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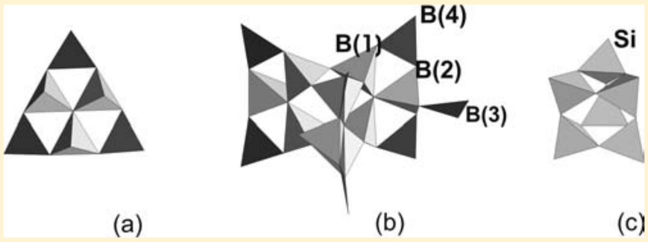
Acentric Polyborate, $Li_3[B_8O_{12}(OH)_3]$, with a New Type of Anionic Layer and Li Atoms in the Cavities

Elena L. Belokoneva* and Olga V. Dimitrova

Department of Crystallography, Geological Faculty, Lomonosov Moscow State University, Leninskije Gory 1, Moscow, 119991 GSP1, Russia

ABSTRACT: Single crystals of $Li_3[B_8O_{12}(OH)_3]$ were synthesized under hydrothermal conditions using a complex initial composition that included SiO_2. The crystal structure is acentric, space group $P\bar{6}2c$, with a = 8.9301(2) Å and c = 15.9962(4) Å, and Z = 4. New double three-membered rings of hexaborate blocks and monoborate triangles are connected into a polyborate anionic layer. Although the new structure is similar to double ring silicate $Na_3Y[Si_6O_{15}]$, detailed comparison of the anionic groups demonstrates principal differences between silicates and borates. Sodium silicate was proposed as an intrinsic fast ion conductor, and for the new borate Li ionic conductivity is very probable, as Li atoms in it are in positions similar to the Na atoms in the silicate.



INTRODUCTION

Compounds containing Li atoms are known as functional materials in electrochemistry (Li batteries). They are also used as components of nonlinear optical devices: among Li-borates LBO-LiB_3O_5 is used in lasers for frequency conversion.[1] There are other polar Li-borates, e.g., $Li_3B_5O_8(OH)_2$ or $Li_2B_4O_7$,[2] that are promising materials for nonlinear optical, acoustic, and thermo luminescence applications.[3] These properties had induced interest in searching for new acentric or polar compounds in borates with Li atoms, which are relatively rare. New borates may be obtained under different reaction conditions: flux or hydrothermal. In the hydrothermal method widely used for borate synthesis initial composition may contain a boron component added with the only lithium-containing component or a complicated multicomponent mixture, which makes such compositions similar to the natural ones.

Within the framework of a systematic search of new promising borates at hydrothermal conditions, here we report the synthesis of a new acentric Li-borate with a unique anionic radical, its crystal structure investigation and crystal chemistry analysis, determination of the position in a system, comparison with Na,Y-silicates, and prediction of possible ion-conducting properties.

