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Abstract

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CRYSTALLOGRAPHY

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CRYSTAL STRUCTURE OF INDERBORITE

$CaMgB_6O_{11} \cdot 11H_2O = CaMg[B_3O_3(OH)_5]_2 \cdot 6H_2O$

The hydrous borate inderborite $CaMgB_6O_{11} \cdot 11H_2O$ was first discovered by K. S. Gorshkov (^{1}) and almost simultaneously by N. Yu. Ikornikova and M. N. Godlevskii (^{2}). The monoclinic symmetry of the spear-shaped crystals was established, as well as the goniometric axial ratio: $a : b : c = 1.6395 : 1 : 2.6346$ at the angle $\beta = 90°44.5'$. Formally, inderborite differs from hydroboracite $CaMgB_6O_{11} \cdot 6H_2O$ (^{3}) only by 5 "extra" particles of H_2O (in connection with which in (^{2}) it appears as "metahydroboracite"). The monoclinic Laue symmetry $2/m$; a centered (C) cell with parameters $a = 12.22$; $b = 7.46$; $c = 19.11$ Å; $\beta = 90°44'$ were independently determined by x-ray methods by M. N. Sotnikova and V. V. Kondrat' eva [^{4}].

For the inderborite specimens studied by us, from the Mineralogical Museum of the Academy of Sciences of the USSR, rotation x-ray photographs and distant pinacoidal Weissenberg reflections gave the parameters $a = 12.15$; $b = 7.46$; $c = 19.05$ Å; $\beta = 90°45'$. At density $d = 1.934$ (^{5}), the cell contains 4 units of $CaMgB_6O_{11} \cdot 11H_2O$.

Using Mo K_α radiation, Weissenberg photographs were taken for the zero and subsequent (1, 2, 3, 4) layer lines of rotation about the b axis, as well as a zero-level rotation pattern about a. Reflection intensities were estimated by comparison with a blackening scale (with a step of $\sqrt{2}$). For overexposed reflections, films with multiple exposures were used. The transition coefficient from a weak film to a stronger one was chosen close to 3. Integral extinctions hkl for $h + k = 2n + 1$ and zonal extinctions $h0l$ for $l = 2n + 1$ determined the diffraction group $2/mC - lc$ with two Fedorov groups Cc and $C2/c$. The test for the piezoelectric effect gave a negative result; however, the final choice of the holohedral group $C2/c = C_{2h}^6$ was made in the course of the structural determination on the basis of the statistics of the quantities F_{h0l}^2 and F_{h2l}^2 (^{6,7}).

The structure of inderborite was solved by the Patterson-function method in combination with partial Fourier syntheses, which had proved effective in the determination of hydroboracite (^{3}). First, the positions of the Mg and Ca cations were found. Attention was drawn to the fact that reflections $h0l$ with $l = 4n$ are, as a rule, stronger than reflections $h0l$ with $l \neq 4n$ (although the pseudoperiod $c' = c/4$ was not observed on the rotation photograph about the z axis). For reflections $h4l$ this difference is weaker; however, the mean value of the structure factor F^2_{h4l} at $l = 4n$ exceeds the values F^2_{h4l} ($l = 4n + 2$) and F^2_{h4l} ($l = 2n + 1$). This regularity compelled the assumption that the Mg and Ca atoms, differing by 1/4 in the z coordinate, occupy fourfold positions of the group $C2/c$, but not Cc. To confirm this assumption, the Patterson projection $P(u, w)$ was constructed, as well as the weighted projections $C_1(u, w)$, $C_2(u, w)$, $C_4(u, w)$. A high peak at the point $0; 0.25$ in the syntheses $P(u, w)$ and

$$C_4(u, w) = \int_0^1 P(u, v, w) \cos 8\pi v \, dv$$

at deep-

failure at the corresponding point of the weighted projection

$$C_2(u, w) = \int_0^1 P(u, v, w) \cos 4\pi v \, dv$$

served as the basis for identifying the vector with its end at 0; 0.25; 0.25 with the vector Ca—Mg. Since in the group $C2/c$ there are only two different kinds of fourfold positions, it is natural to place the usually "more symmetric" Mg at the center of symmetry 000, and the larger cation Ca on the twofold axis $0y\frac{1}{4}$, analogously to what occurs in the structure of hydroboracite (^{3}). The coordinate of the Ca atom, $y \approx \frac{1}{4}$, is established from the weighted Patterson projections $C_2(u, w)$ and $C_4(u, w)$, using the relation $C_2(u, w)/C_4(u, w) = \cos 2\pi \cdot 2v / \cos 2\pi \cdot 4v$.

