Crystal chemistry of hydrous forsterite and its vibrational properties up to 41 GPa

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Abstract

The crystal structure of hydrous pure magnesium forsterite (Mg_2SiO_4) containing 8900 ppmw H_2O, synthesized at 12 GPa and 1250 °C, has been refined. The major hydration mechanism appears to be M1 cation vacancy with protonation of the O1-O2 octahedral edge of M1. Raman spectra up to 41 GPa show strong coupling between the two J_2 modes (824.4 and 856.2 cm⁻¹). Mode Grüneisen parameters γ, related to Mg(2)O translation mode decrease relative to anhydrous forsterite. This is attributed to the fact that the M2 site shows full occupancy compared to the M1 site, and the vacancy predominantly occurs at the M1 site. Pressure dependencies of four OH vibrations in the region 3548–3615 cm⁻¹ suggest that positional ordering of hydrogen ion (proton) takes place with increasing pressure. The OH mode at 3615 cm⁻¹ shows complex response as a function of pressure: the (dν/dP) slope changes from –0.43 below 10 GPa to 1.97 between 10 and 20 GPa, and does not show clear pressure dependence above 20 GPa. Single-crystal X-ray data were used to assign the OH band to the structural sites, O1 and O2. The proton is closer to O2 than O1. The distance between the proton and O2 is 0.96 Å. In view of the empirical relation between OH-stretching frequencies and O···O distances (Libowitzky 1999), the pressure dependence of the OH mode (3615 cm⁻¹) is well correlated with the O1-O2 distance and the degree of hydrogen bonding.

Keywords: Forsterite, X-ray diffraction, Raman spectroscopy, hydration mechanism, high pressure

Introduction

The nominally anhydrous mineral phases—olivine (α-), wadsleyite (β-), and ringwoodite [γ-(Mg,Fe)2SiO_4]—in the Earth’s upper mantle and transition zone (410–660 km depth) may serve as a large internal reservoir of water that has profound implications for Earth’s evolution as a water planet. This concept has generated deep interest in systematic investigations of the various elastic (seismic) properties, as well as the stability of these phases as a function of water content (i.e., H content, or hydration state), crystal structure, oxidation state of Fe, and P-T environments. One of the major findings is that the effect of hydration is to decrease bulk modulus (K_b) and increase K’_0 by increasing the vacancy or unoccupied volume in the structure (e.g., Inoue et al. 1998; Jacobsen and Smyth 2006; Smyth and Jacobsen 2006). This paper represents one such step in a continued systematic investigation of the structure, vibrational properties, and compression behavior of hydrous mantle minerals.

The incorporation of hydrogen in anhydrous mineral phases occurs by bonding to lattice oxygen to form hydroxyl groups (OH⁻) known in the literature as water. Much effort has been put into estimating the OH⁻ storage capacity of nominally anhydrous mineral phases, and to determining the factors controlling OH⁻ substitution and its incorporation mechanism in the lattice (Miller et al. 1987; Mackwell and Kohlstedt 1990; Rossman and Smyth 1990; Skogby et al. 1990; Bai and Kohlstedt 1993; Smyth 1994; Smyth et al. 1997; Kohlstedt et al. 1996; Matveev et al. 2001; Khisina et al. 2001; Bell et al. 2003; Braithwaite et al. 2003; Matsuysik and Langer 2004; Zhao et al. 2004; Koch-Müller et al. 2006; Mosenfelder et al. 2006; Walker et al. 2007; Bali et al. 2008). These studies have revealed that hydroxyl occurrence in mantle phases is closely related to the crystal defect structure, and that it is controlled by the diffusion rates of cations, anions, and point defects.

Although point defects have been linked to hydrogen incorporation, there remain several questions as to which point defect predominates under various conditions. Smyth (2006) has reviewed the crystal structures of the nominally hydrous and anhydrous phases that are likely constituents of Earth’s mantle. In nominally hydrous silicate structures, H normally bonds to a non-silicate oxygen, that is, an oxygen not bonded to Si. There are a few examples of a proton bonded to a silicate oxygen such as in the pyroxenoids, pectolite, and serandite, but these are unusual cases in which there is an anomalously short O-O distance between unshared O atoms. In nominally anhydrous silicates, four protons may replace Si as in the hydro-garnet substitution, but this substitution has a large volume effect and is therefore destabilized by pressure (Withers et al. 1998). In pyroxenes, protonation of an oxygen atom bonded to a tetrahedral site can occur if there is some Al substitution (Smyth et al. 2007), but, again, Al substitution in tetrahedral sites is destabilized by pressure. More commonly, protonation is balanced by an octahedral...