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Refinement of the crystal structure of frolovite $Ca[B(OH)_4]_2$

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(Submitted March 29, 1976)

Dokl. Akad. Nauk SSSR **230**, 91–94 (September 1976)

PACS numbers: 61.50.Qy

The crystal structure of frolovite $Ca[B(OH)_4]_2$, which was deciphered with the participation of the present authors in 1972,[1] has been refined in order to localize the hydrogen atoms and to correlate the results with diffractometric material obtained at ordinary and low temperatures.

The experimental material (parameters of the unit cell and a series of intensities) was obtained from one crystal of isometric form on a $P\bar{1}$ Sintex automatic diffractometer; an LT-1 attachment was used at low temperatures. The crystal was flushed with a stream of nitrogen gas previously cooled to T = −140°C with liquid nitrogen in a heat exchanger.

The parameters of the triclinic frolovite cell (a, b, c in angstroms and α, β, γ in degrees) are: at T = 18°C, a = 7.774(2), b = 5.680(1), c = 8.136(2), α = 113.15(1), β = 101.67(2), γ = 107.87(2), V = 292.2(1) Å^3; at T = −140°C, a = 7.745(2), b = 5.667(1), c = 8.102(2), α = 113.24(2), β = 101.54(2), γ = 107.92(2), V = 289.1(1) Å^3; Z = 2, d_{exper} = 2.14 g/cm^3, d_{calc} (T = 18°C) = 2.259, d_{calc}(T = −140°C) = 2.284 g/cm^3, space group $C_i = P\bar{1}$.

In refining the structure of calcium borate use was made of 3160 [max(sin θ)/λ = 0.77] and 2858 [max(sin θ)·(λ)$^{-1}$ = 0.66 Å^{-1}] independent nonzero ($I \geq 1.96\sigma I$) reflections, recorded by the $2\theta:\theta$ method at variable scanning speeds (Mo Kα radiation, plane graphite monochromator) at T = 18 and −140°C, respectively. Recalculation of I and $|F_{hkl}|$ (without allowance for absorption, μr = 0.09) and all subsequent mathematical operations were carried out with an XTL special-purpose structure-decoding computing system.

Comparison of the numbers of reflections recorded at ordinary and low temperatures (Table 1) reveals that they increase with (sinθ)/λ for T = −140°C. Comparison of the mean values of the signal-to-background ratio [$C/\Phi = \langle F^2_{exp}/\sigma^2(F_{exp})\rangle$] as a function of sin$^2\theta$ for chosen intervals (Fig. 1) demonstrates that C/Φ improves (increases) at low temperatures, especially for large values of θ.

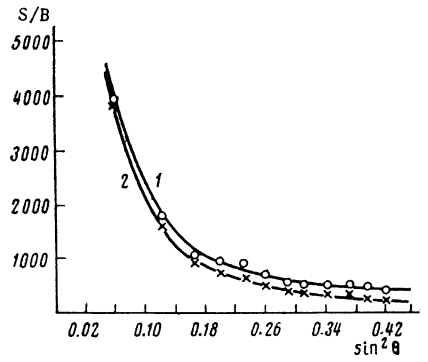

Fig. 1. Plot of the signal-to-background ratio as a function of sin$^2\theta$ for T = 18°C (1) and T = −140°C (2), according to experimental data for frolovite.

The coordinates of the basis atoms Ca, B, and O, taken from Egorov-Tismenko,[1] were refined by the least squares method to R_{hkl} = 5.4% (T = 18°C) and R_{hkl} = 4.0% (T = −140°C) in a full-matrix isotropic approximation and to R_{hkl} = 4.2% (T = 18°C) and R_{hkl} = 3.6% (T = −140°C) in an anisotropic approximation. The construct zero difference syntheses of the electron density according to the experimental data, taken at T = 18°C, show on four clearly defined maxima identified with hydrogen atoms; the four missing hydrogen atoms were fixed from the data of the low-temperature experiment.

The positions of the hydrogen atoms found were refined by the least-squares method in an isotropic approximation in two stages: In the first, only the position parameters were refined while B_j was fixed at 2.0 Å, and in the second stage only B_j was refined.

