Incorporation of water in iron-free ringwoodite: A first-principles study

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ABSTRACT

The structures, infrared active OH stretching modes, and relative energies of OH-defects in ringwoodite (γ-Mg2SiO4) have been studied by first-principles calculations based on density functional theory (DFT). Two types of fully protonated cationic defects in normal spinel were considered at 0 and 20 GPa, i.e., [V_{bgd}(OH)]\textsuperscript{x}, [V_{sd}(OH)]\textsuperscript{x} defects. In addition, two defects associated with the partial inversion of the spinel structure have been investigated. The first one corresponds to two protons compensating a Mg substituted for Si in tetrahedral site, [Mg(OH)]\textsuperscript{x}, whereas the second defect corresponds to a Mg vacancy located nearby a Mg-Si substitution, [Mg(OH)]\textsuperscript{x}Mg_{bgd}Si_{bgd}. The infrared spectrum and evolution with pressure of these OH-defects make it possible to interpret the major IR absorption bands experimentally observed. The main absorption band at ~3150 cm\textsuperscript{-1} corresponds to protons located between the O-O pairs shared by 16c and 16d octahedra, instead of OH along the tetrahedral edges as usually proposed in the literature. The large width of this band is most likely related to the association of OH defects with the various cationic configurations related to the partial inversion of a vacancy-bearing spinel structure. The less intense band at ~3675 cm\textsuperscript{-1} is assigned to hydrogarnet-type defects with a protonation of the tetrahedral edges. This interpretation is consistent with an Mg/Si ratio lower than 2 and its weak variation as a function of water concentration, as experimentally observed. These results emphasize the importance of taking into account the structural relaxation experienced by defects, instead of using empirical correlation, to assign OH stretching bands to specific O-O pairs of the structure.

Keywords: Ringwoodite, Mg2SiO4 spinel, hydrogen, DFT, infrared spectroscopy

INTRODUCTION

Ringwoodite (γ-Mg2SiO4) is considered to be the most abundant mineral in the lower part of the transition zone (520–660 km depth). Solubility studies performed at high pressure from natural or synthetic materials have shown that ringwoodite can incorporate a significant amount of water (up to ~2.7 wt% H2O) in the form of OH groups within its crystal structure (Kohlstedt et al. 1996; Bolfan-Casanova et al. 2000). The presence of water modifies the physical and chemical properties of the mineral and, in turn, the dynamics of the transition zone. The incorporation of water (~2.2 wt% H2O) decreases aggregate elastic moduli by about 10% (Inoue et al. 1998; Wang et al. 2003; Smyth et al. 2004; Jacobsen et al. 2004), which leads to a substantial reduction of the seismic velocity (~5%). Thus hydration would have a larger effect on seismic velocity than temperature at mantle conditions. The presence of water also has a strong effect on electrical conductivity (Huang et al. 2005; Yoshino et al. 2008) and significantly weakens ringwoodite (Chen et al. 1998; Kavner 2003). Therefore the interpretation of geophysical data needs to account for the effect of water not only in terms of the degree of hydration but also the incorporation mechanism. Sinogeikin and Bass (1999) have shown that the incorporation mechanism itself influences the elastic properties. However, the nature of hydrogen sites in ringwoodite remains unclear as well as the origin of the very broad band between 3800 and 2500 cm\textsuperscript{-1} associated with OH in infrared spectra (e.g., Smyth et al. 2003).

Ringwoodite has a cubic spinel structure (space group Fd\textbar{3}m) such that there is only one crystallographically distinct site for each element. Oxygen is close-packed with silicon in tetrahedral sites (8a), and magnesium in octahedral sites (16d). The spinel structure also contains another octahedral site, i.e., 16c, which is vacant. The structure consists of two types of layers stacked alternately along the [111] direction, one made of MgO\textsubscript{6} tetrahedra and SiO\textsubscript{4} tetrahedra (OT layer), and the other made of MgO\textsubscript{6} octahedra (O layer). The location of the 16c octahedral site is between two tetrahedra in the OT layer (Fig. 1). The structure of hydrous ringwoodite single crystals was analyzed by X-ray diffraction (Kudoh et al. 2000; Smyth et al. 2003, 2004). These studies mainly indicate the presence of octahedral vacancies and also report a small degree of Mg-Si disorder. By looking at the correlation between the Mg/Si ratio and the water content, Kudoh et al. (2000, 2001) suggest that hydrogen is accommodated via a combination of two types of substitution: type A involving only Mg vacancies (Mg ↔ 2H) and type B corresponding to a coupled substitution with both Mg vacancies and Mg in Si sites (Mg\textsubscript{Si} ↔ 8H). Finally, based on infrared and Raman spectra, and on correlations between the O-O distance and the OH stretching frequency (Nakamoto et al. 1955; Libowitzky 1999), these authors discuss the proton locations. According to Kudoh et al. (2000), possible sites for hydrogen are between O-O pairs...