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Hydroxylborite, $Mg_3(BO_3)(OH)_3$, a New Mineral Species and Isomorphous Series Fluoborite–Hydroxylborite[1]

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Abstract—Hydroxylborite, a new mineral species, an analogue of fluoborite with OH > F, has been found at the Titovsky deposit (57°41′ N, 125°22′ E), the Chersky Range, Dogdo Basin, Sakha-Yakutia Republic, Russia. Prismatic crystals of the new mineral are dominated by the $\{10\bar{1}0\}$ faces without distinct end forms and reach (1–1.5) × (0.1–0.2) mm in size. Radial aggregates of such crystals occur in the mineralized marble adjacent to the boron ore (suanite–kotoite–ludwigite). Calcite, dolomite, Mg-rich ludwigite, kotoite, szaibelyite, clinohumite, magnetite, serpentine, and chlorite are associated minerals. Hydroxylborite is transparent colorless, with a white streak and vitreous luster. The new mineral is brittle. The Mohs' hardness is 3.5. The cleavage is imperfect on $\{0001\}$. The density measured with equilibration in heavy liquids is 2.89(1) g/cm^3; the calculated density is 2.872 g/cm^3. The wave numbers of the absorption bands in the IR spectrum of hydroxylborite are (cm^{-1}; sh is shoulder): 3668, 1233, 824, 742, 630sh, 555sh, 450sh, and 407. The new mineral is optically uniaxial, negative, $\omega = 1.566(1)$, and $\varepsilon = 1.531(1)$. The chemical composition (electron microprobe, H_2O measured with the Penfield method, wt %) is 18.43 B_2O_3, 65.71 MgO, 10.23 F, 9.73 H_2O, 4.31 $-O = F_2$, where the total is 99.79. The empirical formula calculated on the basis of 6 anions *pfu* is as follows: $Mg_{3.03}B_{0.98}[(OH)_{2.00}F_{1.00}]O_{3.00}$. Hydroxylborite is hexagonal, and the space group is $P6_3/m$. The unit-cell dimensions are: $a = 8.912(8)$ Å, $c = 3.112(4)$ Å, $V = 214.05(26)$ Å^3, and $Z = 2$. The strongest reflections in the X-ray powder pattern [*d*, Å (*I*, %)(*hkil*)] are: 7.69(52)$(01\bar{1}0)$, 4.45(82)$(11\bar{2}0)$, 2.573(65)$(03\bar{3}0)$, 2.422(100)$(02\bar{2}1)$, and 2.128(60)$(12\bar{3}1)$. The compatibility index $1 - (K_p/K_c)$ is 0.038 (excellent) for the calculated density and 0.044 (good) for the measured density. The type material of hydroxylborite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow (inventory number 91968) and the Geological Museum of the All-Russia Institute of Mineral Resources, Moscow (inventory number M-1663).

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INTRODUCTION

Hydroxylborite is an OH-dominant (OH > F) magnesium orthoborate, a member of the isomorphous series fluoborite $Mg_3(BO_3)F_3$–hydroxylborite $Mg_3(BO_3)(OH)_3$ with an inferred complete substitution of F for OH. The mineral is named after its chemical composition.

Minerals of the fluoborite group are abundant, although they infrequently form large segregations. These minerals are most typical of ore and mineralized calciphyre at Sn–B and B–Fe magnesian skarn deposits (Tilley, 1951; Gramenitsky, 1966; Pertsev, 1971, Alexandrov, 1982; Marincea, 2000). They also occur in skarnified rocks and related ore at Sn deposits (Ahifeld et al., 1938; Sergeev and Novikova, 1969; Kwak and Nicholson, 1988; Šrein et al., 2000); base-metal deposits (Bauer and Berman, 1929); in apodolomitic greisen (Gulyaev, 1971); serpentinite (Oidup and Kudryavtseva, 1999); in metalimestone xenoliths hosted in volcanic tuff (Brisi and Eitel, 1957); and halite–anhydrite and halite–calcite rocks (Apollonov et al., 1988).

Magnesium fluorhydroxylorthoborate was described for the first time by Geijer (1929) from the Norberg iron deposit (Mine Tallgruvan) in Sweden, and was named *fluoborite*. The borate was identified in association with magnetite, humite-group minerals, forsterite, and ludwigite and characterized by the significant predominance of OH over F (h = OH/(OH + F) ratio is about 70 mol %). The high-fluorine (F > OH) mineral of this group was found in limestone xenoliths in the Nocera volcanic tuff near Naples, Italy by A. Scacchi in 1881 and F. Zambonini in 1919 and originally regarded as a mineral species $Mg_3Ca_3O_2F_8$ named nocerite. Brisi and Eitel (1957) established that this composition corre-

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sponds to a mixture of fluoborite and fluorite. Despite the name *nocerite* that was initially given to a mineral mixture, Brisi and Eitel kept this name for the identified borate, which is not correct in our opinion.

