American Mineralogist, Volume 94, pages 83–89, 2009

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

Marc Blanchard,[1,2,*] Etienne Balan,[1,2] and Kate Wright[3]

[1]IRD, 209 rue La Fayette, 75480 Paris cedex 10, France
[2]IMPMC, UMR CNRS 7590, Universités Paris VI et VII, IPGP, 140 rue de Lourmel, 75015 Paris, France
[3]Nanochemistry Research Institute, Curtin University of Technology, P.O. Box U1987, Perth 6845, Australia

Abstract

The structures, infrared active OH stretching modes, and relative energies of OH-defects in ringwoodite (γ-Mg_2SiO_4) 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., $[V_{Mg}(OH)_2]^x$, $[V_{Si}OH)_4]^x$ 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, $[Mg_{Si}(OH)_2]^x$, whereas the second defect corresponds to a Mg vacancy located nearby a Mg-Si substitution, $[V_{Mg}(OH)_2Mg_{Si}Si_{Mg}]^x$. 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^{-1} corresponds to protons located between the O-O pairs shared by 16*c* and 16*d* 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^{-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, Mg_2SiO_4 spinel, hydrogen, DFT, infrared spectroscopy