CRYSTALLOGRAPHY

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1962

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Abstract

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CRYSTAL STRUCTURE OF HYDROBORACITE

$CaMgB_6O_{11} \cdot 6H_2O = CaMg[B_3O_4(OH)_3]_2 \cdot 3H_2O$

Hydroboracite—a hydrated calcium and magnesium borate, $CaMgB_6O_{11} \cdot 6H_2O$—was first investigated by X-ray methods in 1958 by L. V. Petrova (^{1}), who determined the parameters of the monoclinic cell: $a = 11.64$, $b = 6.62$, $c = 8.24$ Å; $\beta = 102°54'$ and the diffraction group of the crystal $(2/mP-/c)$.

The objects of our investigation were specimens from the Mineralogical Museum of the Academy of Sciences of the USSR. The preliminarily determined cell parameters of hydroboracite were: $a = 11.54$, $b = 6.56$, $c = 8.18$ Å; $\beta = 102°40'$. The cell contains 2 formula units of $CaMgB_6O_{11} \cdot 6H_2O$ (specific gravity 2.167 according to (^{1})). We recorded (Mo K_α radiation) Weissenberg diagrams of five layer lines of rotation about the axes b and c, and on them fixed 146 nonzero F^2_{hk0}, $260F^2_{hk1}$, $216F^2_{hk2}$, $183F^2_{h0l}$, and $253F^2_{h1l}$; the intensities were estimated from blackening standards. Analysis of extinctions, in agreement with (^{1}), indicated two possible symmetry groups, Pc and $P2/c$. A test for the piezoelectric effect gave a negative result. However, the final conclusion in favor of the higher group $P2/c = C^4_{2h}$ was made in the course of deciphering the structure on the basis of the statistics of the quantities F^2_{hk1} (^{2}).

The structure was solved by the Patterson-function method in combination with difference Fourier syntheses. We would consider the use of difference Fourier syntheses with enhanced black-white symmetry (the substructure (^{3})) to be a distinguishing feature of the interpretation. Initially the positions of the Ca and Mg cations were determined. The presence of a noticeable pseudoperiod $c' = c/2$ on the rotation X-ray photograph about the z axis made it possible to assume that the Ca and Mg atoms are located in double positions, each with close (x, y) coordinates and z coordinates differing by $c/2$.

Attention was drawn to the fact that to a strong peak at the center $[1/2, 1/2]$ of the Patterson projection $P(u, v)$ there corresponded, on the (second) weighted Patterson projection

$$C_2(u, v) = \int P(u, v, w) \cos 4\pi w \, dw$$

an equally large hollow at the analogous point $[1/2, 1/2]$, which was the basis for identifying the vector $[1/2, 1/2, 1/4]$ with the vector Ca–Mg. From these data, within the group $P2/c$, it followed that one pair of cations is located in the centers of symmetry 000, $00\frac{1}{2}$ (we assumed that this is the "always more symmetrical" Mg), and the other (Ca) on 2-fold axes: $\frac{1}{2}y\frac{1}{4}$, $\frac{1}{2}y\frac{3}{4}$ (with a y coordinate close to 1/2). (The statistics of the intensities F^2_{hk1}, to which Ca cations make almost no contribution and Mg do not contribute at all, confirmed the centrosymmetric arrangement of the remaining atoms, i.e., the group $P2/c$.) In the Patterson syntheses, pseudocenters of symmetry linking the vectors Ca–O and Mg–O appeared very clearly at the point $[\frac{1}{4}, \frac{1}{4}]$ of the xy projection and $[\frac{1}{4}, \frac{1}{8}]$ of the xz projection. Moreover, the heights of the Patterson peaks associated with pseudosymmetry were very close because of the overlap of a number of vectors with close components. At the next stage of the interpretation, the method of successive difference Fourier syntheses with symmetry enhanced by taking the pseudocenters initially as true centers of symmetry proved very fruitful. In this way the arrangement of a doubled number of atoms was outlined.

connected by a pseudocenter (the substructure according to (3)). As a result of several (machine) cycles of refinement, the discrepancy coefficients R_{hk0} for $h + k = 2n$ and R_{h0l} for $h + l/2 = 2n$ decreased to 20%.

Fig. 1. Projection of the structure of hydroboracite in polyhedra along the c axis. Numerals without primes correspond to basis atoms; with one prime, to atoms related to the basis atoms by a glide plane; with two primes, to a twofold screw axis of symmetry; with three primes, to a center of inversion.

To isolate the true positions of the atoms of the structure from the doubled set of the substructure, a Patterson synthesis $P(u, v)$ was constructed from the nonzero reflections $h + k = 2n + 1$, and difference Fourier syntheses $\sigma(x, y)$ and $\sigma(x, z)$ were constructed from zero reflections $h + k = 2n + 1$ and, respectively, $h + l/2 = 2n + l$ (with coefficients $(-F_{\mathrm{Ca,Mg}})_{\mathrm{calc}}$). In these syntheses the pseudocenters were now centers of antisymmetry (cf. (3)), and from them it was possible to outline the true positions of most of the atoms. Subsequent difference Fourier syntheses over all nonzero reflections F_{hk0} $(h + k = 2n + 1)$ and F_{h0l} $(h + l/2 = 2n + 1)$ made it possible finally to localize all atoms of the structure (except H).

Next, a (machine) refinement cycle was carried out using the ordinary projections $\sigma(xy)$ and $\sigma(xz)$; the y-coordinates of the Ca cations and the (x, z)-coordinates of O_9, i.e., of those atoms that overlap in the projections, were refined from the syntheses $S_1(x, y)$, $C_1(x, z)$, and $S(x, z)$.

