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High-pressure single-crystal X-ray and powder neutron study of F,OH/OD-chondrodite: Compressibility, structure, and hydrogen bonding

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ABSTRACT

The crystal structure of a natural F-bearing chondrodite [$Mg_{4.64}Fe_{0.28}Mn_{0.014}Ti_{0.023}(Si_{1.01}O_4)_2F_{1.16}OH_{0.84}$; $a = 4.7328(1)$, $b = 10.2749(2)$, $c = 7.8756(1)$ Å, $\alpha = 109.065(1)°$; space group $P2_1/b$ (a unique)] from the Tilly Foster mine (Brewster, New York) and the structure of a deuterated synthetic analogue [$Mg_5(SiO_4)_2F_{1.10}OD_{0.90}$] were refined at high pressure using single-crystal X-ray and time-of-flight neutron powder diffraction data, respectively. The isothermal equation of state was determined from single-crystal high-precision X-ray diffraction measurements of unit-cell parameters as a function of pressure up to 9.63(1) GPa. A third-order Birch-Murnaghan equation-of-state fit to pressure-volume data results in $V_0 = 362.00(2)$ Å^3, $K_{0,T} = 117.0(4)$ GPa and $K_T' = 5.6(1)$. The larger value of $K_{0,T}$ relative to that determined for the OH end-member confirms that F makes the chondrodite structure less compressible. The axial compressibilities behave anisotropically with fitted parameters $a_0 = 4.73282(9)$ Å, $K(a)_0 = 458(3)$ GPa, and $K(a)' = 28.9(9)$; $b_0 = 10.2759(3)$ Å, $K(b)_0 = 298(1)$ GPa, and $K(b)' = 13.4(4)$; $c_0 = 7.8759(2)$ Å, $K(c)_0 = 316(2)$ GPa, and $K(c)' = 16.7(5)$. X-ray structural investigations at 0.0001, 4.952(7), and 9.550(7) GPa in a diamond-anvil cell reveal a complex compression mechanism. The greatest changes with pressure occur in the M2 octahedra, which are located at the flexion points of the octahedral chain. These octahedra have the longest bonds at ambient conditions due to cation-cation repulsion, which displaces the cation from the centroid of the octahedron. The application of pressure overcomes the effect of cation-cation repulsion inducing a strong bond-length compression. The neutron powder data were collected at 0.0001, 1.26(1), 2.89(2), 3.87(1), 5.27(2), and 7.04(2) GPa in the Paris-Edinburgh cell using a new gasket design and a fluid pressure medium. Changes in the O-D···O/F hydrogen bond geometry with pressure can be interpreted in terms of a rotation of the OD vector and a reduction in the degree of static disorder associated with the hydrogen bond acceptor/donor site. These new crystallographic data are discussed in terms of corresponding spectroscopic measurements reported recently in the literature.