Fluorine members of the considered mineral group occur in nature more frequently than hydroxyl counterparts; however, OH-dominant minerals are not a mineralogical curiosity (Utekhin, 1960; Kwak and Nicholson, 1988; Šrein et al., 2000; our samples from the Verkhoyansk region). Having studied fluoborite from Sterling Hill, New Jersey, the United States, Bauer and Berman (1929) noted that, under appropriate conditions, it was appropriate to expect an F-free "fluoborite." While analyzing the chemical composition and properties of the fluoborite-group minerals with the general formula $Mg_3BO_3(F,OH)_3$, Shaller (1942) and later Brovkin et al. (1967) demonstrated a wide range of replacement of F with OH.

In experiments on the hydrothermal synthesis of the $Mg_3BO_3(F,OH)_3$ fluoborates, a wide range of varieties from a fluorine end member (h = 0) (Flamini et al., 1979) to a hydroxyl-rich (h = 57 mol %) member were synthesized. It was revealed that an increasing pressure favors the synthesis of minerals enriched in hydroxyl (Nekrasov et al., 1970).

We have studied the OH-dominant mineral species (h = 67 mol %) from calciphyre of the Titovsky Sn–B deposit that is typical of the Verkhoyansk–Indigirka metallogenic province (Lisitsyn et al., 1995). On the basis of the results obtained and a survey of published data, we propose recognizing *hydroxylborite*, the hydroxyl mineral species $Mg_3BO_3(OH)_3$ within a continuous isomorphous series of binary compounds, whereas the name *fluoborite* is suggested for the $Mg_3BO_3F_3$ species, which is consistent with the composition of these minerals. The range of compositional variation recommended for definition is the 50% rule. The principal characteristics of the studied hydroxylborite are listed in Table 1.

EXPERIMENTAL

The chemical composition of hydroxylborite was studied with a Superprobe-8100 electron microprobe at the All-Russia Institute of Mineral Resources. The accelerating voltage was 5–10 kV for boron, 10 kV for fluorine, and 15 kV for magnesium; the current is 100, 50, and 20 nA, respectively. The following standards have been used: natural danburite $CaB_2Si_2O_8$ for B and synthetic MgF_2 for Mg and F. The LDE2 crystal was used for the detection of boron, and the TAP crystal, for the detection of magnesium and fluorine. Differential discrimination has been applied to measure the intensity of BK_α and FK_α. In order to minimize the effect of the chemical bond on the results of the boron and fluorine measurements, the K-ratio ($K = S_{sample}/S_{standard}$) was determined by integral intensities. The BK_α and FK_α intensities were measured in the raster regime with an irradiated area of 30 × 30 μm^2 to decrease the thermal diffusion of the atoms during analysis. The thermal stability of the new mineral was controlled by the measurement of the MgK_α intensity for a time, which is necessary for obtaining the integral intensity of BK_α. The variation in the MgK_α intensity did not exceed 2% at the applied analytical conditions.

The concentrations were calculated with a CITZAF Vers. 3.50 program that is included in the software support for the electron microprobe. The B_2O_3 content in the mineral (18.15 wt %, average over 3 point analyses) detected at 5 kV was underestimated in comparison with that at 10 kV.

The H_2O content was measured using the Penfield method at the Institute of Problems of Chemical Physics, Russian Academy of Sciences (analyst A.S. Astakhova). Ignition was carried out at 1000°C in oxygen flowing with anhydron, magnesium perchlorate $Mg[ClO_4]_2$, as an adsorbent.

Infrared spectra were recorded with a SPECORD 75 IR dual-beam spectrophotometer (Carl Zeiss, Jena) within the wave number interval 400–3800 cm^{-1} ranging from 400 to 1400 cm^{-1} at a width of the spectral slit of <2 cm^{-1} and from 1400 to 3800 cm^{-1} at <8 cm^{-1}. Polysterene and gaseous ammonia were used as the standards. The KBr disk with mineral powder was measured. An anhydrous KBr disk without the mineral was placed in a comparison beam during the recording of the spectrum. IR spectroscopy was performed at the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

The density was measured with equilibration in heavy liquids. The optical parameters were determined with immersion liquids.[2] The X-ray powder diffraction pattern of hydroxylborite was recorded with a RIGAKU diffractometer, CuK_{α_1} radiation, at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences.

The X-ray diffraction analysis of hydroxylborite was carried out with a $P\bar{1}$ SYNTEX automatic single-crystal diffractometer at the Laboratory of X-ray Diffraction Analysis, Department of Crystallography and Crystal Chemistry, Moscow State University. The structure of the new mineral was determined by the direct method using the SHELX-97 software package (Sheldrick, 1997). The model obtained was refined with the least-squares method in an anisotropic fit for Mg, B, and O atoms. The position of the H atom was detected on a differential distribution of the electron density. The absence of additional significant maximums on this distribution confirmed the accuracy of the structure model.