EXPERIMENTAL DETAILS

Hydrothermal Synthesis. New borate single crystals were obtained under hydrothermal conditions. As a rule in our synthesis we model processes taking place in the geological environment. It is known that in nature the presence of the SiO_2 component is very common. Therefore, a significant amount of SiO_2 was included in the batch in order to increase the viscosity of the water solution. Thus, the borosilicate system was chosen for synthesis. The initial content was complex because we tried to test the common crystallization of Li-containing components together with the components containing heavy atoms possessing lone pairs such as Pb and Bi. New Li-borate was crystallized at the weight ratio $PbCO_3$:Bi_2O_3:$LiIO_3$:B_2O_3:SiO_2 = 1:1:2:3:1, which corresponds to 0.5 g (~1.9 mmol) of $PbCO_3$, 0.5 g (~1.1 mmol) of Bi_2O_3, 1.0 g (~5.5 mmol) of $LiIO_3$, 1.5 g (~21.6 mmol) of B_2O_3, and 0.5 g (~8.3 mmol) of SiO_2. The ratio of solid and liquid phases was 1:5. The synthesis was performed at 270 °C under a 70 atm pressure. The experiment was carried out in a standard autoclave (volume 5−6 cm^3) lined with Teflon. The temperature was restricted by the kinetics of the hydrothermal reactions and the instrumental capabilities, respectively. The duration of the experiments (18−20 days) corresponded to the completion of the reaction. Final cooling after synthesis to room temperature was done in 24 h. Grown crystals were isolated by filtering the stock solution and washing with hot water. All products of crystallization were colorless. The complexity of the system led to five phases, determined by morphology analysis, X-ray diffraction data on single crystals and powders, composition determination, and nonlinear optical properties measurements. The first three phases contained Bi/I or Pb/I atoms (Leo 1420 VP + INCA350 analytical scanning electronic microscope) and demonstrated different nonlinear optical properties. A recently discovered phase, $BiO(IO_3)$, with a very high optical nonlinearity[4] was repeatedly synthesized in our experiment as a white polycrystalline powder. The identity was confirmed by composition (Bi, I), comparative strong SHG signal, and powder X-ray diffraction data. Crystals of known centrosymmetric iodate $Pb(IO_3)_2$ and its new acentric modification (the results will be presented elsewhere) were identified by composition analysis, unit cell measurements on single crystals, and SHG measurements.

Transparent or semitransparent crystals of the new phase were found among crystallization products as a satellite phase. They were regularly faced by trigonal prisms (110) and pinacoids (001). All small crystals were practically of equal dimensions, with a horizontal edge common for prisms and pinacoids of ~0.18 mm and a prism height of ~0.06 mm. Such an ideal form allowed us to separate the new phase, but the amount of crystals and their dimensions were sufficient neither

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for X-ray powder diffraction nor for measurements of any properties including second-harmonic generation. Colorless massive aggregates found in the products together with the prisms were crystals of sassolite H_3BO_3, identified by unit cell measurements on single crystals. The compositions of trigonal prismatic crystals as well as sassolite blocks were confirmed by EDX carried out on a Jeol JSM-6480LV scanning electronic microscope. The test revealed the presence of any heavy elements, which meant both phases were borates with the only light elements. Thus, in the crystallization products we obtained the borate part without heavy metals (two phases: new borate and sassolite) and a non-borate, namely, an iodate part with lead and bismuth (three phases). The new borate was the object of investigation.

Single-Crystal X-ray Diffraction. A transparent crystal in the form of a regular trigonal prism with an edge size of 0.175 and a height of 0.075 mm was glued on a glass fiber for single-crystal X-ray determination study. The new borate unit cell (Table 1) corresponded to a hexagonal (trigonal) system and had no analogous compounds in the ICSD database. Experimental data were collected at room temperature using an Xcalibur S diffractometer equipped with a CCD area detector using graphite-monochromated Mo Kα radiation. Full spheres of data were collected in omega scan mode for the compound with an exposure time of 1.5 s per frame and with control frame measurements during the process of data collection to check the stability of all measurements. The absorption of the new borate was negligible: μ = 0.198 1/cm (calculated in Table 1). The data were integrated using the CrysAlis program with the intensities corrected for Lorentz and polarization factors. A possible space group suggested by the CrysAlis system was $P6_3mc$: the extinctions of reflections hhl: $l = 2n$ were practically observed, but several 00l reflections did the follow the rule $l = 2n$ and the 6_3-axis. The Patterson function Puvw calculated for the $P3$ space group revealed the horizontal mirror plane m_z, which was also contradictory with the $P6_3mc$ space group. The structure was solved by direct methods using SHELXS-97[5] under the assumption that it is a new modification of sassolite, thus using in the calculations the initial formula H_3BO_3 and the least symmetrical $P3$ space group. The direct method gave a good solution (in contrast to $P6_3mc$) with ~27 O and B atoms, identified by interatomic distances. The list of atoms was added to final 20 O and 12 B atoms in a series of Fourier syntheses.

