

Experimental report

05/03/2024

Proposal: DIR-264

Council: 10/2022

Title: On the complex H-bonding scheme in inderborite, $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2 \cdot 6\text{H}_2\text{O}$

Research area: Other...

This proposal is a new proposal

Main proposer: Giacomo Diego GATTA

Experimental team:

Local contacts: Oscar Ramon FABELO ROSA

Samples: $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2 \cdot 6\text{H}_2\text{O}$

Instrument	Requested days	Allocated days	From	To
D19	6	0		
D9	10	10	06/04/2023	17/04/2023
ORIENTEXPRESS	1	1		

Abstract:

Inderborite, $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2 \cdot 6\text{H}_2\text{O}$, is a complex hydrous borate mineral. Despite the geochemical and industrial interest on this mineral (as source of B, it contains 41 wt% B_2O_3), only a few studies were devoted to it. Its structure was solved years ago by single-crystal X-ray diffraction, and no more recent data are available. The aim of the present study is a reinvestigation of the crystal structure/chemistry of inderborite by single-crystal neutron diffraction (20 K) and other techniques, in order to provide: a) an unambiguous location of all the proton sites and the description of the complex H-bonding network expected in its structure, alongside its low-T induced rearrangement; b) the anisotropic displacement parameters of all the atomic sites, including the H-sites; c) a robust description of the B-coordination environment (e.g. aplanarity of the BO_3 -group, distortion of the BO_4 -tetrahedra); d) a description of the crystal chemistry of this mineral based on modern analytical protocols, with attention to the potential B- and Mg-Ca-substituents. These data are pivotal for a full description of the pressure- and temperature-behaviour of inderborite at the atomic scale.

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On the complex H-bonding scheme in inderborite, $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2 \cdot 6\text{H}_2\text{O}$

The aim of this experiment was to obtain a full structural model of inderborite, including positions and displacement parameters for all hydrogen atoms. The vibrational regime of protons at room- T can give rise to some dynamic or static disorders, which often occur in this class of materials. In order to minimize this effect, we asked for D9 measurements at low- T to better locate the protons. We expected to provide:

- a) an unambiguous location of all the proton sites and the description of the complex H-bonding network expected in inderborite structure, alongside its low- T induced rearrangement;
- b) the anisotropic displacement parameters of all the atomic sites, including the H-sites;
- c) a more robust description of the B-coordination environment (*e.g.*, aplanarity of the BO_3 -group, tetrahedral distortion of the BO_4 -groups);

The diffraction experiment was conducted with a wavelength of 0.8348 Å, obtained from a Cu(220) monochromator, and a small two-dimensional area detector. The data collection strategy was based on a series of ω -scans (for low- Q reflections) or ω - 2θ scans (for high- Q reflections), varying the ω -range as a function of the instrument resolution curve. A total of 4732 Bragg reflections was collected up to $2\theta_{\text{max}}$ of 114.9° (with $-20 \leq h \leq +19$, $0 \leq k \leq +14$ and $-4 \leq l \leq +25$), with $d_{\text{min}} = 0.498$ Å; 4509 reflections were unique for symmetry ($R_{\text{int}} = 0.0304$, Laue class $2/m$) and 3861 with $I_o > 2\sigma(I_o)$. The unit-cell was found to be metrically monoclinic, with $a = 12.047(2)$, $b = 7.399(1)$, $c = 19.157(3)$ Å, $\beta = 90.76(1)^\circ$, and the reflection conditions consistent with the space group $C2/c$. The structure refinement is in progress, but the preliminary data confirm that the principal building block unit of the structure is a $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ ring, consisting of two $\text{BO}_2(\text{OH})_2$ tetrahedra (B-ion in sp^3 electronic configuration) and one planar-triangular BO_2OH group (B-ion in sp^2 electronic configuration). In the $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ ring, all the oxygen atoms that are not shared between two boron atoms are protonated. The building units share corners with the $\text{CaO}_2(\text{OH})_4(\text{OH}_2)_2$ polyhedra and $\text{Mg}(\text{OH})_4(\text{OH}_2)_2$ octahedra, forming hetero-polyhedral sheets parallel to (100). Subsequent hetero-polyhedral sheets are mutually connected only by H-bonding interactions, even mediated by the zeolitic (“interstitial”) H_2O molecules. Ten over eleven independent oxygen sites in the structure of inderborite are involved in H-bonds as *donor* or *acceptors*, and this reflects the pervasive effect of the H-bonding network. The role played by the complex H-bond network is expected to be substantial on the stability of the crystalline edifice, having effects within the single hetero-polyhedral sheet, between subsequent sheets, and to bond the interstitial zeolitic H_2O molecules.

Figure 1. The crystal structure of inderborite (H-free model) viewed down [010] and the configuration of the FBU.