OCCURRENCE

Boron mineralization in the Verkhoyansk–Indigirka ore province (Russian Federation, Sakha-Yakutia

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[2] Measurements of the density and determination of the optical parameters were carried out by A.E. Zadov, NPO Regenerator, Moscow.

Table 1. Main characteristics of the minerals of the fluoborite–hydroxylborite series

Characteristic	Fluoborite (synthesized)	Hydroxylborite (sample B-922)
Formula	$Mg_3BO_3F_3$	$Mg_{3.03}B_{0.98}O_{3.00}[(OH)_{2.00}F_{1.00}]$
h = OH/(OH + F), mol %	0	67
Symmetry	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P6_3/m$
a, Å	$8.805_6 \pm 0.0015$	8.912(8)
c, Å	$3.097_5 \pm 0.001$	3.112(4)
c/a	0.3518	0.3492
V, Å^3	208.08	214.05(26)
Z	2	2
Strongest reflections in X-ray pattern, I, d, $hkil$	30, 7.60, $10\bar{1}0$	52, 7.69, $01\bar{1}0$
	60, 4.38, $11\bar{2}0$	82, 4.45, $11\bar{2}0$
	50, 2.539, $30\bar{3}0$	65, 2.573, $03\bar{3}0$
	–	49, 2.551, $11\bar{2}1$
	100, 2.403, $20\bar{2}1$	100, 2.422, $02\bar{2}1$
	100, 2.108, $31\bar{4}0 + 21\bar{3}1$	44, 2.141, $13\bar{4}0$
		60, 2.128, $12\bar{3}1$
	80, 1.795, $22\bar{4}1$	35, 1.812, $22\bar{4}1$
	50, 1.748, $31\bar{4}1$	22, 1.765, $13\bar{4}1$
	80, 1.549, 0002	22, 1.557, 0002
	100, 1.465, $41\bar{5}1$	36, 1.482, $14\bar{5}1$
	50, 1.0574, $62\bar{8}0$	–
D, g/cm^3	3.012	2.89(1)
Optical character	Uniaxial, negative	Uniaxial, negative
ω	1.503	1.566
ε	1.482	1.531
$\omega - \varepsilon$	0.021	0.035
Wave numbers in IR spectrum	3660, 1237, 851, 825, 740, 640, 616, 525, 460, 403	3668, 1233, 824, 742, 630, 555, 500, 450, 407
Color	Colorless	Colorless
Fluorescence	?	Bluish
Source	Brovkin et al. (1967)	This study

Republic, Chersky Range) has been known since the 1930s (Vakar et al., 1934) and was further studied in detail by many researchers (Pertsev, 1971; Dorofeev, 1979; Aleksandrov, 1982; Lisitsyn et al., 1995). More than 30 boron minerals were described from this region, including new mineral species discovered here: calcium and magnesium carbonate-borates bokarite (Pertsev et al., 1965) and sakhaite (Ostrovskaya et al., 1966), calcium borate ol'shanskite (Bogomolov et al., 1969), silicatian magnesioborate, pertsevite (Schreyer et al., 2003), and Al-rich iron–magnesium borate alumino-magnesiohulsite (Pertsev et al., 2004). In addition, original varieties of borates were established at the deposits of the Verkhoyansk region: Al-rich ludwigite (Pertsev and Alexandrov, 1964) and Zr-bearing nordenskiöldine (Rudnev, 1998).

The studied samples of hydroxylborite were taken from the Visyachy area located in the eastern part of the Titovsky deposit (57°41′ N, 125°22′ E). This area comprises the early Cretaceous amphibole–biotite granite

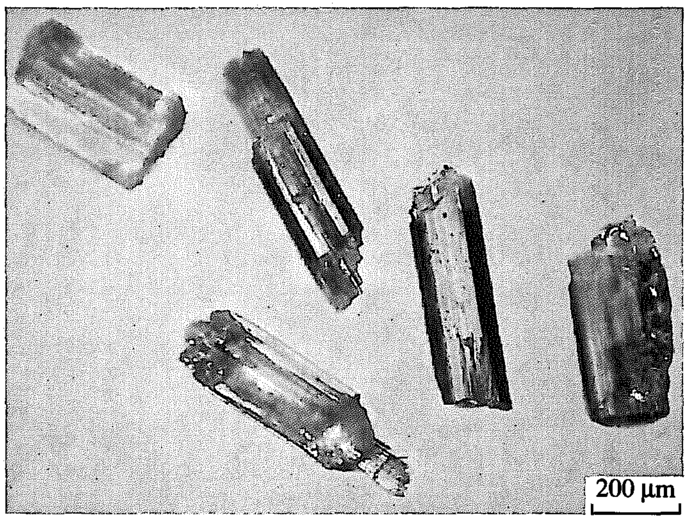


Fig. 1. Crystals of hydroxylborite.