The finally adopted coordinates of all atoms are collected in Table 1. The discrepancy factors calculated over all nonzero reflections, taking into account

Table 1

Coordinates of the basis atoms of the hydroboracite structure

Fig. 2. Projection of the hydroboracite structure along the *b* axis

Figure 1: Fig. 2. Projection of the hydroboracite structure along the *b* axis

Atoms and their multiplicity	x/a	y/b	z/c	Atoms and their multiplicity	x/a	y/b	z/c
Mg (2)	0	0	0	O_6 (4)	0,349	0,272	0,107
Ca (2)	0,5	0,478	0,25	O_7 (4)	0,327	0,385	0,820
O_1^{**} (2)	0	0,120	0,25	O_8^* (4)	0,356	0,027	0,896
O_2^{**} (4)	−0,051	0,274	−0,099	O_9^* (4)	0,508	0,284	−0,024
O_3^* (4)	0,169	0,090	0,035	B_1 (4)	0,226	0,289	0,087
O_4 (4)	0,191	0,340	0,244	B_2 (4)	0,381	0,237	−0,054
O_5 (4)	0,174	0,448	−0,033	B_3 (4)	0,232	0,500	0,842

* O atom from a hydroxyl group.
** O atom in a water molecule.

isotropic temperature corrections, were: $R_{hk0} = 10.8\%$ ($\sin\vartheta/\lambda \leq 1.15$ Å^{-1}, $B_{hk0} = 0.7$ Å^{-2}), $R_{h0l} = 17\%$ ($\sin\vartheta/\lambda \leq 1.15$ Å^{-1}, $B_{h0l} = 0.8$ Å^{-2}).

The main features of the structure of hydroboracite are apparent from Figs. 1 and 2. The most striking characteristic should be considered the infinite boric-acid chains, which extend parallel to the *c* axis and are similar to the chains found in colemanite ([4]). The link of each chain is composed of two BO_4 tetrahedra and one BO_3 triangle, which are joined by common

Fig. 2. Projection of the hydroboracite structure along the *b* axis

vertices into a triple ring $B_3O_4(OH)_3$. The Mg cations are located at centers of symmetry inside octahedra composed of four H_2O molecules and two OH groups. Individual Mg octahedra are linked to one another by common H_2O vertices into chains $[AX_5]_\infty$, which are also elongated along *c*.

There are two Mg octahedra per cell; these are crystallographically related to one another, and also to the other octahedra of the AX_5 chain, by a glide plane

c passing through their centers. Each pair of translationally identical (along b) Mg chains is linked together by two (in

Table 2

Interatomic distances in the structure of hydroboracite (in angstroms)

B_1-tetrahedron		B_2-tetrahedron		B_3-triangle		Mg-octahedron	
$B_1 - O_3^*$	1.48	$B_2 - O_6$	1.46	$B_3 - O_4'$	1.34	$Mg - O_1^{**}$	2.19
$B_1 - O_4$	1.46	$B_2 - O_7$	1.45	$B_3 - O_5$	1.38	$Mg - O_2^{**}$	2.00
$B_1 - O_5$	1.47	$B_2 - O_8^*$	1.45	$B_3 - O_7$	1.37	$Mg - O_3^*$	2.00
$B_1 - O_6$	1.40	$B_2 - O_9^*$	1.46	$O_5 - O_4'$	2.34	$O_1^{**} - O_2^{**}$	2.96
$O_3^* - O_4$	2.34	$O_6 - O_7$	2.42	$O_5 - O_7$	2.38	$O_1^{**} - O_3^*$	2.90
$O_3^* - O_5$	2.42	$O_6 - O_8^*$	2.37	$O_7 - O_4'$	2.38	$O_1^{**} - O_2''^*$	2.98
$O_3^* - O_6$	2.36	$O_6 - O_9^*$	2.32	Ca-polyhedron		$O_1^{**} - O_3''$	3.02
$O_4 - O_5$	2.34	$O_7 - O_8^*$	2.43	$Ca - O_6$	2.30	$O_2^{**} - O_3^*$	2.81
$O_4 - O_6$	2.38	$O_7 - O_9^*$	2.30	$Ca - O_7$	2.37	$O_2^{**} - O_3''^*$	2.84
$O_5 - O_6$	2.38	$O_8^* - O_9^*$	2.42	$Ca - O_9^*$	2.59		
				$Ca - O_9''^*$	2.40		

on both sides of the plane $bc = (100)$ by chains $[B_3O_4(OH)_3]_\infty$. Each Ca is surrounded by eight O atoms, forming a complex 12-hedron with triangular faces. A similar Ca polyhedron is encountered in colemanite (4), although the authors themselves (4) inaccurately indicate sevenfold coordination for Ca. Thus the chemical formula of hydroboracite should be written as $CaMg[B_3O_4(OH)_3]_2 \cdot 3H_2O$. As Fig. 1 shows, two neighboring B chains (in the middle of the unit rectangle) are tightly linked by Ca cations and are very clearly separated from analogous pairs in neighboring cells. This determines the acicular habit of hydroboracite and two mutually perpendicular cleavages, (010) and (100), as in orthoclase. The parallel-running B and Mg chains are the obvious cause of the well-pronounced positive optical character of hydroboracite.

Table 2 collects the principal interatomic distances, which agree well with those found in other borates (4–10). We note that the length of the B–O bond in BO_3

triangles is appreciably shorter than in BO_4 tetrahedra. The distribution of protons among the 9 kinds of oxygen atoms, with separation into H_2O and OH, was carried out on the basis of an analysis of the valence balance.

Received
12 IX 1962

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