the Si defects (Braithwaite et al. 2003; Walker et al. 2006).

In the present paper, we reinvestigate hydrous defects associated with vacant Si and Mg sites in forsterite by first-principles calculations. We propose new hydrogen configurations for the hydrogen-saturated Si vacancy, (4H)ₓSi. These new configurations together are able to explain IR peaks in the Group I spectral region better than other configurations that have been previously considered. The new hydrogen configurations are expected to occur not only in forsterite but also in wadsleyite and ringwoodite, which also contain SiO₄ tetrahedra.

Computational Method

Calculations were performed using the generalized gradient approximation (GGA) (Perdew et al. 1996). The pseudopotentials for Si, O, and H were generated by Vanderbilt’s method (Vanderbilt 1990). The valence electronic configurations used are 3s²3p²3d⁰, 2s²2p⁴, and 1s⁰ for Si, O, and H, respectively. Core radii for all quantum numbers / are 1.6, 1.4, and 0.5 a.u. for Si, O, and H, respectively. The pseudopotential for Mg was generated by von Barth-Car’s method (Karki et al. 2000). The planewave cutoff energy is 544 eV. Forsterite at 0 GPa with 28 atoms and no vacancies was optimized using variable-cell-shape molecular dynamics (Wentzcovitch 1991; Wentzcovitch et al. 1993) with the 4×2×4 k-point mesh. The optimized lattice constants of forsterite without vacancies are a = 4.800 Å,