Fig. 2. Photomicrograph of columnar hydroxylborite aggregates partially replaced by szaibelyite and hosted in clinohumite calciphyre. Crossed polars.

that intrudes the Paleozoic (Ordovician–Silurian–Devonian) cherty–carbonate sequence. The magnesian carbonate rocks were transformed into magnesian skarn (pyroxene, pyroxene–forsterite, forsterite (clinohumite), and phlogopite varieties), calciphyre, and periclase–brucite marble. These rocks are nonuniformly serpetinized. Skarn and calciphyre host ludwigite and suanite–kotoite boron ores; the early borates are replaced by szaibelyite to a variable extent. Al-rich ludwigite with an f_m = Fe/(Fe+Mg) ratio no higher than 9–10 mol % is characteristic of the Visyachy area. The insignificant admixture of hulsite is associated with magnesian ludwigite. Minerals of the fluoborite series occur in mineralized skarn, calciphyre, and marble as nonuniform disseminations, pockets, thin rims at the contact between ludwigite ore and calciphyre, and polymineralic veinlets along with serpentine and chlorite. Apomagnesian calc-skarn with vesuvianite and sakhaite locally occur in the area.

Hydroxylborite was revealed in clinohumite calciphyre adjacent to the ludwigite ore. This rock is mainly composed of calcite locally enriched in hydroxylborite, which is frequently replaced with acicular and fibrous szaibelyite. Ludwigite is associated with these borates as acicular–fibrous segregations. Separate crystals of

Table 2. Chemical composition of hydroxylborite, wt %

Component	Range	Average of 3 analyses	Standard deviation	(O, OH) = 5
B_2O_3	18.20–18.61	18.43	0.2	0.98
MgO	65.13–66.03	65.71	0.4	3.03
F	10.04–10.48	10.23	0.2	1.00
H_2O	9.59–9.87	9.73		2.00
Total		104.10		
$-O=F_2$		–4.31		
Total		99.79		

Note: A Superprobe-8100 electron microprobe, analyst G.N. Nechelyustov. Ca, Fe, Mn, Al, Cl, Ti, and Zn contents are below detection limits. H_2O content is determined using the Penfield method.

hydroxylborite contain acicular inclusions of ludwigite oriented along the elongation of the host mineral. Small grains of clinohumite with a simple or polysynthetic twinning (extinction angle of the twins is 9–12°) are nonuniformly scattered through the carbonate matrix.

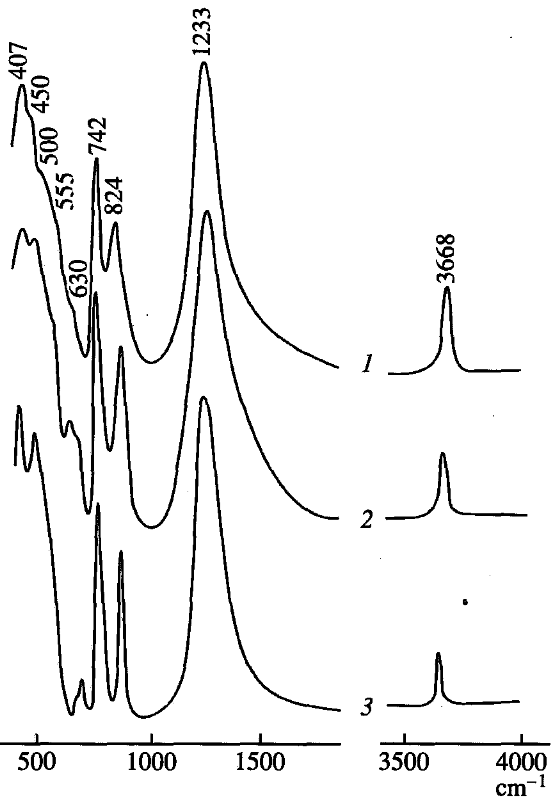


Fig. 3. (*1*) IR spectrum of hydroxylborite, sample B-922 compared with that of fluoborite from (*2*) Pöhla, Saxony, Germany, containing 20.09 wt % F and from (*3*) Boden (New Jersey, the United States) containing 23.2 wt % F.

PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION

The typical crystals of hydroxylborite are hexagonal prisms $\{10\bar{1}0\}$ without end faces and reach 1–1.5 × 0.1–0.2 mm^2 in size (Fig. 1). They commonly occur as radiaxial and fanlike aggregates (Fig. 2). The new mineral is colorless, transparent, and with a vitreous luster. The cleavage is imperfect on {0001}; parting is absent; and fracture is conchoidal. Hydroxylborite is brittle. The Mohs' hardness is 3.5. The measured density is 2.89(1) g/cm^3; the density calculated on the basis of the chemical composition and unit-cell dimensions is 2.872 g/cm^3. The new mineral is optically uniaxial, negative, $\omega = 1.566(1)$, $\varepsilon = 1.531(1)$, and $\omega - \varepsilon = 0.035$. The elongation is negative. Hydroxylborite is characterized by a bluish fluorescence in ultraviolet light (λ = 246 nm). The new mineral dissolves in concentrated H_2SO_4, readily reacts with quinalizarin, and remains insoluble in water and dilute HCl.

