

Crystal structure analysis of post δ -AlOOH at 8.2 GPaTakahiro Kuribayashi^{1*}, Asami, Sano-Furukawa² and Toshiro Nagase³¹Department of Earth Science, Graduate School of Science, Tohoku Univ., Sendai 980-8578, Japan²JAEA, Tokai, Ibaraki, 319-1106, Japan³The Tohoku University Museum, Tohoku Univ., Sendai 980-8578, Japan**Introduction**

δ -AlOOH was first synthesized by Suzuki et al. (2000) [1] at 1600°C and 21 GPa conditions using a Kawai type multi-anvil apparatus. δ -AlOOH is stable under wide PT conditions such as 18-130 GPa and < 2300 K [2, 3]. The phase is, therefore, recognized as an important phase in the view of the carriers and reservoirs of hydrogen in the Earth's deep interior.

Crystal structure of δ -AlOOH is a distorted rutile type structure with space group $P2_1nm$, and has hydrogen bonding. According to Ab-initio calculations [4, 5], the space group of δ -AlOOH would be changed from $P2_1nm$ to $Pnmm$ by re-arrangements of hydrogen, yielding symmetric hydrogen bonding at around 30 GPa. Recently, our research group confirmed the phase transition of δ -AlOOH around 8.2 GPa [6]. The next step is to clarify whether hydrogen bond in the post-phase is symmetric or not. In this report, we conducted high-pressure single-crystal X-ray diffraction measurements on the post-transition phase at 8.2 GPa to refine its crystal structure.

Experimental Procedure

The sample used for this study was synthesized at 18 GPa and 900-1000°C kept by 1 hour using a Kawai-type multi-anvil apparatus installed in Tohoku University. A single crystal of δ -AlOOH (30 $\mu\text{m} \times 30\mu\text{m} \times 20\mu\text{m}$ in size) was mounted in a modified Merrill-Bassett type diamond anvil cell. A fluid mixture of 4:1 Methanol and Ethanol was used for the pressure medium and a SUS301 stainless plate was used for a gasket. Pressure was determined by using the EOS of δ -AlOOH [7]. X-ray diffraction experiments were performed using the automated four-circle X-ray diffractometer installed at the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization. The wavelength ($\lambda = 0.6489\text{ \AA}$) of synchrotron radiation was calibrated by the unit cell volume of the NIST ruby standard crystal at ambient temperature. Unit cell parameters of δ -AlOOH at 8.2 GPa were determined from 50 centered reflections in the 2θ range between 12.1° and 36.7° . The X-ray reflection intensity data were collected up to $\sin\theta/\lambda < 0.99$ by ω -scan method with fixed ϕ mode for all reciprocal regions. The SHELX97 software with WinGX was used for all structure refinements [8, 9]. Structure refinements for three models ($Pnmm$, $Pnn2$ and $P2_1nm$) were conducted. Structural parameters of H could not be refined.

Results and Discussion

The unit cell parameter of post δ -AlOOH phase at 8.2 GPa are as follows: $a = 4.6379(19)\text{ \AA}$, $b = 4.1342(15)\text{ \AA}$, $c = 2.7990(8)\text{ \AA}$. As the results from the analysis of X-ray diffraction intensity dataset, the candidates for space group of post δ -AlOOH phase were $Pnmm$, $Pnn2$ and $P2_1nm$. Structural refinements for three models were suggested that the $Pnmm$ model is most suitable as the post-transition phase. The R and wR^2 values for $Pnmm$ model with anisotropic displacement parameters were 4.42 % and 10.4%, respectively. The O-O distance related to hydrogen bond is changed from 2.548(1) \AA to 2.439(6) \AA , which shows very large compressibility. The O-O distance of the symmetric hydrogen bond would be around 2.27 \AA . The obtained O-O distance is significantly longer than 2.27 \AA . That is to say, hydrogen bond of the post-transition phase at 8.2 GPa is not symmetric. Refined structure was corresponding to the completely disordered hydrogen bond model.

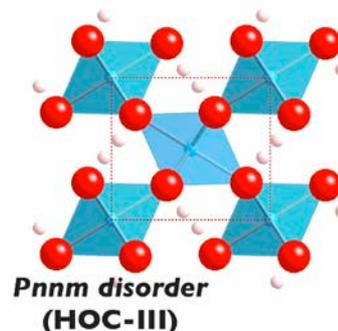


Figure 1 Crystal structure of post-transition phase. Red spheres represent O atom, small balls indicate H atoms. H would be located disorderly at the equivalent positions.

References

- [1] Suzuki et al. (2000) *Phys. Chem. Mineral*, **27**, 689-693. [2] Ohtani et al. (2001) *Geophys. Res. Lett.*, **28**, 3991-3993. [3] Sano et al. (2008) *Geophys. Res. Lett.*, **35**, L03303. [4] Tsuchiya et al. (2002) *Geophys. Res. Lett.*, **29**, 1909. [5] J. Tsuchiya and T. Tsuchiya (2002) *Phys. Rev. B.*, **83**, 054115. [6] Kuribayashi et al. (2013) *PF Activ. Rep. 2012 B*, 243. [7] Sano-Furukawa et al. (2009) *Amer. Mineral.*, **94**, 1255-1261. [8] Sheldrick and Schneider (1997) *Methods in Enzymo.*, **277**, 319-343. [9] Farrugia (1999) *J. Appl. Cryst.*, **32**, 837-838.

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