CRYSTAL STRUCTURE OF THE NEW NATURAL BORATE VIMSITE Ca[B$_{2}$O$_{2}$(OH)$_{4}$]

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Abstract

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CRYSTAL STRUCTURE OF THE NEW NATURAL BORATE VIMSITE $Ca[B_2O_2(OH)_4]$

In 1967, during a single-crystal investigation of uralborite, we discovered a new Ca borate—vimsite (^{1})*—in the form of elongated crystals with perfect cleavage along the elongation. The dimensions of individual crystals reach 2 mm; well-bounded forms are not observed.

According to chemical-analysis data by T. I. Stolyarova (in wt.%): SiO_2 2.18; Al_2O_3 0.57; Fe_2O_3 1.63; CaO 36.14; MgO 0.92; B_2O_3 37.36; H_2O^+ 20.86; $\Sigma =$ 99.66%—the approximate gross chemical formula $CaB_2O_4 \cdot 2.2H_2O$ was adopted, and this served as the basis for a detailed X-ray structural study of vimsite. Single-crystal fragments with linear dimensions of $0.2 \times 0.2 \times 0.25$ mm^3 were selected and adjusted by Laue photographs using the Umanskii–Kvitka method. From oscillation radiographs the monoclinic syngony of the mineral (Laue class $2/m$) was established, and the unit-cell parameters were determined, then refined by the powder method (RKU-114): $a = 10.02 \pm 0.02$ Å; $b = 9.71 \pm 0.02$ Å; $c = 4.440 \pm 0.005$ Å; $\beta = 92°$.

In accordance with the specific gravity $d = 2.54$ g/cm^3, determined by the heavy-float method, the monoclinic cell contains $Z = 4$ formula units of the indicated composition.

The principal experimental material for deciphering the structure of vimsite consisted of layer-line photographs (Weissenberg photographs, Mo K_α radiation) about the b and c axes: $h0l$, $h1l$, $hk0$, $hk1$, $hk2$, $hk3$ ($\max \sin\vartheta/\lambda = 1.08$ Å^{-1}). Intensities were estimated visually by blackening marks with a step of $\sqrt[4]{2}$. The systematic extinctions on the layer-line photographs lead to the X-ray group $C/-c$, i.e., to two Fedorov groups: $C_{2h}^6 = C2/c$ and $C_s^4 = Cc$. Intensity statistics were carried out according to Howells, Phillips, and Rogers (^{2}). The distribution functions $N(Z)$, constructed from the intensities $h0l$, $hk0$, $hk1$, indicate the presence of a center of symmetry, and accordingly the subsequent investigation was performed within the group $C_{2h}^6 = C2/c$, which was later confirmed.

The structure of vimsite was solved from the xy, xz projections and refined from a three-dimensional set of intensities. For the 4 Ca, 8 B, 16 O, and 8 H_2O atoms contained in the unit cell, the centered group $C2/c$ permits special fourfold positions: at inversion centers $4(a, b, c, d)$; on second-order axes $(4e)$; and general eightfold positions. In accordance with this, the Ca atoms must occupy a special position. The 4 parameterless complexes at inversion centers are divided into 2 subsorts: centers on glide planes $c(4a, b)$ and on clinoplanes $n(4c, d)$. The small parameter c (4.44 Å) and the glide along it exclude the location of Ca at centers on the c plane.

The absence of a maximum with coordinates $u = 0$, $v = 1/2$ in the Patterson projection uv showed that the Ca atoms also cannot occupy the second system of centers on the clinoplanes n, and, consequently, for the atoms

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* Named in honor of the 50th anniversary of the All-Union Scientific Research Institute of Mineral Raw Materials (VIMS).

Ca remains a one-parameter complex $(4e)$ on twofold rotation axes.