The chemical composition (Table 2, sample B-922) of the studied hydroxylborite is identical to that of samples from the Tallgruvan Mine in Norberg, Sweden (Geijer, 1926), from the central Transbaikalian region, Russia (Kanishchev, 1966), and from tin deposits in the NW Tasmania, Australia (Kwak and Nicholson, 1988) and Bohemia, Czech Republic (Šrein et al., 2000).

The empirical formula of hydroxylborite calculated on the basis of the standard (oxygen) method for

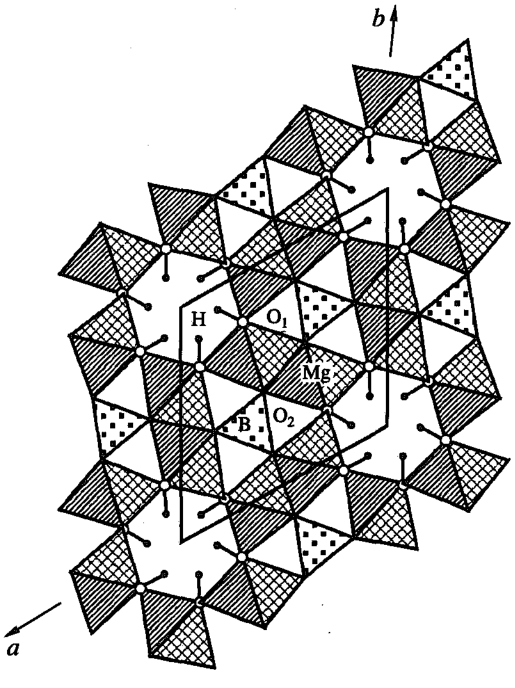


Fig. 4. Projection of the hydroxylborite structure along [001]. Heavy lines show $H-O_1$ bonds.

Table 3. X-ray powder diffraction data for hydroxylborite

I, %	d_{meas}, Å	d_{calc}, Å	*hkil*	*I*, %	d_{meas}, Å	d_{calc}, Å	*hkil*
52	7.69	7.72	$01\bar{1}0$	22	1.765	1.764	$13\bar{4}1$
82	4.45	4.46	$11\bar{2}0$	8	1.685	1.684	$14\bar{5}0$
1	3.860	3.859	$02\bar{2}0$	11	1.640	1.640	$04\bar{4}1$
42	2.916	2.917	$12\bar{3}0$	22	1.557	1.556	0002
28	2.886	2.886	$01\bar{1}1$	17	1.540	1.539	$23\bar{5}1$
65	2.573	2.573	$03\bar{3}0$	14	1.486	1.485	$33\bar{6}0$
49	2.551	2.551	$11\bar{2}1$	36	1.482	1.481	$14\bar{5}1$
100	2.422	2.422	$02\bar{2}1$	9	1.470	1.469	$11\bar{2}2$
7	2.228	2.228	$22\bar{4}0$	6	1.459	1.459	$24\bar{6}0$
44	2.141	2.141	$13\bar{4}0$	9	1.387	1.386	$15\bar{6}0$
60	2.128	2.128	$12\bar{3}1$	8	1.384	1.383	$05\bar{5}1$
4	1.983	1.983	$03\bar{3}1$	5	1.341	1.341	$33\bar{6}1$
17	1.930	1.929	$04\bar{4}0$	10	1.332	1.331	$03\bar{3}2$
35	1.812	1.812	$22\bar{4}1$	5	1.321	1.321	$24\bar{6}1$
17	1.771	1.771	$23\bar{5}0$				

(O,OH)$_5$ is $Mg_{3.03}(B_{0.98}[(OH)_{2.00}F_{1.00}]O_{3.00}$. The simplified formula—$Mg_3(BO_3)(OH)_3$. The theoretical chemical composition calculated from this formula is (wt %): 66.16 MgO, 19.05 B_2O_3, 14.79 H_2O, where the total is 100.00 wt %.

The compatibility index of the chemical composition, optical parameters, and density is good: $1 - (K_p/K_C) = 0.038$ for the calculated density and $1 - (K_p/K_C) = 0.044$ for the measured density.

X-RAY DIFFRACTION AND IR SPECTROSCOPY

Hydroxylborite crystallizes in a hexagonal symmetry, and the space group is $P6_3/m$. The unit-cell parameters determined from the X-ray powder pattern are (Table 3): $a = 8.912(8)$ Å, $c = 3.112(4)$ Å, $V = 214.05(26)$ Å^3, $c/a = 0.3492$, and $Z = 2$.

