

OH⁻ in synthetic and natural coesite

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ABSTRACT

The incorporation of hydrogen into the coesite structure was investigated at pressures ranging from 4.0–9.0 GPa and temperatures from 750–1300 °C using Al and B doped SiO₂ starting materials. The spectra show four sharp bands (ν_1 , ν_{2a} , ν_{2b} , and ν_3) in the energy range of 3450–3580 cm⁻¹, consistent with the hydrogarnet substitution [$\text{Si}^{4+(T2)} + 4\text{O}^{2-} = \text{va}^{T2} + 4\text{OH}^-$], two weak sharp bands at 3537 and 3500 cm⁻¹ (ν_{6a} and ν_{6b}) attributed to B-based point defects, and two weaker and broad bands at 3300 and 3210 cm⁻¹ (ν_4 and ν_5) attributed to substitution of Si⁴⁺ by Al³⁺ + H. More than 80% of the dissolved water is incorporated via the hydrogarnet substitution mechanism. The hydrogen solubility in coesite increases with pressure and temperature. At 7.5 GPa and 1100 °C, 1335 H/10⁶ Si is incorporated into the coesite structure. At 8.5 GPa and 1200 °C, the incorporation mechanism changes: in the IR spectra four new sharp bands appear in the energy range of 3380–3460 cm⁻¹ (ν_7 – ν_{10}) and the ν_1 – ν_3 bands disappear. Single crystal X-ray diffraction, Raman spectroscopy, polarized single-crystal and in situ high-pressure FTIR spectroscopy confirm that the new bands are due to OH⁻ in coesite. The polarization and high-pressure behavior of the ν_7 – ν_{10} OH bands is quite different from that of the ν_1 – ν_3 bands, indicating that the H incorporation in coesite changes dramatically at these *P* and *T* conditions. Quantitative determination of hydrogen solubility in synthetic coesite as a function of pressure, temperature, and chemical impurity allow us to interpret observations in natural coesite. Hydrogen has not previously been detected in natural coesite samples from ultra high-pressure metamorphic rocks. In this study, we report the first FTIR spectrum of a natural OH-bearing coesite. The dominant substitution mechanism in this sample is the hydrogarnet substitution and the calculated hydrogen content is about 900 $\zeta \pm 300$ H/10⁶ Si. The coesite occurs as an inclusion in diamond together with an OH-bearing omphacite. The shift of the OH-bands of coesite and omphacite to lower energies indicates that the minerals are still under confining pressure.