The final divergence factor with allowance for the localized hydrogen atoms R_{hkl} = 3.2% (T = −140°C) corresponds to the coordinates of the basis atoms and the ir

TABLE 1. Number of Reflections in Intervals of (sinθ)/λ, Recorded at −140 and 18°C

Intervals of (sin θ)/λ	No. of reflections		Intervals of (sin θ)/λ	No. of reflections	
	−140° C	18° C		−140° C	18° C
0–0.355	590	578	0.513–0.565	450	379
0.0281–0.408	569	576	0.540–0.587	452	367
0.355–0.450	539	507	0.565–0.608	462	355
0.408–0.484	521	480	0.587–0.627	426	330
0.450–0.513	513	470	0.608–0.645	384	317
0.484–0.540	492	432	0.627–0.663	176	256

Note: The relative decrease in the number of reflections, recorded in the last two intervals at low temperatures, is related to the angular limitations in work with the LT-1 low-temperature attachment.

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TABLE 2. Frolovite $Ca[B(OH)_4]_2$. Coordinates of Basis Atoms and Individual Isotropic and Anisotropic Temperature Factors

Atoms	x/a	y/b	z/c	B_j	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	0.23651(5)	0.01813(7)	0.18818(5)	0.36(0)	0.35(1)	0.35(1)	0.40(1)	0.15(1)	0.11(1)	0.20(1)
	79(6)	1781(8)	18910(6)	0.73(1)	0.72(1)	0.69(1)	0.81(1)	0.31(1)	0.22(1)	0.39(1)
B_1	0.0287(3)	0.4076(4)	0.2353(3)	0.52(2)	0.57(5)	0.48(5)	0.56(5)	0.23(4)	0.24(4)	0.28(4)
	78(3)	2(4)	49(3)	0.84(3)	0.83(6)	0.80(6)	0.88(6)	0.35(5)	0.28(5)	0.43(5)
B_2	0.4383(3)	0.3149(4)	0.7119(3)	0.48(2)	0.49(5)	0.42(5)	0.50(5)	0.17(4)	0.17(4)	0.21(4)
	8(3)	51(4)	20(3)	0.76(3)	0.77(6)	0.76(6)	0.76(6)	0.34(5)	0.28(5)	0.35(5)
H_1	0.020(4)	0.292(5)	0,688(4)	10.1(9)						
H_2	0.191(4)	0.416(5)	0.078(4)	2.9(5)						
H_3	0.232(4)	0.485(5)	0.415(4)	12(1)						
H_4	0.793(4)	0.107(5)	0,202(4)	3.5(6)						
H_5	0.183(4)	0,027(6)	0.581(4)	3,0(6)						
H_6	0.541(4)	0.277(5)	0.926(4)	3.0(5)						
H_7	0.198(4)	0,15(5)	0.520(4)	13(1)						
H_8	0.609(4)	0,346(4)	0.204(4)	2.7(5)						
O_1	0.0660(2)	0.7080(3)	0.3016(2)	0.58(2)	0.70(4)	0.44(4)	0.64(4)	0.26(3)	0.29(3)	0.26(3)
	55(2)	60(3)	14(2)	0.99(2)	1.11(5)	0.67(4)	1.16(5)	0.36(4)	0.40(4)	0.38(4)
O_2	0.0830(2)	0.2948(3)	0.0654(2)	0.54(2)	0.53(4)	0.50(4)	0.51(4)	0.17(3)	0.21(3)	0.19(3)
	30(2)	48(3)	54(2)	1.00(2)	1.03(5)	0.87(4)	0.93(5)	0.31(4)	0.40(4)	0,32(4)
O_3	0.1433(2)	0,3739(3)	0.3859(2)	0.60(2)	0.61(4)	0.70(4)	0.55(4)	0.32(3)	0.13(3)	0.35(3)
	18(2)	11(3)	41(2)	1,10(2)	1.25(5)	1.40(5)	1.05(5)	0.71(4)	0,27(4)	0,70(4)
O_4	0.1820(2)	0.7724(3)	0,8306(2)	0.56(2)	0.51(4)	0.49(4)	0.77(4)	0.22(3)	0.27(3)	0.35(3)
	19(2)	8(3)	15(2)	1.00(2)	0.75(4)	0.94(4)	1.42(5)	0.30(4)	0.40(4)	0.67(4)
O_5	0.2384(3)	0.1414(3)	0,6825(2)	0.61(2)	0,48(4)	0.59(4)	0.67(4)	0,13(3)	0,21(3)	0.28(3)
	92(2)	36(3)	8(2)	1.11(2)	0.79(4)	1.02(5)	1.37(5)	0.22(4)	0.43(4)	0,55(4)
O_6	0.4243(2)	0.7353(3)	0.1606(2)	0.51(2)	0.53(4)	0,59(4)	0.47(4)	0.28(3)	0.14(3)	0.31(3)
	5(2)	49(4)	12(2)	0,90(2)	0.96(5)	1.05(5)	0.90(4)	0.56(4)	0,29(4)	0.57(4)
O_7	0.4675(2)	0.2288(3)	0.5267(2)	0.51(2)	0.59(4)	0,55(4)	0,40(4)	0.26(3)	0.18(3)	0,23(3)
	2(2)	91(3)	74(2)	0.91(2)	1,09(5)	0,94(4)	0.72(4)	0,46(4)	0,34(4)	0,38(4)
O_8	0.4858(2)	0.6236(3)	0.8092(2)	0.53(2)	0.52(4)	0.38(4)	0.62(4)	0.19(3)	0.17(3)	0.18(3)
	62(2)	27(3)	83(2)	0.92(2)	0.92(5)	0.62(4)	1.11(5)	0,32(4)	0.33(4)	0.30(4)

