

Single crystal X-ray diffraction study of high pressure phase of gibbsite

Kazuki KOMATSU*¹, Takahiro KURIBAYASHI¹, Yasuhiro KUDOH¹

¹ Institute of Mineralogy, Petrology, and Economic Geology, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Introduction

The minerals of the alumina–water system, which have the composition $\text{Al}(\text{OH})_3$, are gibbsite [$\gamma\text{-Al}(\text{OH})_3$], bayerite [$\alpha\text{-Al}(\text{OH})_3$], nordstrandite [$\beta\text{-Al}(\text{OH})_3$], and doyleite. Among them, gibbsite has been studied intensively both from experimental and theoretical viewpoints. In 1983, two new polymorphs was found in the alumina-water system [1]. Over the past 10 years, a number of studies have investigated gibbsite using *in situ* high-pressure powder X-ray diffraction analysis [2,3]. However, the crystal structures of the two polymorphs remain yet to be determined.

In this study, one of the two polymorphs, which is termed as $\eta\text{-Al}(\text{OH})_3$, was investigated by single crystal X-ray diffraction method to determine its crystal structure.

Experimental details and Results

In this analysis we used a colorless platy single crystal (0.2 x 0.1 x 0.1 mm) of natural gibbsite from Langesundfjord, Oslo Region, Norway. The sample was loaded into a modified Merrill–Bassett type DAC that consists of a pair of Type Ia diamonds with 600 μm flat culets. As gibbsite has strong (001) cleavage, the (001) plane of the sample was placed parallel to the diamond culet. An SUS 301 stainless steel plate of 250 μm thickness and with a 300- μm diameter hole in the center was used as a gasket. FluorinertTM (FC-40, 3M) was used as a fluid pressure transmitting medium. No ruby chip for determining pressure was mounted to avoid extra spots. The wavelength of the synchrotron radiation was calibrated to $\lambda = 0.7003(1)$ \AA from lattice constants of a ruby standard crystal at ambient conditions. The four-circle angles of 45 reflections in the 2θ range between 9° and 31° were centered for determining the correct crystal system and lattice constants. Lattice constants refined assuming a triclinic unit cell were $a = 8.612(3)$, $b = 5.013(2)$, $c = 9.194(5)$, $\alpha = 90.34(7)$, $\beta = 90.00(6)$, and $\gamma = 90.00(4)$. The obtained α angle was significantly different from 90° ; thus $\eta\text{-Al}(\text{OH})_3$ is unequivocally confirmed as a monoclinic phase. Lattice constants with constraints of a monoclinic cell were $a = 8.612(3)$ \AA , $b = 5.013(2)$ \AA , $c = 9.194(5)$ \AA , and $\alpha = 90.34(6)^\circ$. Reflection conditions derived from the indexed reflections were $0kl$: $k=2n$ and $h00$: $h=2n$. According to reflection conditions, the space group of $\eta\text{-Al}(\text{OH})_3$ was determined uniquely as $P2_1/b11(\#14)$. X-ray diffraction intensities were collected up to $\sin\theta/\lambda < 0.603$ (maximum $2\theta = 50^\circ$) by ω scan with the fixed ϕ method. Although a relatively large crystal (0.2 x 0.1 x 0.1 mm) and synchrotron radiation were used, the observed reflections were weak and broad; this means that $\eta\text{-Al}(\text{OH})_3$ has low crystallinity. Extinction and

absorption corrections for the crystal were not applied. Data were corrected for Lorentz and polarization effects.

The model of crystal structure except for H atoms was solved by a direct method using the Sir2004 program package [4]. Atomic coordinates and isotropic atomic displacement parameters except for hydrogen atoms were refined using SHELXL from the SHELX-97 program package [5]. We were unable to resolve the H positions of $\eta\text{-Al}(\text{OH})_3$ in the D-Fourier map. This may be due to factors such as weak and broad reflections with large uncertainties, noise from Be backing plates or the stainless steel gasket, or the effect of unobserved 00/ reflections related to the sample setting in DAC.

The solved crystal structure of $\eta\text{-Al}(\text{OH})_3$ consists of an Al octahedral layer as well as gibbsite [$\gamma\text{-Al}(\text{OH})_3$]. Comparing the crystal structures between gibbsite and $\eta\text{-Al}(\text{OH})_3$ (see Fig. 1), it is expected that the mechanism of the transition from gibbsite to $\eta\text{-Al}(\text{OH})_3$ approximately involves a shift of Al octahedral layers with respect to each other by the vector $\mathbf{a}/2$ or $\mathbf{b}/2$.

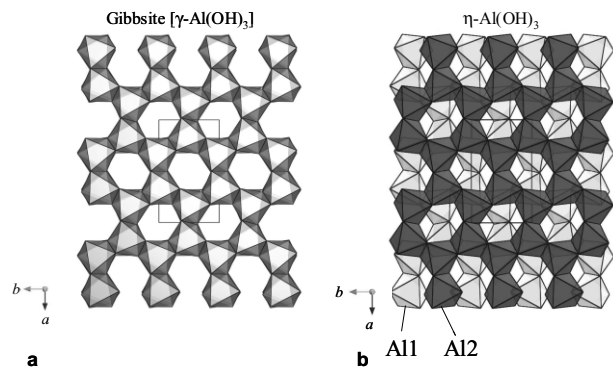


Fig. 1: Crystal structure of (a) gibbsite [$\gamma\text{-Al}(\text{OH})_3$] and (b) $\eta\text{-Al}(\text{OH})_3$. The solid line denotes the unit cell. To clarify Al octahedral stacking, H atoms are not described here.

References

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* komatsu@ganko.tohoku.ac.jp