Table 1. Crystal Data and Structure Refinement for $Li_3B_8O_{12}(OH)_3$

formula	$Li_3B_8O_{12}(OH)_3$.
fw (g/mol)	347.3
T (K)	293
cryst syst	hexagonal
space group	$P\bar{6}2c$
a (Å)	8.9301(2)
b (Å)	8.9301(2)
c (Å)	15.9962(5)
V (Å^3)	1104.73(5)
Z	4
ρ_{calcd} (g/cm ^{3})	2.088
μ (mm^{-1})	0.198
F(000)	676
θ range (deg)	2.63−32.59
reflns collected	22 081
indep reflns	1343
R(int)	0.1094
completeness to θ = 32.59 (%)	97.7
data/restraints/params	1383/0/86
GOF	1.115
R_1, wR_2[a] [$I > 2\sigma(I)$]	0.0515, 0.1070
R_1, wR_2 (all data)[a]	0.0634, 0.1119
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e·Å^{-3})	0.419 and −0.363

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

B atoms had both triangle and tetrahedral coordination. The analysis of the structure drawn in ATOMS[6] revealed a higher symmetry than $P3$: it was the m_z plane, proposed before, the vertical c-glade plane, and the resulting 2-fold axis on coordinate positions with the final group $P\bar{6}2c$. The origin on the space group was shifted from the first to the final models to satisfy the correct setting of the space group with fewer independent atoms than before. The residual electron density showed two additional electron density peaks coordinated by O atoms with the distances corresponding to Li−O. Initial components in our experiment, composition of crystals, and height of the peaks allowed us to introduce Li atoms into the model in special positions. Taking into account the multiplicity of the common and special positions in the space group $P\bar{6}2c$ occupied by basal O, B, and Li atoms, the charges in the resulting chemical formula were balanced by introduction of one O6 atom to the (OH) group: $Li_{12}B_{32}O_{48}(OH)_{12}$ or $Li_3B_8O_{12}(OH)_3$ with Z = 4. The analysis of polyhedral connections and the Pauling valence sum on oxygens in the structure confirmed this assumption. The final structural model, corresponding to the given formula, was refined using the least-squares procedure in the anisotropic approximation of thermal displacement for all atoms and by refinement of the weighting scheme (SHELXL-97).[7] It was found (Flack test) that the crystal is a racemic twin (−1 0 0/0 −1 0/0 0 −1/), which was introduced into the refinement. Crystallographic data, atomic coordinates, and selected bonds are presented in Tables 1, 2, and 3.

Table 2. Atomic Coordinates (×10 ^{4}) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $Li_3B_8O_{12}(OH)_3$[a]

atom	Wyckoff position and point symmetry	x	y	z	U_{eq}
O(1)	6h, m	0553(2)	6144(3)	1/4	7.7(4)
O(2)	12i, 1	03200(19)	60817(18)	40329(8)	11.1(3)
O(3)	12i, 1	82668(18)	6388(2)	17839(8)	12.6(3)
O(4)	6h, m	0562(3)	8827(3)	1/4	13.1(4)
O(5)	12i, 1	19385(17)	49711(17)	33888(8)	8.5(3)
O(6)−OH	12i, 1	7808(2)	5873(2)	46509(9)	24.3(4)
B(1)	12i, 1	1564(3)	6349(3)	33422(13)	8.1(4)
B(2)	2b, −6	0	0	1/4	9.9(9)
B(3)	6h, m	9415 (4)	6946(4)	1/4	9.1(5)
B(4)	12i, 1	8809(3)	6118(3)	39562(14)	11.4(4)
Li(1)	6h, m	3081(7)	9686(7)	1/4	17.3(11)
Li(2)	6g, 2	5704(11)	5704(11)	1/2	67(3)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Interatomic Distances for $Li_3B_8O_{12}(OH)_3$