Note: Standard deviations are given in parentheses. The first and second columns give the results obtained in experiments at −140 and 18°C, respectively. The anisotropic temperature factors were calculated with the formula $T=\exp[-1/4\ (B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

TABLE 3. Frolovite $Ca[B(OH)_4]_2$. Interatomic Spacings (standard deviations in parentheses).

B_1-tetrahedron	B_2-tetrahedron	Ca-polyhedron		
B_1-O_1 1.477(3)	B_2-O_5 1.467(3)	Ca−O_1 2.451(2)		
1.472(3)	1.468(3)	2.462(2)		
$-O_2$ 1.485(2)	$-O_6$ 1.502(3)	$-O_2$ 2.432(1)		
1.486(3)	1.499(3)	2.437(2)		
$-O_3$ 1.473(3)	$-O_7$ 1.472(2)	$-O_2$ 2.595(2)		
1.475(3)	1.472(3)	2.613(2)		
$-O_4$ 1.478(3)	$-O_8$ 1.489(3)	$-O_3$ 2.441(2)		
1.477(3)	1.488(3)	2.443(2)		
		$-O_4$ 2.544(1)		
		2.556(2)		
Average 1.478	Average 1.482	$-O_6$ 2.453(2)		
1.478	1.481	2.459(2)		
		$-O_7$ 2.507(1)		
		2.513(1)		
		$-O_8$ 2.451(2)		
		2.461(2)		
		Average 2.484		
		2.493		
O_1-O_2 2.438(2)	O_5-O_6 2.403(2)	O_1-O_2 2.960(2)	O_2-O_3 2.374(2)	O_3-O_8 3.543(2)
2.436(2)	2.406(2)	2.972(2)	2.374(2)	3.554(2)
$-O_3$ 2.442(2)	$-O_7$ 2.415(2)	$-O_3$ 3.388(2)	$-O_4$ 2.362(2)	O_4-O_6 3.055(2)
2.442(3)	2.416(2)	3.397(3)	2.358(2)	3.075(2)
$-O_4$ 2.430(2)	$-O_8$ 2.443(2)	$-O_4$ 4.319(3)	$O_2'-O_3$ 3.635(2)	$-O_8$ 3.247(2)
2.429(2)	2.439(2)	4.336(3)	3.636(2)	3.260(2)
O_2-O_3 2.374(2)	O_6-O_7 2.408(2)	$-O_6$ 3.189(2)	$-O_4$ 2.284(2)	O_6-O_7 3.035(2)
2.374(2)	2.407(2)	3.205(2)	3.250(2)	3.053(2)
$-O_4$ 2.362(2)	$-O_8$ 2.424(2)	$-O_7$ 3.089(2)	$-O_8$ 3.107(2)	$-O_8$ 3.379(2)
2.358(2)	2.421(2)	3.107(2)	3.124(2)	3.394(2)
O_3-O_4 2.431(2)	2.428(2)	O_2-O_2' 2.822(2)	$-O_8-O_7$ 3.024(2)	O_7-O_8 3.200(2)
2.429(2)	O_7-O_8 2.426(2)	2.829(2)	3.035(2)	3.213(2)
Average 2.413	Average 2.420			Average 3.165
2.411	2.419			3.171