The wave numbers of the absorption bands in the infrared spectrum of hydroxylborite are (cm^{-1}; sh is shoulder): 3668, 1233, 824, 742, 630sh, 555sh, 500sh, 450sh, and 407 (Fig. 3). Hydroxylborite differs from fluoborite in a higher integral intensity of the O–H-stretching vibration band with a maximum at 3668 cm^{-1} and the absence of distinct maximums within the range 500–700 cm^{-1}.

CRYSTAL STRUCTURE

The principal parameters of XRD experiments, refinement results, and crystal characteristics are presented in Table 4. The final reliability factor (R_1 = 0.054) corresponds to the coordinates of the basic atoms and interatomic distances given in Tables 5 and 6. The refined population value of size O(1) equals 0.52(2) suggested statistic occupation of this position by O (~68%) and F (~32%) atoms. According to this relationship, the crystallochemical formula is $Mg_3(BO_3)[(OH)_{2.04}F_{0.96}]$ ($Z = 2$, $D_{\text{calc}} = 2.85$ g/cm^3). The resolution of the hydroxylborite structure confirmed its belonging to the mineral of the structural type of fluoborite $Mg_3(BO_3)F_3$ (Takeuchi, 1950; Dal Negro and Tadini, 1974). At the same geometry of the atom location in the hydroxylborite structure and the refined structure of fluoborite ($a = 8.86$ Å, $c = 3.10$ Å, $V = 211$ Å^3, space group $P6_3/m$ (Cámara and Ottolini, 2000)), these models differ in the choice of horizontal axes (*X*, *Y*, *U*) of the hexagonal unit cell. The transition from the hydroxylborite cell to the fluoborite cell is reflected in the matrix ($100/\bar{1}10/00\bar{1}$). In addition, OH-groups are dominant in site O(1) (F/OH ~ 0.3/0.7) of the hydroxylborite structure, whereas according to (Cámara and Ottolini, 2000), this site is dominated by F (F/OH ~ 0.8/0.2) in the structure of fluoborite.

Table 4. Main crystal data of hydroxylborite and characteristics of the experiment on the refinement of its structure

Characteristic	Formula and value
Chemical formula	$Mg_3BO_3[(OH)_{2.04}F_{0.96}]$
Symmetry	Hexagonal
Space group, Z	$P6_3/m$, 2
Unit-cell dimensions, Å:	
a	8.924(5)
c	3.116(1)
Volume of unit cell, V, Å^3	214.9(2)
D_{calc}, g/cm^3	2.85
μ, mm^{-1}	0.67
Crystal size, mm	0.075 × 0.125 × 0.300
Diffractometer	$P\bar{1}$ "SYNTEX"
Radiation, wavelength, Å	MoK_α, 0.71069
Scanning method	$2\theta : \theta$
Scanning ranges	$0 \le h \le 14$ $-14 \le k \le 12$ $0 \le l \le 6$
$\sin\theta/\lambda_{max}$	0.99
Number of recorded reflections	678
Number of independent reflections with $I \ge 2\sigma(I)$	238
$R_1/wR_2[I \ge 2\sigma(I)]$	0.054/0.115
Weight scheme in least-square method, w	$w = 1/[\delta^2(F^2) + (0.0742P)^2 + 0.00P]$, $P = (\max F_o^2 + 2F_c^2)/3$
s	0.974
$\Delta\rho_{max}$(cÅ^{-3})/$\Delta\rho_{min}$(cÅ^{-3})	1.23/–1.10
Number of refined parameters	33

Decreasing the F content in the hydroxylborite structure leads to an increase in the Mg–O(1) distances up to 1.998–2.039 Å and in parameter a of the unit cell (8.924 Å) as compared with fluoborite, where for the two studied samples, the Mg–F(O$_1$) distances are 1.9711–2.0115 Å and 1.9707–2.0115 Å, while parameters a equal 8.8612 Å and 8.8602 Å. Parameters c, which are 3.116 Å in hydroxylborite and 3.1021 Å in fluoborite, as well as the B–O distances in B-triangles, which are equal to 1.389 Å (hydroxylborite) and 1.389–1.387 Å (fluoborite), vary to a lesser extent, while F is replaced with the OH-groups.

Table 5. Atom coordinates and equivalent displacement parameters for hydroxylborite

Position	Multiplicity	x/a	y/b	z/c	$U_{eq} \times 100$, Å^2
Mg	6	0.3721(1)	0.3395(1)	0.25	1.00(4)
B	2	0.3333	0.6667	0.25	1.3(1)
O(1)	6	0.7924(3)	0.7053(3)	0.25	1.17(5)
O(2)	6	0.4462(3)	0.6020(3)	0.25	1.05(5)
H	6	0.90(1)	0.81(2)	0.25	5(3)

Note: Standard deviations are given in parentheses. Value U_{iso} is shown for position H.

