The crystal structure of $\delta$-Al(OH)$_3$; Neutron diffraction measurements and ab initio calculations

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ABSTRACT

$\delta$-Al(OH)$_3$ powders were synthesized from Al(OD)$_3$ bayerite at 4 GPa and 523 K using a cubic press apparatus. Neutron powder diffraction analyses of $\delta$-Al(OH)$_3$ at ambient conditions revealed that the crystals are orthorhombic with space group $P2_12_12_1$, not $Pnma$ as reported previously based on X-ray diffraction data. The $P2_12_12_1$ $\delta$-Al(OH)$_3$ structure contains seven independent atoms in the asymmetric unit, including one Al, three O, and three H atoms. The initial lattice parameters and the atomic positions of both Al and O were taken from previous X-ray structural analyses of the $Pnma$ structure, while the positions of H were determined in the present study using ab initio calculations to (1) give the least energy among trial structural models for $P2_12_12_1$ $\delta$-Al(OH)$_3$, (2) accurately reproduce the measured lattice parameters of $\delta$-Al(OH)$_3$, and (3) show reasonable energetic relations between the Al(OH)$_3$ polymorphs; namely, gibbsite is stable at ambient pressure, $\delta$-Al(OH)$_3$ has the lowest enthalpy at pressure greater than 1.1 GPa, and both bayerite and $\eta$-Al(OH)$_3$ are metastable over the entire pressure range. Furthermore, we found that the structure of $\delta$-Al(OH)$_3$ obtained from ab initio calculations is in good agreement with that derived from a Rietveld refinement of $\delta$-Al(OH)$_3$, based on the present powder neutron diffraction data. The $\delta$-Al(OH)$_3$ structure possesses one relatively long and two short O-H⋯O hydrogen bonds. Ab initio calculations also reveal that $\delta$-Al(OH)$_3$, with space group $P2_12_12_1$, transforms to another high-pressure polymorph with space group $Pnma$ at around 67 GPa, and that the two short hydrogen bonds in $\delta$-Al(OH)$_3$ become both symmetric through the $P2_12_12_1$ to $Pnma$ transformation, in which the protons are located at the midpoints of the O⋯O hydrogen bonds.

Keywords: Al(OH)$_3$, high pressure, neutron diffraction, ab initio calculations, symmetrical hydrogen bond

INTRODUCTION

Aluminum trihydroxide Al(OH)$_3$ has four polymorphs in nature: gibbsite, bayerite, doyleite, and nordstrandite. Of these, gibbsite is the most common, and is an important constituent of bauxite. Both gibbsite and bayerite are monoclinic, whereas doyleite and nordstrandite are triclinic. Using a high-pressure opposed-anvils apparatus, Dachille and Gigl (1983) synthesized two new Al(OH)$_3$ polymorphs, the $\eta$ (called $\beta'$ by the authors) and $\delta$ phases. Based on powder X-ray diffraction analyses, the authors reported that the $\eta$ phase is monoclinic, while the $\delta$ phase is orthorhombic with space group $Pna2_1$, or $Pnma$; in the present study, the axis directions are changed from those reported by Dachille and Gigl to give the standard setting, $Pnma$.

The structure of the high-pressure $\eta$ phase was much in debate. Huang et al. (1996, 1999) reported that gibbsite transforms to nordstrandite with triclinic unit cell at approximately 3 GPa and room temperature, based on Raman spectra and X-ray diffraction measurements. Subsequently, Liu et al. (2004, 2005) reindexed this high-pressure phase as orthorhombic with space group $Pbca$, using in situ high-pressure synchrotron X-ray diffraction combined with infrared absorption experiments. However, Komatsu et al. (2007a) successfully obtained a single crystal of this phase (called $\eta$) at 3 GPa and determined it to be monoclinic with space group $P2_1/c$ and a monoclinic $\beta$ angle of 90.34(6)$^\circ$ at 3 GPa and room temperature, consistent with the earlier report by Dachille and Gigl (1983); here, the axis directions are changed from those reported by Komatsu et al. (2007a) to give the standard setting, $P2_1/c$. We note that the $P2_1/c$ structure of the $\eta$ phase at 3 GPa, as obtained by Komatsu et al. (2007a), is very similar to the $Pnma$ structure proposed by Liu et al. (2005), with the monoclinic $\beta$ angle for the former [90.34(6)$^\circ$] being close to 90$^\circ$.

A deuterated high-pressure phase, called $\delta$-Al(OD)$_3$, was synthesized at 18 GPa and 973 K using a Kawai-type multi-anvil apparatus (Komatsu et al. 2007b). Based on powder X-ray diffraction at ambient conditions, Komatsu et al. (2007b) confirmed $\delta$-Al(OD)$_3$ is isostructural with $\delta$-Al(OH)$_3$ with space group $Pnma$, previously synthesized at high temperatures and high pressures by Dachille and Gigl (1983). Based on Rietveld and difference-Fourier analyses using powder X-ray data, Komatsu et al. (2007b) reported a structural model for $\delta$-Al(OD)$_3$, in which positional disorders of the D atoms were proposed in their hydrogen bonds.

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