

## Poster Presentation

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### *Structure and H position of tetragonal hydrogarnet derived from CaGeO<sub>3</sub> garnet*

A. Nakatsuka<sup>1</sup>, H. Matsutomi<sup>1</sup>, K. Fujiwara<sup>1</sup>, N. Nakayama<sup>1</sup>, O. Ohtaka<sup>2</sup>, K. Sugiyama<sup>3</sup>

<sup>1</sup>Yamaguchi University, Graduate School of Science and Engineering, Ube, Japan, <sup>2</sup>Osaka University, Graduate School of Science, Toyonaka, Japan,

<sup>3</sup>Tohoku University, Institute for Materials Research, Sendai, Japan

Hydrogarnets, represented by hydrogrossular, are produced by the replacement of (ZO<sub>4</sub>)<sup>4-</sup> in garnets by (H<sub>4</sub>O<sub>4</sub>)<sup>4-</sup> (Z: tetrahedral cation) and the vacancies of tetrahedral cations are created by this replacement. Most of reported hydrogarnets crystallizes with cubic symmetry (space group Ia-3d). To our knowledge, Ca<sub>3</sub>Mn<sub>2</sub>[SiO<sub>4</sub>]<sub>2.07</sub>[H<sub>4</sub>O<sub>4</sub>]<sub>0.93</sub> with space group I41/acd (tetragonal) [1] has been only reported as a low-symmetry hydrogarnet. In the cubic hydrogarnets, all O atoms are crystallographically equivalent, whereas in low-symmetric one, they can be located at non-equivalent sites. Therefore, the investigation of low-symmetry hydrogarnets is important to gain knowledge of the site preference of H atoms. Recently, we have successfully synthesized the single crystal of a new low-symmetry hydrogarnet CaGe<sub>0.924</sub>O<sub>3</sub>H<sub>0.304</sub> (= Ca<sub>3</sub>(CaGe)[GeO<sub>4</sub>]<sub>2.696</sub>[H<sub>4</sub>O<sub>4</sub>]<sub>0.304</sub>) with tetragonal space group I41/a, at 3 GPa and 1273 K under the presence of H<sub>2</sub>O component. This tetragonal hydrogarnet is produced by the partial replacement of (GeO<sub>4</sub>)<sup>4-</sup> in high-pressure CaGeO<sub>3</sub> garnet, Ca<sub>3</sub>(CaGe)[GeO<sub>4</sub>]<sub>3</sub>, by (H<sub>4</sub>O<sub>4</sub>)<sup>4-</sup>. In the present study, we report the single crystal X-ray diffraction study of this hydrogarnet at 98 and 298 K. In the structure refinement at 298 K, the occupancy parameters resulted in 0.393(2) for tetrahedral Z2(Ge) site, coordinated only by O<sub>6</sub> atoms, and showed no significant deviation from 1.0 for the remaining cation sites. The bond valence sums of each atom except O<sub>6</sub> atom agree with the valences of occupied atoms, whereas that of O<sub>6</sub> atom are 1.50, deviating largely from oxygen valence. Thus, the substitution of OH groups for O atoms in the present sample occurs only at O<sub>6</sub> site, which indicates that O<sub>6</sub> is the most preferential site for the OH substitution. The position of H atom will be examined from the residual electron density distributions at a low temperature of 98 K, and the hydrogen bonding in the crystal structure will be discussed.

[1] T. Armbruster, T. Kohler, E. Libowitzky et al., *Am. Mineral.*, 2001, 86, 147-158.

**Keywords:** hydrogarnet, hydrogen bonding, single crystal X-ray diffraction