The main attention was devoted to analysis of the xy projection along the short edge of the cell, with minimal probability of atom overlap. In accordance with the symmetry of this projection, Cmm, and the position of $\mathrm{Ca}(0, y)$, a maximum corresponding to the Ca—Ca vector with coordinates $u = 0$, $v = 2y = {}^{24}/_{60}$ was found on the Patterson map. Comparison of the structural factors, experimental and calculated from the coordinates of one Ca: $x = 0$ and $y = {}^{12}/_{60}$ (25% of the scattering matter), gave an R-factor of 40%. In the electron-density synthesis, maxima corresponding to oxygen atoms and OH groups were clearly revealed. Some difficulty arose with regard to the boron atoms, which were localized from difference Fourier syntheses calculated with subtraction from the experimental F contributions of Ca and two O atoms, with the result being a fairly significant maximum clearly corresponding to the B atom. Refinement of the x, y coordinates of the independent atoms in this projection, carried out automatically on the M-20 computer at the Computing Center of Moscow State University by the least-squares method using the programs of B. L. Tarnopol' skii and V. I. Andrianov (^{3}), with introduction of an isotropic temperature correction $B = 0.92$, led to a decrease of the discrepancy factor to 12.6%.

Table 1

Coordinates of the basis atoms of vimssite

Atoms	x/a	y/b	z/c
Ca	0	0.208	0.250
O_1	0.165	0.048	0.114
O_2 (OH)	0.359	0.084	0.799
O_3 (OH)	0.142	0.201	0.705
B	0.209	0.070	0.813

Table 2

Interatomic distances in vimssite (Å)

B-tetrahedron		Ca-polyhedron	
B –O_1	1.43	Ca –O_1 (2) ***	2.36
B –O_2 (OH)	1.51	Ca –O_2 (OH) (2)	2.50
B –O_3 (OH)	1.50	Ca –O_3 (OH) (2)	2.43
B –O_4 (O_1)*	1.50	Ca –O_4 (OH) (2)	2.84
O_1 –O_2 (OH)	2.45	O_1 –O_3 (OH)* (2)	2.35
O_1 –O_3 (OH)	2.35	O_1 –O_3 (OH)** (2)	3.03
O_1 –O_4	2.40	O_2 (OH) –O_3 (OH)** (2)	3.07
O_2 (OH) –O_3 (OH)	2.48	O_2 (OH)* –O_4 (OH)* (2)	3.03
O_2 (OH) –O_4 (O_1)	2.45	O_3 (OH) –O_4 (OH)* (2)	2.88
O_3 (OH) –O_4 (O_1)	2.46	O_1 –O_1*	3.56
		(O_2OH) – O_2(OH)*	2.90
Avg. B –OOH = 1.485 Å		Avg. Ca – OOH = 2.54 Å	
Avg. O –OOH = 2.43 Å		Avg. O –OOH = 2.93 Å	

* Atoms which are related to the corresponding basis atoms by symmetry elements of the group.
** Atoms taken from neighboring cells.
*** The position of Ca on the twofold axis divides its 8 neighbors into 4 pairs of equidistant ones.

The fixed position of the Ca atoms in the *xz* projection, with known *x* coordinates of the basis atoms, made it possible to proceed to a detailing of the electron-density distribution in *xz*. By the method of successive approximations, taking into account the solved *xy* projection, the x, z coordinates of all O atoms were found. To localize the light B atom, a difference Fourier synthesis was also constructed, on which the peak identified as the boron atom was clearly preserved; allowance for its coordinates improves the discrepancy factor by 2%. The fixed, ultimately refined x, z coordinates of the basis atoms O and B were re-

Fig. 1. Vimsite. yz projection of its structure. Light Ca polyhedra are singled out. B tetrahedra connected into metachains parallel to the z axis are shaded

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Fig. 2. Vims e. Projection xz with alternating packets of B tetrahedra and layers of Ca polyhedra

Figure 2: Fig. 2. Vims e. Projection xz with alternating packets of B tetrahedra and layers of Ca polyhedra

were refined by the least-squares method with a final
$R_{h0l} = 10.1\%$ ($B = 1.07$).

