CRYSTAL STRUCTURE OF CALCIBORITE

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CRYSTAL STRUCTURE OF CALCIBORITE

$CaB_2O_4 = Ca_2[BO_3BO]_2$

The mineral calciborite—a new anhydrous Ca borate, discovered in 1951 by E. S. Petrova in skarnified limestones of the Novofrolovskoe deposit—was named in accordance with the chemical formula she proposed, $5CaO \cdot 4B_2O_3 = Ca_5B_8O_{17}$ ([1,2]).

Data from microchemical analysis, obtained with allowance for mineral impurities during a reexamination of the mineral by S. V. Malinko et al. ([3]) (wt.%): SiO_2 0.55; Fe_2O_3 0.22; Al_2O_3 0.18; CaO 44.08; MgO 0.81; B_2O_3 47.58; CO_2 6.07; As_2O_5 0.30; H_2O^+ 0.17; H_2O^- 0.50; $\Sigma = 100.46\%$, led to the simpler ratio $CaO : B_2O_3 = 1 : 1$ in calciborite, and consequently to the formula $CaO \cdot B_2O_3$, or CaB_2O_4.

In addition to the mineral calciborite, 4 polymorphic modifications of the same composition have been obtained synthetically (phases I, II, III, and IV). The structures of phases I, III, and IV have been solved; for phase II only the unit-cell dimensions have been determined, which coincide, within the limits of accuracy, with the parameters of the mineral calciborite we studied, namely, of its specimens kindly provided by S. V. Malinko to the crystal-chemistry laboratory of VIMS ([4–9]).

The parameters of the orthorhombic cell (Laue class *mmm*), refined by the powder method (RKU-114), are:

$$a = 8.38 \pm 0.01 \text{ Å};$$

$$b = 13.82 \pm 0.01 \text{ Å};$$

$$c = 5.006 \pm 0.002 \text{ Å}.$$

Table 1

Calciborite, coordinates of the basis atoms

Atoms	x/a	y/b	z/c
Ca	0.386	0.143	0.123
B_1	0.537	0.139	0.624
B_2	0.742	0.052	0.365
O_1	0.391	0.185	0.633
O_2	0.742	−0.009	0.144
O_3	0.596	0.112	0.365
O_4	0.885	0.112	0.378

The best agreement of the experimental density with the X-ray density for the formula CaB_2O_4 made it possible to adopt the latter as the starting formula in solving the structure ($d = 2.88$ g/cm^3; $\rho_x = 2.90$ g/cm^3). The unit cell of the indicated dimensions contains $Z = 8$ units of CaB_2O_4.

The main experimental material for deciphering the structure of calciborite was provided by layer-line developments (Weissenberg photographs, MoK_α radiation) about the principal crystallographic directions: $hk0$–$hk4$, $0kl$, $h0l$, $h1l$ ($\max \sin\theta/\lambda = 0.9$ Å^{-1}).

The intensities of the reflections were estimated by blackening standards with a step of $\sqrt[4]{2}$. Systematic absences on the layer-line developments unambiguously determine the most probable Fedorov group $D_{2h}^{10} = Pccn$.

The solution of the structure of calciborite in accordance with the previously calculated gravity criterion ($r' = 1.55$) was carried out by the (semi-)heavy-atom method ([10]).

The short edge $c = 5.0$ Å excludes the possibility of placing Ca in special positions with multiplicity 4 (a, b, c, d). Analysis of Patterson synthesis ···

projections $P(uv)$, $P(vw)$, and then of the entire three-dimensional Patterson function $P(uvw)$ made it possible to localize the Ca atoms in a general position. The pseudoperiod $c' = c/2$ considerably hindered localization of the oxygen and boron atoms, and the positions of the latter were found by constructing three-dimensional full and difference syntheses of the electron density. In the course of successive approximations the discrepancy factor R_{hkl} improved from 42.5%, taking into account one independent Ca atom, to 25.2% for all atoms. Refinement of the coordinates of the basis atoms, carried out automatically on the M-20 computer at the Computing Center of Moscow State University by the least-squares method (programs of B. A. Tarnopol' skii and V. I. Andrianov ([11])) for a three-dimensional

Fig. 1. Calciborite; calcium atoms are shown as spheres, and for two of them the associated polyhedra are indicated

set of intensities (300 independent and nonzero reflections), with the introduction of an isotropic temperature correction $B = 0.56$, reduced the discrepancy

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factor to $R_{hkl} = 12.2\%$ (Table 1).

The interatomic distances calculated from the final coordinates are given in Table 2.