Table 6. Interatomic distances in the structure of hydroxylborite

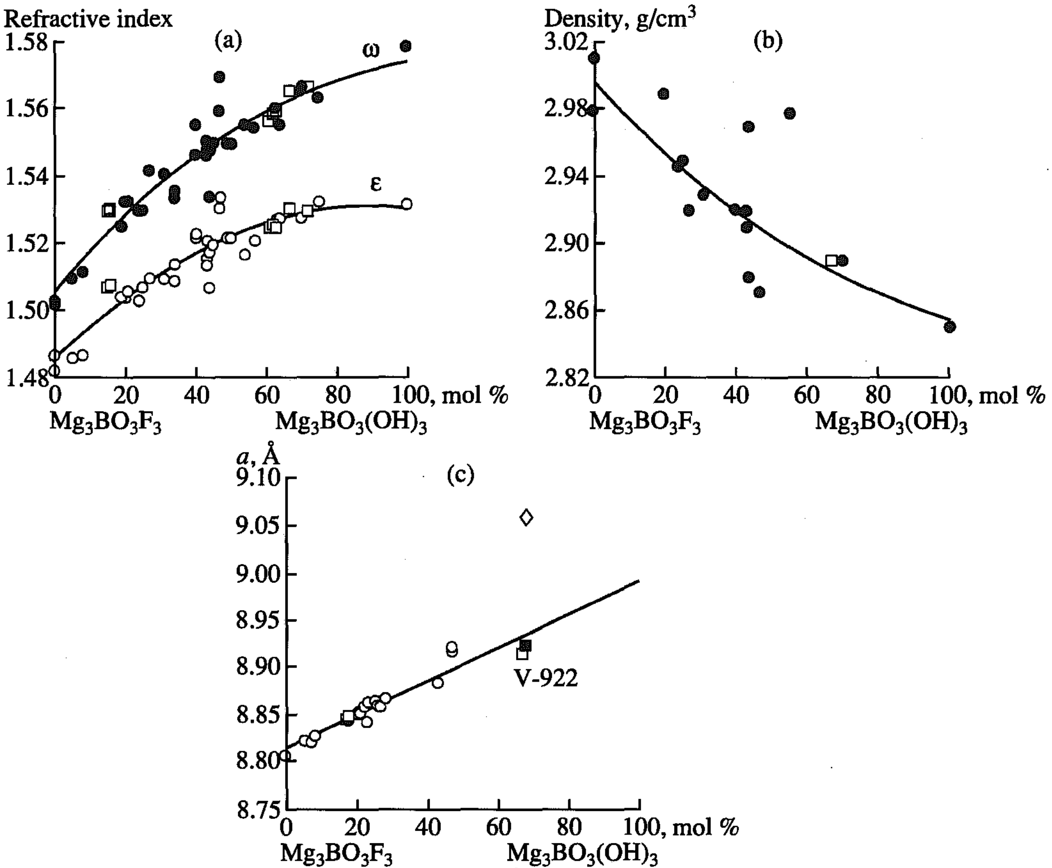
Configuration	Distance	Configuration	Distance
Mg–O(1)* × 2	2.039(2)	B–O(2) × 3	1.389(2)
O(1)**	1.998(3)		
O(2)* × 2	2.117(2)	O(1)–H	0.95(12)
O(2)	2.092(3)	H–H	2.16(12)
	⟨2.067⟩		

Note: * $-x + 1, -y + 1, -z$; ** $-y + 1, x - y, z$.

The columns that run along the c axis of the unit cell and are formed by the edge-shared pairs of Mg-octahedrons combined in a three-dimensional framework with two types of through channels of hexagonal and trigonal cross sections make up the basis of the hydroxylborite structure (Fig. 4) like in other compounds allied to fluoborite. Six hydrogen atoms forming OH-groups and bonded by screw axis 6_3 are located around site (00z) in the broad (empty) channels of the first type, whereas BO$_3$-triangles are located around sites (1/3 2/3 z) and (2/3 1/2 –z) in the narrow channels of the second type. The crystallochemical analysis of orthotriborates, diorthosilicates, and zirconoborates allied to fluoborite revealed their common architectonic basis as an octahedral framework with the formula $[M_9X_{18}]$ (M = Mg^{2+}, Ca^{2+}, Al^{3+}; X = O^{2-}, F$^-$, OH$^-$), where the occupation of narrow channels with isolated B-triangles, Si-pyrogroups, or Zr-trigonal prisms creates a diversity of the structural types among the above groups of compounds (Belov, 1976; Moore and Araki, 1976; Yamnova et al., 1993).

