

Structural Properties of Al-replaced Phase D

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Phase D, ideally $\text{MgSi}_2\text{H}_2\text{O}_6$, is one of dense hydrous magnesium silicate (DHMS) minerals. DHMS phases are stable under cold slab conditions, and are important to understand the transportation of H into deep Earth's interior. Two research groups first synthesized phase D at the almost same time [1, 2]. Although one of the groups described the new phase as "phase G" because the name "phase D" was already used for other phase, "phase D" was adopted. Phase D is generally synthesized with non-stoichiometric chemical formula like phase E, which is other DHMS phase. Crystal structure of phase D has the

trigonal symmetry with the space group $P\bar{3}1m$ (#162). One of the important structural properties of the phase is that Si atom occupies in six-coordinated site like in the stishovite structure [1, 3]. Although the chemical formula is non-stoichiometric, the crystal structure of the phase does not show any modulated structures. Recently, phase D including Al was synthesized at the conditions of 25-26 GPa and ~ 1600 °C coexisting bridgmanite [4, 5]. Also, Al-phase D, which is perfectly replaced Mg by Al, was reported [5], but structural information remains unclear. Although the behavior of Al in phase D structure is paid attention to, the structural information on Al-containing phase D is insufficient.

In this report, we conducted single-crystal X-ray diffraction measurements to investigate Al-site in phase D structure, and to clarify the replacement mechanism in the structure.

2. Experimental Procedure

The samples used for this study were synthesized by [4] at the conditions of 26 GPa and 1200 °C for sample #1 and 25 GPa and 1600 °C for sample #2, respectively. The chemical compositions of the synthesized phases were briefly checked by [4] with EDS-SEM. The chemical formulae of the samples (#1 and #2) were $\text{Mg}_{0.99}\text{Si}_{1.41}\text{Al}_{0.47}\text{H}_{3.00}\text{O}_6$ and $\text{Mg}_{0.91}\text{Si}_{1.28}\text{Al}_{0.73}\text{H}_{2.85}\text{O}_6$, respectively. Hydrogen contents were estimated from total deficit. After we checked the quality of crystals by taking oscillation photos, single crystal of each run were selected. Single-crystal X-ray diffraction experiments were performed using an automated four-circle X-ray diffractometer installed at the beam line BL-10A, PF,

KEK. The wavelength ($\lambda = 0.7012$ Å for #1 and $\lambda = 0.7123$ Å for #2) of synchrotron radiation in each run was calibrated by the unit cell volume of the NIST standard ruby at ambient temperature. The unit cell parameters of the samples were determined from the centered reflections in the 2θ range between 35° and 69°.

The X-ray diffraction intensity data were collected up to $2\theta_{\text{max}}=116^\circ$ for both experiments ($\sin\theta/\lambda = 1.18$ for #1 and $\sin\theta/\lambda = 1.16$ for #2) by using ω -scan method. Structural refinement for #2 was conducted using SHELX97 with WINGX software [6, 7]. The latest R and $wR2$ values are 2.04 % and 5.51 %, respectively.

3. Results and Discussion

The lattice constants of each sample are determined as follows: $a = 4.7892(20)$ Å and $c = 4.3145(9)$ Å for #1; $a = 4.7987(15)$ Å and $c = 4.3106(4)$ Å for #2. The a -axis length is increasing with an increase of Al content. On the other hand, the a -axis length of a perfectly Al-replaced phase D is 4.7114(6) Å [5]. This finding indicates the existence of the local maximum of the a -axis length in the Al incorporation stage, and suggests that the Al replacement mechanism into phase D structure should be changed beyond the local maximum point.

As the results from structure refinement of the sample #2, the mean M-O distances of two octahedral sites are 2.1026(6) Å for Mg-octahedral site and 1.8279(5) Å for Si-octahedral site. These averaged M-O distances shows that the Al replacement mechanism of phase D structure preferably occurs at Si-octahedral site ($\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{H}^+$) up to the local maximum point (half of Si is probably replaced). Beyond the point, $3\text{Mg}^{2+} \leftrightarrow 2\text{Al}^{3+}$ and/or $2\text{Mg}^{2+} \leftrightarrow \text{Al}^{3+} + \text{H}^+$ replacement would be predicted.

References

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