

## Estimation of hydrogen position in (Fe, Al)-bearing phase E structure using single-crystal diffraction data

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### Introduction

Phase E (ph E), Mg<sub>2</sub>SiH<sub>4</sub>O<sub>6</sub> (ideal), is known as one of the dense hydrous magnesium silicate minerals (DHMS). According to several previous researches<sup>[1][2]</sup>, this phase is stable under high-PT conditions such as 9 GPa and 800°C. DHMS phases are important in the view of the carriers and reservoirs of water in the Earth's subduction zone.

Ph E structure (space group is  $R\bar{3}m$ ) has a cubic closest packing of oxygen with a tetrahedral T site and two octahedral M1 and M2 sites. The crystal structure of ph E consists of brucite-like layers cross-linked by SiO<sub>4</sub> tetrahedra and MgO<sub>6</sub> octahedra with weak hydrogen bonds<sup>[3]</sup>. Adjacent T and M2 sites cannot be occupied simultaneously to avoid face-sharing, these cation sites are distributed statistically. Ph E has hydrogen bonds in its structure. Hydrogen bond is influenced on its thermodynamic properties, especially under high-PT conditions, however, the detail information on hydrogen positions in ph E structure was not obtained. We try to investigate hydrogen position in ph E using a single crystal diffraction intensity data set. Also we try to visualize the electron distributions in its structure by the ME (Maximum Entropy) analysis.

### Experimental Procedure

The sample used for this study was synthesized by Kawamoto et al.<sup>[4]</sup> at conditions 9.3 GPa and 875°C using a multi anvil apparatus. Chemical formula of this sample was Mg<sub>1.98</sub>Fe<sub>0.23</sub>Al<sub>0.17</sub>Si<sub>1.15</sub>O<sub>6</sub>H<sub>2.47</sub>. A blue transparent single crystal of ph E (0.06×0.04×0.03 mm<sup>3</sup> in size) was used for the experiment. The wavelength of synchrotron radiation ( $\lambda=0.7014$  Å) was calibrated by the unit cell volume of a ruby standard crystal (NIST, SRM 1990) at 25°C. The X-ray diffraction intensities were measured using an automated four-circle X-ray diffractometer installed at the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization. The unit cell parameters of ph E were  $a=2.9686(5)$  Å,  $c=13.795(3)$  Å,  $V=105.28(4)$  Å<sup>3</sup>. The X-ray reflection intensity data were collected up to  $\sin\theta/\lambda < 1.01$  Å<sup>-1</sup> (maximum  $2\theta$  is 116.0°). Corrections for background and Lorentz-polarization were applied to all measured reflections. Space group was determined as  $R\bar{3}m$  from the extinction rule. The symmetrically equivalent reflections were averaged by the Laue symmetry of  $\bar{3}m$ . 175 reflections ( $F_o > 4.0\sigma(F_o)$ ) were used for the structure refinement. Final agreement factors were  $R=4.5\%$ ,  $wR^2=10.4\%$  and  $GoF=1.230$ . Small

amount of Fe and Al in each site cause instability for site occupancy refinements in each octahedral site, therefore, only Mg scattering factor was used in this report. All calculations were performed using SHELXL97<sup>[5]</sup>. PRIMA<sup>[6]</sup> was used for ME analysis. The initial phase for ME analysis was calculated from the result of structure refinement. In ME analysis, unit cell was divided into 48×48×100 sections. Reflections having  $F_o < 1.5\sigma(F_o)$  do not use for ME analysis, yielding  $R_{MEM}=1.7\%$  and  $wR_{MEM}=0.67\%$ . Main crystallographic structural information was summarized in Table 1.

### Results and Discussion

The difference Fourier map at convergence of refinement of this specimen showed characteristic residual peak at (0, 0, 0.1928) with 0.54 e/Å<sup>3</sup> due to hydrogen. O-H distance was 0.82 Å, which was slightly short but was consistent to the estimated values from FT-IR spectra. Site occupancies of T, M1 and M2 sites were 0.18(4), 0.83 and 0.01(1), respectively. The occupancy of each site in this sample was similar to those of pure ph E<sup>[3]</sup>. There is no significant difference in both the M2 sites. The bond distances of M1-O and M2-O were 2.050(1)Å and 2.077(1)Å, respectively. M1-O distance of this sample was smaller than that (2.076Å) of pure ph E<sup>[3]</sup> due to the replacement of Mg<sup>2+TM</sup> Al<sup>3+</sup>. These results indicate that trivalent cation is occupied in M1 site mainly with vacancy. The electron distribution map of ph E after ME analysis was shown in Figure 1.

Table 1. Latest atomic coordinate and  $U_{eq}$

| Occ.       | x | y | z         | $U_{eq}$  |
|------------|---|---|-----------|-----------|
| M1 0.83(7) | 0 | 0 | 0         | 0.0182(3) |
| M2 0.01(1) | 0 | 0 | 0.5       | 0.0182(4) |
| T1 0.18(4) | 0 | 0 | 0.1298(1) | 0.0106(6) |
| O 1        | 0 | 0 | 0.2517(1) | 0.0277(4) |
| H 0.33     | 0 | 0 | 0.1928    | 0.05(3)   |

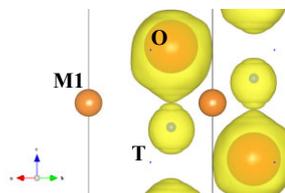


Figure 1 Electron distribution map around oxygen site in ph E viewed down on (110) calculated by PRIMA using single-crystal diffraction data set. Smallest ball is for T site, largest one is for O site and the other is for M1 site. Visualized by VESTA<sup>[7]</sup>.

### References

- [1] Gaspruk, T. *Contrib. Mineral. Petrol.*, **132**, 111-120, 1990; [2] Kanzaki, M., *Phys. Earth Planet. Interior.*, **66**, 307-312, 1991; [3] Kudoh et al., *Phys. Chem. Mineral.*, **19**, 357-360, 1993; [4] Kawamoto et al. 1995; [5] Sheldrick, 1997; [6] Izumi and Dilanian, 2002; [7] Momma and Izumi, *J. Appl. Cryst.*, **41**, 653-658, 2008.

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