teratomic spacings, listed in Tables 2 and 3.

Comparison of the coordinates and interatomic spacings and the individual temperature factors reveals a decrease in the standard deviations for the low-temperature experiment and a difference between the values of the isotropic temperature factors for the hydrogen atoms which showed up in the ordinary-temperature (smaller B_j) and low-temperature experiments. Refinement of the position parameters of the hydrogen atoms by the data of the low-temperature experiment brought the donor-H spacings closer to the standard distance (Table 4).

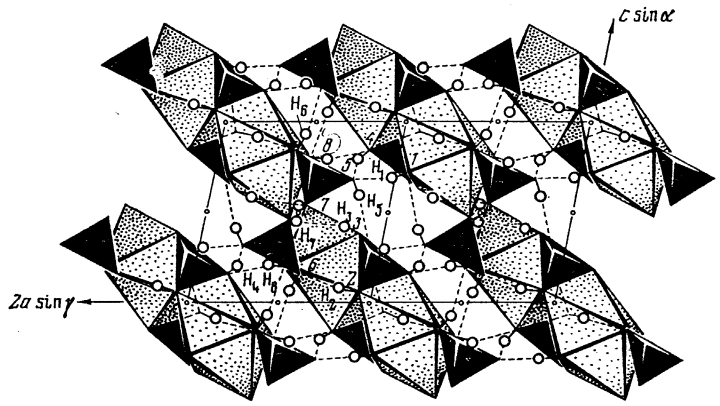

Fig. 2. Frolovite $Ca[B(OH_4)]_2$. xz projection. The solid line shows the donor-H bonds and the dashed line, the acceptor H bonds.

TABLE 4. Hydrogen Bonds in the Structure of Frolovite $Ca[B(OH)_4]_2$

D-N...A	D−N	N...A	D−N	Angle DNA	D-N...A	D−A	N...A	D−A	Angle DNA
	Å					Å			
$O_1-H_1...O_5$	0.83	2.12	2.753	171.7°	$O_5-H_5...O_1$	0.75	2.04	2.774	166.6
$O_2-H_2...O_6$	0.89	1.88	2.716	165.8	$O_6-H_6...O_8$	0.78	2.06	2.836	169.4
$O_3-H_3...O_7$	0.78	2.16	2.893	157.3	$O_7-H_7...O_7'$	0.66	2.08	2.678	164.1
$O_4-H_4...O_5$	0.81	1.96	2.763	173.7	$O_8-H_8...O_4$	0.80	1.97	2.747	165.5

This refinement of the crystal structure of frolovite confirmed the structural motif earlier described and the assumption, based on analysis of the valence force balance, that the entire anionic part of the structure of the borate under study is represented by OH groups. The xz projection of the structure in Fig. 2 demonstrates the binding of the Ca−B−O layers through fixed H bonds.

[1)] This is in agreement with data obtained by A. Christiansen for the org: compound $C_7H_{12}N_2O_2$ (oral communication).

[1] Yu. K. Egorov-Tismenko, A. E. Gushchina, et al., Dokl. Akad. Nauk SS 202 (1972).

Translated by Eugene Lepa

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