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Infrared signatures of OH-defects in wadsleyite: A first-principles study

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ABSTRACT

The structure and the polarized infrared absorption spectrum of OH-defects in wadsleyite (β-Mg_2SiO_4) are studied, at 0 and 15 GPa, by first-principles calculations based on density functional theory (DFT). Four types of OH-defects are considered: fully protonated magnesium vacancies, fully protonated silicon vacancies, silicon vacancies compensated by a magnesium cation and two protons, and OH-defects associated with the migration of a silicon cation to a normally vacant site, as reported by Kudoh and Inoue (1999). The results suggest that the main absorption band constituted by a doublet (3326 and 3360 cm^{-1}) corresponds to at least two types of OH-defects involving M3 vacancies with protonation of the O1-type O atoms along the O1···O4 edges. The main contribution of the less intense band at 3581 cm^{-1} is likely related to the partial protonation of a silicon vacancy (protonation of the O3-type oxygen) associated with the migration of the silicon cation to the Si2 site. This assignment is consistent with several experimental constraints: wavenumber and pleochroism of infrared OH-stretching bands, pressure-dependence of the band wavenumber, evidence from X-ray diffraction of magnesium vacancies in M3 site, and increase of the *b*/*a* axial ratio with water content. The integrated absorption coefficients of the corresponding OH-defects are also calculated and thus complement the set of data obtained previously for forsterite and ringwoodite. Absorption coefficients of wadsleyite computed at 0 and 15 GPa indicate that for a precise quantification of the hydrogen content in in situ experiments, one must consider higher absorption coefficients than those determined at 0 GPa after quench. It is also shown that a single theoretical relation can account for the three Mg_2SiO_4 polymorphs at 0 GPa: $K_{int} = 278.7 \pm 18.1\ (3810 \pm 465 - x)$, where K_{int} is the integrated molar absorption coefficient of the OH stretching modes and x is the average wavenumber in cm^{-1}. Absorption coefficients are significantly lower than the general calibrations, the use of which would lead to an underestimation of the water concentrations.

Keywords: Wadsleyite, OH-defect, IR spectroscopy, ab initio calculations, DFT