The final coordinates of all atoms (Table 1), obtained in solving the xy and xz projections, were refined against a three-dimensional set of intensities (580 independent and nonzero reflexes) by the least-squares method to a discrepancy factor
$R_{hkl} = 13.1\%$ ($B = 0.93$). Analysis of distances, the valence balance, and the gross chemical formula excluded the possibility of "whole" H_2O molecules and separated the O and OH groups in the anionic part. It is evident that the anions common to two B tetrahedra and the Ca polyhedron must be O^{2-}, and not OH^-; otherwise the valence balance on them would be too strained. This may also be considered confirmed by the shortened distance $B—O_1 = 1.43$ Å, with an average $B—(O, OH) = 1.48$ Å. From the distances given in Table 2 it is clear that the B atoms are located inside a slightly distorted tetrahedron. The coordination of the Ca atom is eightfold, in the form of a cube deformed in the direction of a second-order axis.

Fig. 1. Vims e. Projection yz of its structure. Light Ca polyhedra are singled out. B tetrahedra, connected into metachains parallel to the z axis, are shaded

The basis of the structure of vims e may be considered to be infinite columns ("rods") along the c axis, consisting of calcium cubes (Fig. 1) set on an edge common to two neighboring polyhedra, slightly inclined to the c axis.

Fig. 2. Vims e. Projection xz with alternating packets of B tetrahedra and layers of Ca polyhedra

Each column is surrounded on four sides by infinite boron-oxygen chains with the metaformula
$[B_2O_2(OH)_4]^{2-}$ of the pyroxene type with two B tetrahedra in the repeat unit. Such a type of chain is encountered in borates for the first time, although it may be compared with the metachain ($B : O = 1 : 3$) in the rare-earth borosilicate—stillwellite (4), where, however, the unit $[B_3O_9]$ is composed of three tetrahedra,

Fig. 3. Vimsite. Projection xy. The Ca cations are shown as spheres between packets of B tetrahedra, which are broken into chains, looking at the reader with their ends

Figure 3: Fig. 3. Vimsite. Projection xy. The Ca cations are shown as spheres between packets of B tetrahedra, which are broken into chains, looking at the reader with their ends

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···wrapping around the screw axis 3_1, whereas in vimsite the B atoms are connected by the plane c. From Figs. 1 and 2 it is clearly seen that each of the B tetrahedra of the vimsite chain has an edge in common with a Ca polyhedron, shortened in accordance with Pauling’ s rule to 2.35 Å, and a diorthogroup of two B tetrahedra is joined to the elongated edge (rules of Chapters 1 and 2 of silicate crystal chemistry). From the ratio $\mathrm{Ca} : \mathrm{B_2O_3} = 1 : 1$ it follows that, if a Ca column is surrounded on four sides by boron-oxygen chains, then each chain is also common to four Ca columns.

Fig. 3. Vimsite. Projection xy. The Ca cations are shown as spheres between packets of B tetrahedra, which are broken into chains, looking at the reader with their ends

In Fig. 3 the ends of the boron-oxygen chains are visible, i.e., they are directed perpendicular to the plane of the drawing, and the Ca atoms shown as spheres are arranged in the xy projection according to the centered law, in agreement with the symmetry of the group.

Thus, purely geometrically, rods of calcium polyhedra form the basis of the structure, and metaborate chains rigidly cement it. In accordance with the structure determined, the chemical formula of vimsite should be written as $\mathrm{Ca[B_2O_2(OH)_4]}$. The crystal structure found explains well the physical properties of vimsite. The elongation of its crystals coincides with the direction of the columns of Ca polyhedra and metachains along the axis [001]. The optical axis N_p coincides with this same direction. The perfect cleavage (100) permits one to speak of the mica-like character of this borate* and to see in Fig. 3 the packets of B tetrahedra (broken into chains), separated by a layer of large Ca cations, which here play a role similar to K in micas (Ca in margarite). The optically negative character of vimsite is also consistent with this representation. The crystal-structure analysis performed showed that there are no discrete water molecules in the mineral, while the OH groups play a very large role in the structure, which also explains the comparatively high dehydration temperature (about 350°) (1).

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* The closeness of the parameters of the unit cells of vimsite and muscovite is also worthy of attention.

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