To reveal the center of symmetry linking the light atoms, we resorted to modeling the known functions $N(z)$ (^{7}). Knowing the positions of the Ca and Mg atoms, it was possible to construct theoretical curves $N(z)$ for the reflections $h0l$ and $h2l$ in two variants. In both, the fixed positions of Ca and Mg were taken into account, but in the first variant $N(z)$ was calculated for a centrosymmetric structure with an arbitrary arrangement of three B and eleven O atoms in general eightfold positions, and in the second—for a noncentrosymmetric structure with likewise arbitrary arrangement of the B and O atoms. Comparison with the two variants showed close agreement of $N(z)_{\text{exp}}$ with the curve for the centrosymmetric arrangement of the light atoms (for $h0l$ and $h2l$), i.e., the group $C2/c$.

Table 1

Coordinates of the basis atoms of the inderborite structure

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Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Mg	0	0	0	O_7^*	0.299	0.371	0.177
Ca	0	0.229	0.250				
O_1	−0.016	−0.030	0.163	O_8^*	0.392	0.375	0.064
O_2^*	0.122	0.006	0.077	O_9^{**}	0.445	0.743	0.039
O_3^*	0.160	0.077	0.199	O_{10}^{**}	0.357	0.825	0.170
O_4	0.135	0.776	0.162	O_{11}^{**}	0.165	0.450	0.022
O_5	−0.055	0.661	0.157	B_1	0.095	0.962	0.150
O_6^*	0.087	0.471	0.180	B_2	0.405	0.352	0.140
				B_3	0.053	0.648	0.166

The positions of the light components could not be found from Patterson syntheses, and the coordinates of all the remaining 14 atoms in the asymmetric part of the cell were determined successively by the method of Fourier syntheses with increased (single-color or black-and-white) symmetry ([3]). Partial syntheses $\sigma(x,z)_{l=4n}$, $C_2(x,z)_{l=4n+2}$, $C_4(x,z)_{l=4n}$, constructed from the structure factors F_{h0l} $(l=4n)$, F_{h2l} $(l=4n+2)$, F_{h4l} $(l=4n)$, whose signs were fixed from Ca and Mg (the contributions of these two atoms to the indicated factors are added, i.e., $F_{\mathrm{Ca,Mg}} = 4(f_{\mathrm{Ca}} + f_{\mathrm{Mg}})$); the y-coordinates were refined from the Fourier projection $\sigma(y,z)$.

Table 2

Interatomic distances in the inderborite structure (in angstroms)

B_1-tetrahedron	B_2-tetrahedron	B_3-triangle	Mg-octahedron
B_1–O_1 1.48	B_2–O_1 1.48	B_3–O_4 1.37	Mg–O_2^* 2.08
B_1–O_2^* 1.46	B_2–O_5 1.50	B_3–O_5 1.34	Mg–O_8^* 2.01
B_1–O_3^* 1.50	B_2–O_7^* 1.43	B_3–O_6^* 1.42	Mg–O_9^{**} 2.09
B_1–O_4 1.48	B_2–O_8^* 1.48	Ca-polyhedron	O_2^*–O_8^* 2.93
		Ca–O_1 2.58	O_2^*–O_9^{**} 2.91
		Ca–O_3^* 2.46	O_2^*–O 2.84
		Ca–O_6^* 2.65	O_2^*–O^* 2.95
		Ca–O_{10}^{**} 2.43	O_8^*–O_9^{***} 2.82
			$O_8^{\prime\prime *}$–O_9^{**} 2.95

* Oxygen of a hydroxyl group.
** Oxygen of a water molecule.

Table 1 gives the coordinates of the basis atoms. The discrepancy factors (over all nonzero reflections): $R_{h0l} = 19.6\%$; $\sin\vartheta/\lambda \leq 1.0$ Å^{-1}, $B_{h0l} = 0.5$ Å^2; $R_{0kl} = 19.9\%$, $\sin\vartheta/\lambda \leq 0.93$ Å^{-1}, $B_{0kl} = 0.8$ Å^2.

The main features of the structure of inderborite are visible from Figs. 1 and 2. Four Mg are located at centers of symmetry inside octahedra formed

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Fig. 1. Projection of the inderborite structure in polyhedra along the y axis. One stroke denotes atoms related by a glide plane, two by a twofold rotation axis, three by centers of symmetry. The y-coordinates of the Mg and Ca atoms are indicated.

