

## **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 ( $\text{Mg}_2\text{SiO}_4$ ) containing 8900 ppmw  $\text{H}_2\text{O}$ , 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  $\text{cm}^{-1}$ ). Mode Grüneisen parameters  $\gamma_i$  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  $\text{cm}^{-1}$  suggest that positional ordering of hydrogen ion (proton) takes place with increasing pressure. The OH mode at 3615  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ ) 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