

Temperature-dependent single-crystal neutron diffraction study of natural chondrodite and clinohumites

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ABSTRACT

The crystal structures of natural F-bearing chondrodite [$\text{Mg}_{4.64}\text{Fe}_{0.28}\text{Mn}_{0.014}\text{Ti}_{0.023}(\text{Si}_{1.01}\text{O}_4)_2\text{F}_{1.02}\text{OH}_{0.97}$] from the Tilley Foster mine (Brewster, New York), F-bearing titanian clinohumite [$\text{Mg}_{8.805}\text{Fe}_{0.006}\text{Ti}_{0.214}(\text{Si}_{0.993}\text{O}_4)_4\text{F}_{0.484}\text{OH}_{0.516}$] from Kukh-i-Lal (Tadjikistan) and F-free titanian hydroxylclinohumite [$\text{Mg}_{7.378}\text{Fe}_{1.12}\text{Mn}_{0.052}\text{Ni}_{0.014}\text{Ti}_{0.453}(\text{Si}_{0.996}\text{O}_4)_4\text{OH}_{1.0}$] from Val Malenco (Italy) were refined in space group $P2_1/b$ (unique axis a) from single-crystal neutron diffraction data, collected on a four-circle diffractometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory. Accurate H atom positions were determined at 295 K, 100 K, and 20 (10) K. Only one H position of approximately 50% occupancy was observed for each structure, which confirms a disordered H model. Time-of-flight single-crystal neutron data were also collected at 295 K and 20 K for the Val Malenco clinohumite as an additional check on space group symmetry. The crystal structure of the Kukh-i-Lal clinohumite was further investigated by X-ray single-crystal refinement at 295 K and by piezoelectric measurements. A few, very weak, symmetry-forbidden reflections were observed for each crystal at both ambient and lower temperatures. The same reflections were observed by all methods used. No temperature dependence is indicated, as no additional peaks appear at low temperature, and the intensity of the reflections are sample dependent. It appears that the real structure is made up of $P2_1$ and Pb domains so that violations are due to ordering of both H and Ti. No distinct piezoelectric effect was observed that would indicate the absence of a center of symmetry. This points to the simultaneous presence of various enantiomorphic domains, which cancels the piezoelectric effect of individual domains. The decrease in unit-cell volume with F substitution in clinohumites can be explained by the higher concentration of H-site vacancies and the coupled cationic and anionic substitution on the M3 and O/F site.