American Mineralogist, Volume 93, pages 1558–1567, 2008

Neutron diffraction study of δ-AlOOD at high pressure and its implication for symmetrization of the hydrogen bond

ASAMI SANO-FURUKAWA,[1,*] KAZUKI KOMATSU,[2,3] CARINE B. VANPETEGHEM,[4] AND EIJI OHTANI[1]

[1]Department of Earth and Planetary Materials Science, Tohoku University, Sendai 980-8578, Japan
[2]Geochemical Laboratory, Graduate School of Science, University of Tokyo, Tokyo 113-0033, Japan
[3]Centre for Science at Extreme Conditions, University of Edinburgh, Mayfield Road, Edinburgh, EH9 3JZ, U.K.
[4]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, U.S.A.

ABSTRACT

We have conducted a powder neutron diffraction study of the distorted rutile-type hydrous phase δ-AlOO($D_{0.74}H_{0.26}$) at pressures up to 9.2 GPa. Rietveld refinement reveals that the observed diffraction data are best fitted by a model with an asymmetric hydrogen bond (space group $P2_1nm$). The Al-O2 bonds of the AlO_6 octahedron remain longer than the Al-O1 bonds up to 9.2 GPa, reflecting the fact that O2 is the donor and O1 is the acceptor of the hydrogen bond of O2-D···O1. As pressure increases, the Al-O1 bond lengths remain almost constant or increase slightly, whereas the longer Al-O2 bonds are more compressible. The O···O distance of the shared edge of the octahedron is almost constant unlike the other O···O distances that decrease during compression. The bulk modulus of the AlO_6 octahedron is determined to be 197.0(4) GPa, where K' is fixed to 4. The AlO_6 octahedron rotates about 1° during compression to 9.2 GPa. As pressure increases and the O2···O1 distance decreases, the D···O1 bond is shortened, whereas the O2-D bond becomes elongated, with pressure dependencies of $-1.81(9) \times 10^{-2}$ Å/GPa and $0.57(8) \times 10^{-2}$ Å/GPa, respectively, implying the symmetrization of the hydrogen bond at high pressure. The decrease in intensity of the 120 reflection as pressure increases suggests that the transition from the structure with space group $P2_1nm$ to that with $Pnnm$ would take place in δ-AlOOD at high pressure. This transition could be attributed to the disorder of deuterium or symmetrization of the hydrogen bond.

Keywords: δ-AlOOD, neutron diffraction, hydrogen bond, symmetrization