atoms	bonds (Å)	atoms	bonds (Å)	atoms	bonds (Å)
B(1) tetrahedron		B(3) tetrahedron		Li(1) tetrahedron	
B(1)–O(5)	1.429(3)	B(3)–O(3)×2	1.449(2)	Li(1)–O(4)	1.981(6)
B(1)–O(5′)	1.435(2)	B(3)–O(4)	1.466(4)	Li(1)–O(5)×2	2.016(4)
B(1)–O(2)	1.499(2)	B(3)–O(1)	1.508(4)	Li(1)–O(3)×2	2.108(5)
B(1)–O(1)	1.580(2)	B(4) triangle		Li(1)–O(1)	2.355(6)
		B(4)–O(3)	1.346(3)	Li(2) tetrahedron	
B(2) triangle		B(4)–O(2)	1.371(3)	Li(2)–O(6)×2	1.892(6)
B(2)–O(4)×3	1.369(2)	B(4)–O(6)	1.373(2)	Li(2)–O(2)×2	2.136(8)

■ RESULTS AND DISCUSSION

Structure. There are four symmetrically independent B atoms in the structure (space group $P\bar{6}2c$); two of them are in triangle coordination and other two are tetrahedral with typical bond lengths. Boron polyhedra are condensed into a polyborate anionic radical, composed of a new hexaborate block complex unit, joined into a new type of layer by additional B-triangles. The term "hexaborate" was introduced by Christ and Clark,[8] as well as other terms: "penta"-, "tetra"-, "tri"-, "di"-, "mono"-borates depending of the type of fundamental building blocks formed by B-polyhedra. A hexaborate block contains six boron polyhedra and is built of three BO_4 tetrahedra (T) connected through one central oxygen atom and three BO_3 triangles (Δ) attached to three terminal O atoms, with a notation after Christ and Clark of 6:[3Δ+3T]. The bridge atoms are O^{2-} and the apical groups are $(OH)^-$. The hexaborate block $[B_6O_7(OH)_6]^{4+}$ with the symmetry $3m$ (Figure 1a) is present in the mineral macallisterite, $Mg_2[B_6O_7(OH)_6]\cdot 9H_2O$, and its varieties are condensed into a ribbon in the mineral aristarainite and into layers in many natural and synthetic compounds.[9] Another type of strongly corrugated hexaborate layer in $Lu(BO_2)_3$ has been obtained at high pressure and high temperature.[10] This layer is built of hexaborate blocks that contain only tetrahedrally coordinated boron atoms (which is typical at high pressure; see publications of Huppertz's group) with the same topology as that for six polyhedra. Framework structures for hexaborates may be considered as well. They are built of typical layers via their condensation with the known or predicted varieties; they are built of blocks condensed directly by an R-lattice via vertices.[11] In the new Li-borate structure three hexaborate blocks in a vertical orientation are linked by a 3-fold axis into double three-membered rings via three pairs of tetrahedral apexes due to loss of one triangle in every hexaborate block (Figure 1b). This complex ring was never found in borates before. It is described as 3×{6:[3T+3Δ]−1Δ} = 15:[9T+6Δ] for a new nonperiodical unit: ring $[B_{15}O_{24}(OH)_6]^{9-}$ (triangle apexes in a new hexaborate block combination are presented by OH groups). An additional independent B-triangle (monoborate unit) connects the complex hexaborate rings into a layer with a new configuration, and the borate is classified as a polyborate, because two different types of initial blocks are presented here: hexaborate and monoborate (Figures 1b, 2a). The B atom in the monoborate triangle unit is coordinated by apical oxygens of new hexaborate rings on special position 2b, 0 0 1/4 with the symmetry -6, and it is simply added to the radical. The crystal chemical formula of the new layer is $[B_{16}O_{24}(OH)_6]^{6-}{}_{\infty\infty}$ with the notation $\{3\times\{6:[3T+3\Delta]-1\Delta\}+1\Delta\}_{\infty\infty}$.

