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Structure, compressibility, hydrogen bonding, and dehydration of the tetragonal Mn^{3+} hydrogarnet, henritermierite

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ABSTRACT

Henritermierite, space group $I4_1/acd$, at 293 K $a = 12.489(1)$, $c = 11.909(1)$ Å, $Z = 8$, with close to end-member composition $(Ca_{2.98}Na_{0.01}Mg_{0.01})^{VIII}(Mn_{1.95}Fe_{0.01}Al_{0.04})^{VI}[SiO_4]_{2.07}[H_4O_4]_{0.93}$ from the N'Chwaning II mine at the Kalahari manganese fields, Republic of South Africa, has been studied by single-crystal X-ray diffraction at 100 and 293 K at ambient pressure and up to 8.7 GPa in a diamond-anvil cell at 293 K. Polarized FTIR spectroscopy at 80 and 293 K was also performed. The $Mn^{3+}O_6$ octahedra display a tetragonally elongated type of Jahn-Teller distortion where the oxygen atoms of the elongated O-Mn-O axis (Mn-O: 2.2 Å) are moderately hydrogen bonded (O-H···O: 2.76 Å) to the H_4O_4 tetrahedra, which replace 1/3 of SiO_4 tetrahedra in an ordered fashion. Thus Jahn-Teller distortion and H_4O_4 arrangement are coupled and both are responsible for the tetragonal bulk symmetry. The H_4O_4 tetrahedra have a center-to-O distance of 1.98 Å and the H atoms are slightly above the tetrahedral faces as similarly observed in the synthetic katoite end-member, $Ca_3Al_2[H_4O_4]_3$. However, in henritermierite the O-H···O hydrogen bond is considerably bent (ca. 131°) and gives rise to an OH stretching mode at 3432(5) cm^{-1}. Additional, though weak, IR absorptions at 3508(2) and 3553(2) cm^{-1} may be due to more remote hydrogen-bond acceptors (O-H···O: 3.29 Å) within the H_4O_4 tetrahedra.

Compressibility data for a third-order Birch-Murnaghan equation of state yield a bulk modulus of $K_0 = 97.9(9)$ GPa with a pressure derivative of $K' = 5.3(3)$. The axial compressibilities indicate a pronounced compressional anisotropy which is explained by the orientation of the elongated axes of the Jahn-Teller distorted MnO_6 octahedra along the slightly more compressible $[100]_{tetr}$ directions compared to the *c*-axis. The crystal structure was refined at a pressure of 8.6 GPa. The MnO_6 octahedra were observed to show anisotropic compression towards a more isometric shape. Calculated spontaneous strain reveals a trend towards a weaker tetragonal distortion.

If henritermierite is heated above 800 K in air it dehydrates and Mn^{3+} is partially oxidized to Mn^{4+}. This topotactic transformation leads to a new garnet-like phase of $Ia3d$ symmetry with $a =$ 12.12 Å and of $Ca_3Mn_{2.26}O_{2.32}[SiO_4]_{2.42}$ composition in which instead of H_4O_4 tetrahedra a new disordered octahedral site is occupied by Mn.