



Coupled Boron and Hydrogen Incorporation in Coesite

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Natural and synthetic coesite are widely known as nominally anhydrous minerals, which incorporate hydrogen mostly via the hydrogarnet substitution $\text{Si}^{4+} + 4\text{O}^{2-} =$

$(4)[\] + 4\text{OH}^-$ (e.g. Koch-Müller et al., 2001 and 2003). In this study we synthesized for the first time coesite which incorporate hydrogen solely via boron based defects.

The syntheses were carried out at relatively high pressures (9 - 12 GPa) and high temperatures (1000 - 2000 °C) using a Multi-Anvil press and H_3BO_3 doped SiO_2 as starting material.

The coesite crystals were characterized by FTIR spectroscopy in the OH stretching region. The spectra show two sharp OH bands at 3500 and 3533 cm^{-1} , respectively ν_{6a} and ν_{6b} , assigned by Koch-Müller et al. (2003) to two different B-based defects according to $\text{B}^{3+} + \text{H}^+ = \text{Si}^{4+}$.

We quantified the hydrogen and boron contents by FTIR spectroscopy and SIMS, respectively. Coesite synthesized at 9 GPa and 1400 °C incorporate $921 \pm 80 \text{ H}/10^6 \text{ Si}$ and $1600 \pm 300 \text{ B}/10^6 \text{ Si}$ in its structure. Thus, the B concentration is about 1.7 times higher than the H concentration and may be linked to the presence of oxygen vacancies (Pawley et al., 2003). Polarized single-crystal IR spectra revealed that the hydroxyl groups must be oriented along the crystallographic direction *a* of the structure. The crystals were further investigated by in-situ high-pressure IR spectroscopy. From the specific response of the OH bands to increasing pressure in combination with literature data on structural changes with pressure, we conclude that ν_{6b} arises either from vibration of a O1-H6b...O4 group with B on the T1 site or O4-H6b...O1 group with

B on the T2 site. Due to its different pressure behaviour compared to ν_{6b} the ν_{6a} band can be assigned either to vibration of a O4-H6a...O5 group with B on the T1 site or O5-H6a...O4 group with B on the T2 site. Most likely the relatively high pressure and temperature used to synthesize coesite in this study, compared to previous studies, favour the forming of the B-based defect, as such a defect is in comparison with the hydrogarnet substitution accompanied by a decrease of the tetrahedral site. Vacant tetrahedral sites are up to 20% larger than occupied sites (e.g. Armbruster and Gnos, 2000). Further investigations are necessary in order to understand the dramatic change in the H incorporation mechanism.

References

- Armbruster, T. and Gnos E. (2000) Tetrahedral vacancies and cation ordering in low temperature bearing vesuvianites: indication of a hydrogarnet like substitution. *Amer. Miner.*, 85, 570-577.
- Koch-Müller, M., Fei, Y., Hauri, E., Liu, Z. (2001) Location and quantitative analysis of OH in coesite. *Phys. Chem. Miner.*, 28, 693-705.
- Koch-Müller, M., Dera, P., Fei, Y., Reno, B., Sobolev, N., Hauri, E., Wysoczanski R. (2003) OH- in synthetic and natural coesite. *Amer. Miner.*, 88, 1436-1445.
- Pawley, A.R., McMillan, P.F., Holloway, J.R. (1993) Hydrogen in stishovite, with implications for water mantle content. *Science*, 261, 1024-1026.