CRYSTALLOGRAPHY

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Abstract

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CRYSTAL STRUCTURE OF LESSERITE $Mg[B_3O_3(OH)_5] \cdot 5H_2O$

The hydrous borate lesserite $Mg_2B_6O_{11} \cdot 15H_2O$ is a colorless transparent mineral, first described in 1956 ([1]). We repeated the determination of the unit-cell dimensions (RKV camera, Cu K_α radiation) and of the symmetry group on specimens obtained from Harvard University (USA) from Prof. K. Frondel:

$a = 12.02 \pm 0.03$, $b = 13.12 \pm 0.04$, $c = 6.84 \pm 0.02$ Å, $\beta = 104°40'$, $C_{2h}^5 - P2_1/a$. A cell of these dimensions contains $2[Mg_2B_6O_{11} \cdot 15H_2O]$; the specific gravity of the specimens is $d_{\text{exp}} = 1.80$, $d_{\text{theor}} = 1.82$.

With Mo K_α radiation, Weissenberg photographs were obtained for the zero and subsequent (1, 2, 3) layer lines of rotation about the c axis, and also the zero and first developments of layer lines of rotation about a. The intensities of the reflections were estimated by comparison with a blackening scale.

The unit cell of lesserite contains a considerable number of atoms (68, not counting hydrogen) with close atomic numbers, and therefore use of the Patterson function did not appear effective. The structure determination was carried out on the basis of direct determination of the signs of F_{hkl}, namely by the method of comparison ([2–4]) in combination with the statistical relations of Sayre–Zachariasen ([5,6]). For the interpretation all the recorded nonzero reflections were used: 147 F_{hk0}, 280 F_{hk1}, 236 F_{hk2}, 171 F_{hk3}, 114 F_{0kl}, and 247 F_{1kl}. From the reference group ([2–4]), which included about 40% of the nonzero reflections of the types $hk0$, $hk1$, and $hk2$ with the largest unit amplitudes, it was possible to establish part of the signs F_{hk0} and F_{hk1} (126 S_{hk0} out of 147, 232 S_{hk1} out of 280), which were used to construct the electron-density synthesis $\sigma(x, y)$ and weighted projections $C_1(x, y)$ and $S_1(x, y)$. From these projections, after a cycle of refinement, the positions of most of the atoms of the structure were found (Mg, 11 O, 2 B); the positions of three atoms remained undetermined (2 O, 1 B).

To identify them, we turned to the remaining experimental material and, using the available S_{hk0} and S_{hk1}, with the aid of the Sayre–Zachariasen relations, ran through the entire array of signs S_{hk2}, the reference signs S_{hk3}, and then, from all the obtained reference signs, the array S_{0kl}. As a result, a total of 87 signs F_{0kl} (out of 114) and 209 S_{hk2} (out of 236) were determined, on the basis of which we constructed the syntheses $\sigma(y, z)$, $C_2(x, y)$, and $S_2(x, y)$. From

Fig. 1. Electron-density projections

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the projection $\sigma(y, z)$, the z-coordinates of the atoms already found were fixed more accurately and, in addition, from these syntheses the position of one more oxygen atom (O_{13}) was determined. The coordinates found for 15 independent atoms made it possible to calculate the signs of the reflections $0kl$, $hk0$, $hk1$, $hk2$, and $hk3$ and to construct the syntheses $\sigma(y, z)$, $C_l(x, y)$, $S_l(x, y)$ $(l = 1, 2, 3)$, as well as the difference synthesis $\Delta\sigma(x, y)$. On the corresponding diagrams most of the coordinates of the atoms found earlier were refined, but in addition the atoms B_3 and O_7, which had not appeared previously and which in the xy projection are overlapped by the previously fixed B_2 and O_8, stood out on them. The coordinates of all atoms were refined once more from the set of syntheses $C_1(y, z)$, $S_1(y, z)$, $\sigma(y, z)$, $\sigma(x, y)$, constructed from signs in the establishment of which all atoms of the structure participated. The diagrams $C_1(y, z)$ and $S_1(y, z)$ proved especially important in the refinement, since in the yz projection most atoms overlap. Figure 1 gives the last two syntheses $\sigma(x, y)$ and $\sigma(y, z)$. The coordinates of the final approximation are collected in Table 1. The discrepancy factors calculated from these coordinates

over all nonzero reflections, with allowance for isotropic temperature corrections:
$R_{hk0} = 20.0\%$ $(\sin\vartheta/\lambda \leqslant 0.8\,\text{Å}^{-1},\ B_{hk0} = 2.00\,\text{Å}^{-2})$,
$R_{0kl} = 19.7\%$ $(\sin\vartheta/\lambda \leqslant 0.9\,\text{Å}^{-1},\ B_{0kl} = 0.9\,\text{Å}^{-2})$.

The main features of the structure of lesserite are seen in Fig. 2. The Mg cations are located inside octahedra formed by two OH groups and four H_2O. The atoms B_1 and B_2 are in tetrahedra, and B_3 is in a triangle of O atoms and OH groups.

Fig. 1. Projections of electron density: A $-\sigma(x, y)$, B $-\sigma(y, z)$. Atoms related by the basic screw axis are denoted by one prime, by a glide plane by two primes, and by a center of symmetry by three primes. Contour lines are drawn at intervals of $2e/\text{Å}^2$; depressions are indicated by a dotted line; regions of negative values are hatched.

