

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

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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 AlO₆ 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 \cdots 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 \cdots O distance of the shared edge of the octahedron is almost constant unlike the other O \cdots O distances that decrease during compression. The bulk modulus of the AlO₆ octahedron is determined to be 197.0(4) GPa, where K' is fixed to 4. The AlO₆ octahedron rotates about 1° during compression to 9.2 GPa. As pressure increases and the O2 \cdots O1 distance decreases, the D \cdots 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 $Pnmm$ 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