DISCUSSION

An analysis of the available publications and our original data on the chemical composition and properties of the minerals pertaining to the fluoborite–hydroxylborite series allow us to speak about the complete isomorphic miscibility of F for OH and the existence of $Mg_3(BO_3)F_3$ and $Mg_3(BO_3)(OH)_3$ end members. The dependence of the optical parameters and density of the fluoborite-group minerals on the chemical composition once reported by Schaller (1942) was con-



$a = 0.0018h + 8.8142$, $R^2 = 0.9041$

◇ Tallgruvan, Norberg, Sweden (Geijer, 1926; Takeuchi, 1950)

Fig. 5. (a) Refractive indexes, (b) density, and (c) parameter *a* of unit cell versus the chemical composition of the minerals pertaining to the fluoborite–hydroxylborite series. The data taken from the literature are designated by circles: Schaller, 1942 (*h* = 0 and 1, extrapolated values); Brisi and Eitel, 1957 (0 – synthesis, 5 and 8); Brovkin et al., 1967 (0 – synthesis, 15, 20, 21, 31, 43, and 47); Dal Negro and Tadini, 1964 (9); Lisitsyn et al., 1991 (18, 20, 22, 24); Gulyaev, 1971 (19); Pertsev and Nikitina, 1959 (24); Johnston and Tilley, 1940 (25), Pertsev, 1971 (27); Cámara and Ottolini, 2000 (28 and 29); Gramenitsky, 1966 (34, 43, 54, and 75); Eskola and Juurinen, 1952 (34); Bauer and Berman, 1929 (40 and 44); Popov, 1975 (40); Edovin and Utekhin, 1962 (43); Sergeev and Novikova, 1969 (44); Oidun and Kudryavtseva, 1999 (45); Segnit and Loancucki, 1963 (47); Tilley, 1951 (49, 64); Watanabe, 1939 (50); Utekhin. 1960 (67); Gillson and Channon, 1925 (63); Kanishchev, 1966 (70); Geijer, 1926 (70). Original data are designated by squares (15 and 16 – 2 samples, 61, 62, 63, 67, 72); open square (B-922) in panel (c) is the calculation of the X-ray powder pattern and the filled square is the result of the X-ray single-crystal structure study.

firmed on the basis of the presently available analytical data (Figs. 5a and 5b). Fitting the experimental data[3] with the Excel program using a polynomial trend line (reliability of smoothing R^2 is given in parentheses) allowed us to obtain equations for each relationship: (1) for refractive indexes (Fig. 5a) ω: $y = -6 \times 10^{-6}x^2 + 0.0012x + 1.5058$ ($R^2 = 0.9187$) and ε: $y = -6 \times 10^{-6}x^2 + 0.001x + 1.486$ ($R^2 = 0.8885$); (2) for density (Fig. 5b) $y = 9 \times 10^{-6}x^2 + 0.023x + 2.9991$ ($R^2 = 0.7348$).

The repetition period on the *a* axis at an isomorphic substitution varies linearly as was shown by Brovkin et al. (1967); Cámara and Ottolini (2000).

A significant difference was established between the unit-cell dimensions of compositionally similar hydroxyldorates from the Tallgruvan Mine [*a* = 9.06 Å at *h* = 70, mol % (Takeuchi, 1950)] and the Titovsky deposit [*h* = 67 mol %, *a* = 8.912(8) Å (sample B-922, our data)] calculated on the basis of X-ray powder pattern and from the results of X-ray single-crystal study [*a* = 8.924(5) Å]. The close values of parameter *a* estimated with independent methods made it possible to use the data on sample B-922 for fitting and to omit the sample from the Tallgruvan Mine. The repeated investigation of the chemical composition and unit-cell

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[3] The *h* values were calculated on the basis of the original data, largely from the chemical compositions of the minerals. In the absence of chemical data, the *h* value was determined from the diagrams published by Schaller (1942) for all indexes (ω, ε, *D*) and the average values of the established parameters.

dimensions of fluorhydroxylborate from Sweden will probably ascertain a cause for controversy with our data.

Taking into account the aforesaid, the relationship between parameter a and the borate chemistry is expressed by the equation $y = 0.0018x + 8.8142$ ($R^2 = 0.9041$), where $y = a$, Å, and $x = h$, mol % (Fig. 5c).

A comparison of the established trend line with that published by Cámara and Ottoline (2000, Fig. 2a) shows that these lines are crossed at $h \sim 0.14$–0.16 mol % and significantly diverge with an increase in h. The location of the curves is largely controlled by data points characterizing OH-dominant compositions. In addition to the different number of analyses used in the calculation (24 and 9 data points, respectively), the curve divergence results from analytical data for samples from Norberg (Geijer, 1926; Takeuchi, 1950) recorded in the cited article; these data were omitted in our variant.

It should be noted that the major refractive index (ω) of the minerals with an h value higher than 0.30, mol % is always higher than the refractive index of canada balsam (1.536), whereas a minor refractive index (ε) does not exceed the refractive index of canada balsam. This correlation may be used for the express identification of the minerals belonging to the isomorphic series under consideration.

The type material of hydroxylborite is deposited in the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow (inventory number 91968) and the Geological Museum of All-Russia Institute of Mineral Resources, Moscow (inventory number M-1663).

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