Table 2

Interatomic distances in calciborite (Å)

B_1-triangle	B_2-tetrahedron	Ca-polyhedron	Ca-polyhedron
B_1—$O_3 = 1.36$	B_2—$O_3 = 1.48$	Ca—$O'_1 = 2.62$	O'''_1—$O'_1 = 3.08$
B_1—$O_1 = 1.38$	B_2—$O_4 = 1.46$	Ca—$O_1 = 2.52$	O'''_1—$O_2 = 3.00$
B_1—$O_4 = 1.44$	B_2—$O_2 = 1.51$	Ca—$O_2 = 2.57$	O'''_1—$O_4 = 2.48*$
O_1—$O_3 = 2.31*$	B_2—$O'_2 = 1.51$	Ca—$O'_2 = 2.45$	O'_1—$O'_1 = 2.97$
O_1—$O_4 = 2.48*$	O_4—$O_3 = 2.42$	Ca—$O''_1 = 2.39$	O'_1—$O_3 = 3.55$
O_3—$O_4 = 2.44$	O_4—$O_2 = 2.44$	Ca—$O'''_1 = 2.37$	O'_1—$O_4 = 3.59$
	O_4—$O'_2 = 2.31$	Ca—$O_3 = 2.23$	O_2—$O_4 = 3.43$
	O_3—$O_2 = 2.42$	Ca—$O_4 = 2.34$	O_2—$O'_2 = 2.51*$
	O_3—$O'_2 = 2.49$	O_1—$O'_1 = 3.08$	O_2—$O''_1 = 2.96$
	O_2—$O'_2 = 2.51*$	O_1—$O''_1 = 3.44$	O'_2—$O''_1 = 3.00$
		O_1—$O'_2 = 2.96$	O'_2—$O_3 = 3.17$
		O_1—$O_3 = 2.31*$	O'_2—$O_4 = 4.13$
		O'''_1—$O''_1 = 3.44$	O_3—$O_4 = 2.57$
Avg. B_1—$O =$	Avg. B_2—$O =$	Avg. Ca—$O =$	Avg. Ca—$O =$
$1.39 O$—$O = 2.41$	$1.49 O$—$O = 2.43$	$2.44 O$—$O = 3.08$	$2.44 O$—$O = 3.08$

* Common edges connecting boron triangles and tetrahedra with calcium polyhedra.

Figure 1 shows a yz projection of the structure of calciborite, with oxygen tetrahedra and shaded triangles around boron specifically distinguished. The spheres shown are calcium atoms.

The cations in the structure of calciborite are located in eight-vertex deltoid dodecahedra. Intersecting pairs of these Ca polyhedra are linked into infinite columns elongated along the short edge c (an end-on projection of the column is shown in Fig. 2). There are two such columns per unit cell, each of which is surrounded by six boron-oxygen chains $[B_4O_8]^{4-}_{\infty}$ (Fig. 2). These columns may be regarded as the principal structural rods of the structure, while the chains of B tetrahedra and especially B triangles cement them into a single framework

Fig. 2. Calciborite; projection of the structure in polyhedra onto the xy plane

Figure 2: Fig. 2. Calciborite; projection of the structure in polyhedra onto the xy plane

(Fig. 2). Along the a axis the entire structure breaks up into two-layer packets joined by common edges of Ca polyhedra (Fig. 1). Within the period b there are two such two-layer packets at the levels $y = 0$ and $y = 1/2$.

This kind of structure is well matched by the planes of perfect cleavage perpendicular to the b axis and of imperfect cleavage perpendicular to the indicated pseudoperiod $c' = c/2$ in the mineral calciborite.

From the standpoint of the systematics of borate structures, the most characteristic feature of calciborite should be considered the previously unknown infinite boron-oxygen chains $[B_4O_8]^{4-}_{\infty}$ (Fig. 1). This radical is a metaborate chain $[B_2O_6]_{\infty}$ of BO_4-tetrahedra (of metagermanate type), incrusted with BO_3-triangles. Thus, in the structure of calciborite, in contrast to the triple coordination of boron proposed *a priori* by A. S. Povarenykh ([12]), but in agreement with Zachariasen ([7]), half of the boron atoms are in tetrahedral coordination. If the meta-chain $[BO_3]_{\infty}$ is taken as the basis, then the incrusting B triangle contributes only one O atom.

Fig. 2. Calciborite; projection of the structure in polyhedra onto the xy plane

In accordance with the structure determined, the crystallochemical formula of calciborite is $Ca_2[B_4O_8] \equiv Ca_2[BO_3BO]_2$, which confirms the correctness of the chemical formula of the mineral given in ([3]).

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