The structure can be described as a packing of isolated groups– "islands" – which include an Mg octahedron, to two vertices of which there adjoins one three-membered boron-oxygen anion $[B_3O_3(OH)_5]^{-2}$, representing a ring of two B tetrahedra and one B triangle that have common O vertices. Such a radical was previously found 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 $Ca[B_3O_3(OH)_5]{\cdot}H_2O$[7–9]. Islands of composition $MgB_3O_3(OH)_5 \cdot 4H_2O$ are connected by numerous hydrogen bonds, both directly and through a buffer water molecule (O_{13}), which does not enter into the coordination polyhedra and participates only in the redistribution of hydrogen bonds that unite the entire architecture of lesserite, being connected

Fig. 2. Structure of lesserite in polyhedra. Projection along the c axis. Circles denote H_2O molecules not included in the polyhedra. Dotted lines correspond to hydrogen bonds

Figure 2: Fig. 2. Structure of lesserite in polyhedra. Projection along the c axis. Circles denote H_2O molecules not included in the polyhedra. Dotted lines correspond to hydrogen bonds

with four different groups (some H_2O molecules play the same role in [7]). Thus, the chemical formula of lesserite should be written as $Mg[B_3O_3(OH)_5] \cdot 5H_2O$, or in detailed form as $[MgB_3O_3(OH)_5 \cdot 4H_2O] \cdot H_2O$.

The interatomic distances in the Mg octahedra are within the following limits: Mg–O 1.98—2.15 Å, O–O 2.84—3.06 Å; the lengths of B–O bonds in tetrahedra are 1.51—1.39 Å, and in triangles 1.48—1.34 Å, which agrees with the results obtained for other borates [6–13].

The hydrogen (proton) bonds were outlined after finding the lengths of those O –O vectors that do not coincide with the edges of the coordination polyhedra, with sufficient confidence that at least one end of such a vector corresponds to atoms belonging to an OH or H_2O group. The data obtained are given in Table 2. Thirteen distances proved not to exceed 2.96 Å, and two more distances are equal to 3.09 and 3.14 Å. The next 4 distances lie within 3.2–3.3 Å; the remaining exceed-

exceed 3.5 Å. Distances greater than 3.2 Å may with certainty be assigned to van der Waals contacts. The distances given in Table 2 are well interpreted as corresponding to hydrogen bonds: the 15 H atoms belonging to the independent part of the cell are distributed among 15 positions–

Fig. 2. Structure of lesserite in polyhedra. Projection along the *c* axis. Circles denote H_2O molecules not included in the polyhedra. Dotted lines correspond to hydrogen bonds.

Table 1

Coordinates of the basis atoms of the structure of lesserite

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Mg	0,119	0,214	0,258	O_9^{**}	0,000	0,199	0,434
O_1^*	0,435	0,145	0,689	O_{10}^{**}	−0,025	0,226	−0,008
O_2^*	0,256	0,209	0,497	O_{11}^{**}	0,109	0,369	0,275
O_3	0,258	0,087	0,773	O_{12}^{**}	0,229	0,239	0,072
O_4	0,305	0,035	0,464	O_{13}^{**}	0,410	0,022	0,170
O_5^*	0,207	−0,108	0,283	B_1	0,308	0,118	0,599
O_6	0,141	−0,042	0,541	B_2	0,198	−0,014	0,381
O_7^*	0,105	0,000	0,873	B_3	0,170	0,020	0,727
O_8^*	0,118	0,059	0,233				

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

Table 2

O–O distances taken as hydrogen-bond lengths

O–O vector	Length of O –O vector, Å	$OH(H_2O)$ –proton donor	O–O vector	Length of O –O vector, Å	$OH(H_2O)$ –proton donor
O_1^*—$O_{13}'''^{**}$	2,87	O_1^*	O_3—O_{12}^{**}	2,94	O_{12}^{**}
O_7^*—O_8^*	2,54	O_7^* or O_8^*	O_4—O_{13}^{**}	2,61	O_{13}^{**}
O_7^*—$O_8'''^*$	2,68	$O_8'''^*$ or O_7^*	O_3—O_{13}^{**}	2,96	O_{13}^{**}
O_6—$O_9'''^{**}$	2,70	$O_9'''^{**}$	O_2^*—O_5^*	2,81	O_2^*
O_1^*—$O_9'''^{**}$	2,92	$O_9'''^{**}$	O_5^*—$O_{10}'''^{**}$	2,92	$O_{10}'''^{**}$
O_1^*—$O_{10}'''^{**}$	2,61	$O_{10}'''^{**}$	O_5^*—O_7^*	3,09	O_5^*
O_{11}^{**}—$O_{13}'''^{**}$	2,72	O_{11}^{**}	O_{10}^{**}—$O_{12}'''^{**}$	3,14	$O_{12}'''^{**}$
O_4—$O_{11}'^{**}$	2,84	$O_{11}'^{**}$			

* O atom from an OH group.
** O atom from an H_2O molecule.

arrangements, if the 2 distances greater than 3.00 Å are taken into account (hydrogen-bond lengths exceeding 3.00 Å are also indicated in (13)); thus, apparently, all H atoms participate in proton bonds. Each O atom is in a tetrahedral or triangular environment, which is typical of many other structures; in the same Table 2, OH and H_2O—the proton donors in each particular case—are indicated. In the structure of lesserite there is no disorder of the H atoms, such as has been found in some other borates (8, 12).

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Note: Figure translations are in progress. See original paper for figures.