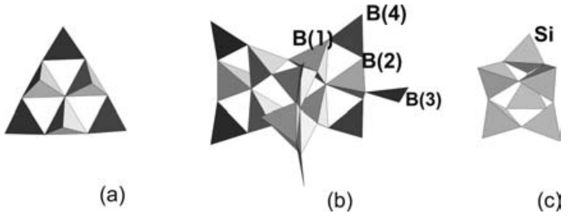

Figure 1. Structural blocks: isolated hexaborate block 6:[3T+3Δ] = $[B_6O_7(OH)_6]^{2-}$ (a); complex double hexaborate ring 3×{6[3T+3Δ]−1Δ} = $[B_{15}O_{24}(OH)_6]^{9-}$ of B(1), B(2), and B(4) polyhedra with additional B(3) triangle for condensation into the layer (b); double "dreier" ring 6:[6T] = $[Si_6O_{15}]^{6-}$ in Na,Y-silicate (c).

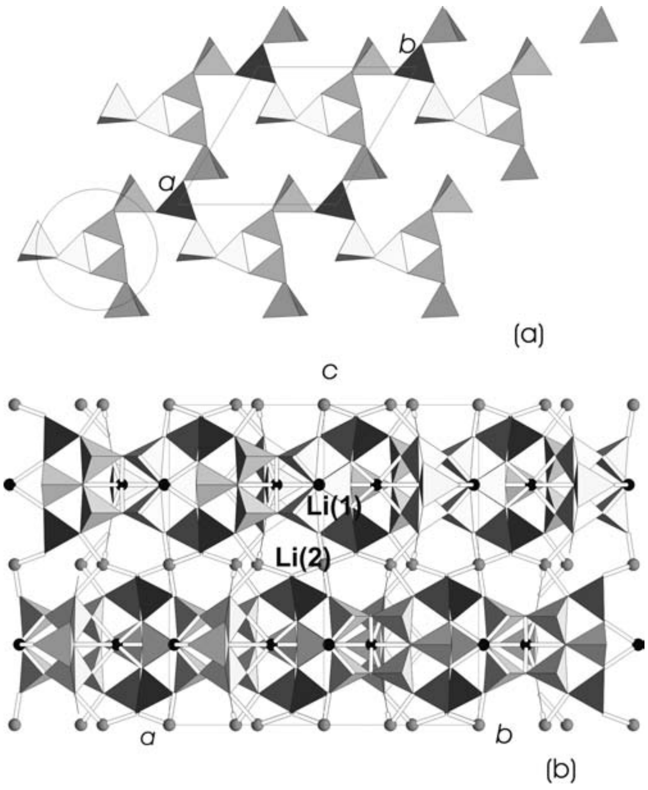

Figure 2. Crystal structure of $Li_3B_8O_{12}(OH)_3$ in two projections: (a) *ab*-projection with one layer (complex hexaborate ring is shown by the circle); (b) side projection with two layers (Li atoms and Li–O bonds are given in ball-and-stick presentation).

The borate structure $Li_3B_8O_{12}(OH)_3$ has a remarkable similarity to the silicate $Na_3YSi_6O_{15}$ despite the difference in the chemical formula.[12] Both compounds share many structural features. The silicate structure is orthorhombic, but is close to pseudohexagonal. A unique double "dreier" ring $[Si_6O_{15}]^{6-}$ built only of tetrahedra is discovered in the silicate (Figure 1c). The new hexaborate ring is an "extension" of the silicate ring because it contains as a core the double "dreier" ring, topologically equal to that the silicate. Every vertical pair of tetrahedra in the borate ring adds a third tetrahedron (to the central bridge oxygen) and two triangles (to the apexes) (Figure 1b). The new, enlarged ring with the symmetry point group 3 has the formula $[B_{15}O_{24}(OH)_6]^{9-}$, in contrast to

$[Si_6O_{15}]^{6-}$. The topology of the new borate ring is not possible in the silicate because the charge of the central atom Si^{4+} in the tetrahedra is too high, and only two tetrahedra may condense on one bridge oxygen. In contrast to that up to four tetrahedra with B^{3+} in the center may condense on one bridge oxygen in borates (cubic boracite's structure).[11] In the silicate, the rings are on two levels in the unit cell along the axis $b = 15.25$ Å, and in the new borate the layers with the rings are also on two levels along axis $c = 15.99$ Å (Figure 2b).

