

Effect of chemical environments on hydrogen related defects in wadsleyite

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Recent observations and high-pressure experiments have suggested that the order of 0.1 wt% water is stored in the Earth's mantle transition zone. Since state and amount of hydrogen in crystal change type and concentration of defects, these have significant influence on rheological and other defect-related properties of material. Therefore, for accurate understanding of material behavior in the mantle transition zone, it is important to clarify the state of hydrogen related defects in wadsleyite as a function of chemical environments (etc. water fugacity and oxygen fugacity). In this study, we have investigated the effects of chemical environments on state of hydrogen related defects in wadsleyite by FTIR analyses of samples annealed at wide range of hydrogen and oxygen fugacities.

Experiments were carried out using Kawai-type multi-anvil apparatus, KIWI, installed at Yale University. Starting materials for the subsequent annealing experiments were synthesized from San Carlos olivine powder. The synthesis conditions are $P = 14-15$ GPa, $T = 1230-1573$ K and $t = 1-2$ h.

The annealing experiments were carried out by using the synthesized samples. In the annealing experiments, we used three different types of capsule assembly depending on target water content. The sintered wadsleyite samples were embedded in 1) a AuPd capsule for 'dry' experiments, 2) a metal foil capsule for 'nominally dry' experiments and 3) a AuPd capsule with surrounding talc + brucite mixture for 'wet' experiments. In order to address effect of oxygen fugacity, each sample was surrounded by Mo, Ni or Re foil. Oxygen fugacity during annealing experiments is considered to be kept at each metal-oxide buffer. The conditions of annealing are $P = 15-16$ GPa, $T = 1450-2173$ K and $t = 0.25-48$ h. Water content of recovered samples ranges from below detectable limit (less than 50 ppm H/Si) to 240,000 ppm H/Si. FTIR measurements were carried out using doubly polished thin sections with thickness of 50-200 microns.

As a result, state of hydrogen in wadsleyite was found to highly depend on both water content and capsule material suggesting influences of water and oxygen fugacities (f_{H_2O} and f_{O_2}). At first, water-rich samples which contain more than 10,000 ppm H/Si show largest peak at 3330 cm^{-1} and 2 medium size peaks at around 3600 cm^{-1} regardless of capsule material. This FTIR pattern is consistent with spectra of wadsleyite reported by various papers. In the case of Mo capsule experiments (with low f_{O_2}), relative height of a peak at 3200 cm^{-1} increases with decreasing water content, and, finally, only this peak survives at less than 200ppm H/Si. On the other hand, in the case of Re capsule experiments (with high f_{O_2}), relative height of a peak at 3620 cm^{-1} increases with decreasing water content, and only this peak survives at at less than 1,000 ppm H/Si. In the case of Ni capsule experiments, the intermediate behavior (between Mo and Re experiments) was observed.

Previous studies on crystal chemistry of water-rich wadsleyite revealed that majority of hydrogen is incorporated by substituting an Mg atom by 2 H atoms. In this study, we found that peaks at 3200 and 3620 cm^{-1} show distinct behavior. These peaks may be related to hydrogen incorporated as other types of defect.