Figure 1: Fig. 1. Projection of the inderborite structure in polyhedra along the y axis. One stroke denotes atoms related by a glide plane, two by a twofold rotation axis, three by centers of symmetry. The y-coordinates of the Mg and Ca atoms are indicated.

by two H_2O and four OH. The Ca atoms are located inside 8-vertex polyhedra with 12 triangular faces (a slightly distorted Thomson cube with broken pseudo-square bases). Four vertices of this polyhedron are OH groups, two are O atoms, and two are H_2O molecules. An analogous

Fig. 1. Projection of the inderborite structure in polyhedra along the y axis. One stroke denotes atoms related by a glide plane, two by a twofold rotation axis, three by centers of symmetry. The y-coordinates of the Mg and Ca atoms are indicated.

Ca polyhedron has been encountered in hydroboracite (^{3}), colemanite (^{8}), and kurnakovite (^{9}). On two sides of the Mg octahedron (at the OH vertices) there adjoin island three-nuclear boron-oxygen anions $[B_3O_3(OH)_5]^{2-}$, each of which is a ring consisting of two (B_1 and B_2) tetrahedra and one B_3 triangle, linked by common O vertices. A similar radical has been found in inderite $Mg[B_3O_3(OH)_5] \cdot 5H_2O$ (^{10}), and also in Ca borates: inyoite $Ca[B_3O_3(OH)_5] \cdot 4H_2O$, synthetic $Ca[B_3O_3(OH)_5] \cdot 2H_2O$, and meyerhofferite $Ca[B_3O_3(OH)_5] \cdot H_2O$ ($^{11-13}$). The architectural basis of the inderborite structure consists of parallel to the c axis, infinite "branching" rods made up of alternating Mg octahedra and Ca polyhedra, connected ("transposed") by ring-shaped (island) radicals $[B_3O_3(OH)_5]^{2-}$. In the corresponding period $c = 19.05$ Å, for one increment of such a rod with two Mg and two Ca, the upper and lower halves are related by the glide plane c. The rods are arranged according to the law of closest packing (of rods of circular cross-section), since $a : b = 1.64 \approx \sqrt{3}$. On two sides of each rod, pairs of B triangles extend in the form of branches (spikes), to the free OH vertices of which Ca polyhedra from neighboring rods adjoin. Thus the rods interlock into an openwork wall (layer) parallel to (100). Translationally identical openwork walls in the direction [100] are connected only by numerous hydrogen bonds, both directly and through buffer molecules

water molecules (O_{11}^{**}), which do not enter into the coordination polyhedra and serve only for the redistribution of hydrogen bonds, as occurs in inderite (^{10}). The comparatively weak bonding of the walls to one another determines the perfect cleavage (100) and the negative optical sign (^{5}). The expanded chemical formula of inderborite is:

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Fig. 2. One openwork wall of the structure of inderborite and free H_2O molecules linking two neighboring walls. Projection onto the yz plane.

Figure 2: Fig. 2. One openwork wall of the structure of inderborite and free H_2O molecules linking two neighboring walls. Projection onto the yz plane.

$$\mathrm{CaMg}\left[\mathrm{B_3O_3(OH)_5}\right]_2 \cdot 6\mathrm{H_2O} = (\mathrm{Ca} \cdot 2\mathrm{H_2O})(\mathrm{Mg} \cdot 2\mathrm{H_2O})\left[\mathrm{B_3O_3(OH)_5} \cdot \mathrm{H_2O}\right]_2 .$$

According to Table 2, the distances in the Mg octahedra remain within narrow limits: Mg—O = 2.01—2.09 Å with O—O = 2.82—2.96 Å; the bond lengths B—O in tetrahedra are 1.43—1.50 Å, and in triangles 1.34—1.42 Å. We postpone a detailed analysis of the hydrogen bonds until refinement of the structural parameters. Comparison of the structures of inderborite (metahydroboracite) $CaMgB_6O_{11} \cdot 11H_2O$ and hydroboracite $CaMgB_6O_{11} \cdot 6H_2O$ shows that the removal of five H_2O units has substantially changed the character of the hydrated boron-oxygen anion. From an island anion in inderborite it becomes an infinite chain anion in hydroboracite through condensation of three-membered rings. In hydroboracite even the Mg octahedra, which remain isolated in inderborite, are condensed into a chain $[AX_5]_\infty$.

Fig. 2. One openwork wall of the structure of inderborite and free H_2O molecules linking two neighboring walls. Projection onto the yz plane.

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