OH– in synthetic and natural coesite

MONIKA KOCH-MÜLLER,1,* PRZEMYSLAW DERA,2 YINGWEI FEI,2 BARRY RENO,3 NIKOLAI SOBOLEV,4 ERIK HAURI,5 AND RICHARD WYSOCZANSKI6

1GeoForschungsZentrum Potsdam, Sektion 4.1, Telegrafenberg, Potsdam D-14473, Germany
2Carnegie Institution of Washington, Geophysical Laboratory, 5251 Broad Branch Road N.W., Washington, D.C. 20015-1305, U.S.A.
3Trinity University, Department of Geosciences, 1932-715 Stadium Drive, San Antonio, Texas 78212-7200, U.S.A.
4Russian Academy of Science, Siberian Branch, Institute of Mineralogy and Petrography, 3 Koptyug Avenue, Novosibirsk 90, 630090, Russia
5Carnegie Institution of Washington, Department of Terrestrial Magnetism, 5251 Broad Branch Road N.W., Washington, D.C. 20015, U.S.A.
6Smithsonian Institution, Department of Mineral Sciences, National Museum of Natural History, Washington, D.C. 20560-0119, U.S.A.

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 (ν1, ν2, ν3, and ν4) in the energy range of 3450–3580 cm–1, consistent with the hydrogarnet substitution [Si4+(T2) + 4O2– = vaT2 + 4OH–], two weak sharp bands at 3537 and 3500 cm–1 (νa and νb) attributed to B-based point defects, and two weaker and broad bands at 3300 and 3210 cm–1 (ν1 and ν2) 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 (ν7–ν10) and the ν1–ν4 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 ν7–ν10 OH bands is quite different from that of the ν1–ν4 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 ± 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.

INTRODUCTION

Recent experimental studies have shown that the SiO2 polymorph coesite belongs to the group of nominally anhydrous minerals which incorporate hydrogen in the form of hydroxyl groups (Li et al. 1997; Mosenfelder 2000; Koch-Müller et al. 2001). Mosenfelder (2000) investigated the pressure dependence of OH solubility in coesite at 1200 °C and found that OH incorporation increased with pressure. FTIR spectra from OH-bearing coesite samples published to date show at least six bands: four intense bands at 3575, 3528, 3508, and 3459 cm–1, and two weak bands at 3296 and 3210 cm–1. All six bands are due to OH-stretching vibrations (Koch-Müller et al. 2001). In addition to these bands Mosenfelder (2000) observed a weak shoulder on the high energy side of the band at 3575 cm–1. Using ion probe analyses along with polarized and in situ high-pressure FTIR spectroscopy, Koch-Müller et al. (2001) concluded that hydrogen incorporation into coesite was consistent with the hydrogarnet substitution mechanism, Si4+(T2) + 4O2– = vaT2 + 4OH–. The vibrations of the low symmetry (OH)2 group in coesite (point symmetry 1) must give rise to four bands as observed. According to Koch-Müller et al. (2001) O2, O3, O4, and O5 are the proton accepting O atoms. This is in excellent agreement with the results of Gibbs et al. (2002) based on mapping of the electron localization function for coesite. Although the mechanism of hydrogen incorporation in coesite can be explained by the hydrogarnet substitution, the arrangement of the four OH-groups in the coesite structure is quite different from the arrangement of the OH-groups in garnet. As shown from X-ray and neutron diffraction studies of hydrogarnets (Lager et al. 1987, 1989), removal of the highly charged Si atom from the center of the tetrahedron and its replacement by four H atoms leads to an expansion of the tetrahedron by about 20%. In such a large tetrahedron the hydrogen atoms exhibit only intra-tetrahedral hydrogen bondings, with O–H···O distances of 3.05 and 3.26 Å (Lager et al. 1989). Such a large expansion of the vacant Si tetrahedron is not expected for the framework-like structure of coesite. Indeed the polarization and high-pressure behavior of the OH-stretching bands...