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Pressure dependence of the hydrogen-bond geometry in topaz-OD from neutron powder diffraction

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ABSTRACT

The crystal structure of deuterated topaz [topaz-OD; $Al_2SiO_4(OD)_2$], synthesized at 10 GPa and 800 °C, has been determined using neutron powder diffraction at pressures up to 7.5 GPa. The linear axial compressibilities obtained from regressions of the lattice constants vs. pressure are $\beta_a = 1.87(1) \times 10^{-3}$ GPa^{-1}, $\beta_b = 1.71(1) \times 10^{-3}$ GPa^{-1}, and $\beta_c = 2.73(1) \times 10^{-3}$ GPa^{-1}. The occupancy of the D1 site was found to be greater than that of D2, as shown independently using neutron diffraction and infrared spectra at ambient conditions. A bifurcated hydrogen bond involving the D1 site, O4-D1···O2 and O4-D1···O3, and a trifurcated hydrogen bond involving D2 site, O4-D2···O1, O4-D2···O2, and O4-D2···O4 are proposed for hydrogen-bond donor and acceptor pairs in addition to those reported previously. The observed pressure dependences of the hydrogen-bonding geometry show that these donor and acceptor pairs are classifiable into two types of interaction: (1) those that strengthen as a function of pressure (O4-D1···O3, O4-D2···O2, and O4-D2···O4) and (2) those that weaken (O4-D1···O1 and O4-D2···O1). These results also demonstrate that the reason for the contrasting behavior of the ν(OH) between F-rich natural topaz and topaz-OH are both the cooperative effect, O4-D2···O4-D1···O3, and the increasing Al-O4 distance.

Keywords: Topaz-OD, hydrogen bond, neutron powder diffraction, high pressure