

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

ANWAR HUSHUR,¹ MURLI H. MANGHNANI,^{1,*} JOSEPH R. SMYTH,² FABRIZIO NESTOLA,³ AND DANIEL J. FROST⁴

¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.

²Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309, U.S.A.

³Department of Geosciences, University of Padova, Via Giotto 1, I-35137 Padova, Italy

⁴Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

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 A_g modes (824.4 and 856.2 cm^{-1}). Mode Grüneisen parameters γ_i related to $\text{Mg}(2)\text{O}_6$ 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 $(\partial\nu/\partial P)$ 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 $\text{O}\cdots\text{O}$ 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