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Abstract's title: High-pressure and low-temperature behavior of colemanite: in situ synchrotron X-ray diffraction experiments

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Abstract

Colemanite, $\text{CaB}_3\text{O}_4(\text{OH})_3 \times \text{H}_2\text{O}$, is one of the most important mineral commodities for the extraction of boron. Despite a recent interest on its potential applications in ceramic processes, very few was known on the behavior of the colemanite crystal structure at non-ambient conditions of temperature and pressure.

An in situ low-temperature X-ray diffraction experiment was performed down to 104 K at the XRD1 beamline of the Elettra synchrotron source. A displacive phase transition from the centrosymmetric $P2_1/a$ colemanite to a ferroelectric polymorph with $P2_1$ symmetry was long time known to occur in the T -range between 273 and 263 K (e.g. [1]). Thermal analysis and in situ single-crystal X-ray diffraction data confirmed the transition, which was found to occur between 275 and 263 K. Single crystal X-ray and neutron diffraction data (down to 104 and 20 K, respectively) showed that the asymmetric distribution of ionic charges along the b crystallographic axis is likely responsible for the observed ferroelectric behavior.

On the other hand, in situ high-pressure single-crystal X-ray diffraction experiments [2], performed up to 24 GPa at the P02.2 beamline of the Petra-III synchrotron source (Hamburg, Germany), disclosed a much more complex scenario, with a first-order reconstructive phase transition occurring between 13.95 and 14.91 GPa, toward a denser polymorph with $\mathbf{a} = 3 \times \mathbf{a}_{\text{COL}}$, $\mathbf{b} = \mathbf{b}_{\text{COL}}$ and $\mathbf{c} = 2 \times \mathbf{c}_{\text{COL}}$. Despite reconstructive, the transition is single crystal-to-single crystal and involves an increase in the average coordination number of both the Ca and B sites. The tripling of the a -axis and the doubling of the c -axis imply the split of every independent atomic site of colemanite in six new independent positions in the high- P polymorph. In particular, three of the six new sites, generated from the parent triangularly coordinated B, increase their coordination number from three to four, gaining a bond with a H_2O oxygen. The elastic behavior of colemanite and of the high- P polymorph have been described by means of III- and II-order Birch-Murnaghan equations of state, respectively, yielding the following bulk moduli: 67(4) GPa (colemanite, $K_{V\phi} = 5.5(7)$) and 50(8) GPa (high- P colemanite).

[1] F.N. Hainsworth, H.E. Petch *Can. J. Phys.* **1966**, *44*, 3083.

[2] P. Lotti, G.D. Gatta, D. Comboni, G. Guastella, M. Merlini, A. Guastoni, H-P. Liermann *J. Am. Cer. Soc.* **2017**, *in press*, DOI: 10.1111/jace.14730.