

The behavior at non-ambient conditions of colemanite: a hydrous Ca-borate

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Colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, is a common hydrous borate of large economic relevance, as it is one of the major commodities of boron with applications in the fields of glass and ceramic industries. Colemanite-rich layers are usually found in stratigraphic successions related to lacustrine basins in semi-arid to arid environments, associated to a local volcanic activity, which provides the source for boron. Despite the large economic relevance, the behavior of this mineral at non-ambient conditions of temperature and pressure was almost unexplored, which can provide a basis for understanding its stability during diagenetic and metamorphic processes. In this contribution, we report the high-pressure behavior of colemanite (Lotti et al., 2017), based on *in situ* single-crystal synchrotron X-ray diffraction data up to 24 GPa, and its low-*T* behavior by *in situ* X-ray and neutron single-crystal diffraction.

Colemanite was found to be stable up to ~ 14.5 GPa, where a reconstructive phase transition towards a high-pressure polymorph (colemanite-II) with same symmetry (space group $P2_1/a$), but a six times larger unit cell volume, occurs. The elastic behavior of colemanite was described by fitting the experimental data with a III-order Birch-Murnaghan equation of state, yielding the following refined elastic parameters: $K_{V0} = 64(4)$ GPa and $K' = 5.5(7)$. The colemanite-to-colemanite-II phase transition induces an increase in the average coordination number of both the Ca and B cations. In particular, a fraction of the boron sites increases its coordination from triangular to tetrahedral by making a further bond with a H_2O -oxygen atom. Although the phase transition occurs (at ambient temperature) at pressures far from those associated with the usual geologic environments of colemanite, the reported results disclosed flexible deformation mechanisms that borate compounds may adopt to accommodate pressure, thus providing new insights on the behavior of borate minerals at non-ambient conditions. The complex hydrogen-bonding network of colemanite has also been characterized, at ambient and low temperature conditions, by means of *in situ* single-crystal synchrotron X-ray and neutron diffraction experiments. A positional disorder, related to the presence of two mutually exclusive configurations of the H_2O -molecule hydrogen atoms, was found both above and below $\sim 0^\circ\text{C}$, where a displacive phase transition from the $P2_1/a$ to the $P2_1$ space group occurs.

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