Lithium Coordination and Possible Ionic Conductivity. Li atoms compensate the effective charge of the borate anionic layer in $Li_3B_8O_{12}(OH)_3$ and occupy large cavities: cages inside the layer (Li(1) special position on mirror plane *m*) and interlayer space with only Li atoms (Li(2) special position on the 2-fold axis) (Figure 2b). Li atoms in the first positions have distorted octahedral coordination with one longer distance (half-octahedra); the second position has regular tetrahedral coordination. Li−O distances correspond to the typical ones (Table 3) found recently in other compounds for four-, five-, and six-coordinate environments. Thermal vibration parameters for Li atoms are significantly enlarged especially for Li(2) (Table 2) and mostly along the *c*-axis. Nevertheless the positions are not split. The significant amount of Li atoms in the structure and their positions in the cavities allow the proposal that new crystals may possess ionic conductivity, observed in a number of alkali silicates and phosphates. This assumption found confirmation by structural comparison because for silicate $Na_3YSi_6O_{15}$ possible conductivity was discussed and its pathway was predicted. In the silicate, Na atoms occupy positions between levels with the rings together with Y-octahedra, and in cages inside levels with rings, exactly like Li atoms in the new borate. No splitting of Li(1) positions is found in the borate, in contrast to an equal Na(2) position in the silicate, but this does not exclude possible Li-ion transportation, despite that the interlayer space in the borate contains only Li atoms. As for Na atoms in the silicate, thermal vibration parameters for both Li atoms are enlarged mainly in the *c*-axis direction especially for Li(2) in the interlayer space (Table 2). A possible pathway could be along the channel in the *c*-axis direction, as in silicate, with the greatest contribution from Li(2) atoms.

CONCLUSION

Single crystals of the new borate $Li_3B_8O_{12}(OH)_3$ were synthesized in a complex borosilicate system. A layered anionic radical of new type is characterized as a polyborate. It is built from a new complex hexaborate ring with the notation $3\times\{6[3T+3\Delta]-1\Delta\}$ added to a monoborate unit, a boron triangle that is constructed from the apical oxygens of the hexaborate rings. The notation for the layer with the crystal chemical formula $[B_{16}O_{24}(OH)_6]^{6-}{}_{\infty\infty}$ is $\{(3\times\{6[3T+3\Delta]-1\Delta)+1\Delta\}_{\infty\infty}$. The new structure is related to the double ring silicate $Na_3YSi_6O_{15}$; however comparison of the anionic groups demonstrates a principal difference between the silicates and borates depending on the charge of the atoms in the center of the tetrahedra. Sodium silicate was proposed as an intrinsic fast ion conductor, and the borate crystals should also possess ionic conductivity because Li atoms occupy similar positions in the borate structure to Na atoms in the silicate. This may be tested on larger crystals obtained by hydrothermal synthesis without heavy metal components under similar conditions of pressure and temperature. It is worthwhile to say that the silicate crystals were also grown by the hydrothermal method because of its effectiveness in inducing crystallization in glass-forming systems, and that led to a double "dreier" ring, found only in this silicate. We suppose that for synthesis of a new borate relative to a silicate with the unique ring, it is important to introduce the silicon component and to increase the viscosity of the water solution.

Crystallographic data for the structure reported in this paper have been deposited with the Karlsruhe Inorganic Crystallographic Structural Data Centre as supplementary publication CSD number 425207 for $Li_3B_8O_{12}(OH)_3$. Copies of the data can be obtained free of charge on application to ICSD FIZ Karlsruhe−Leibnitz Institut fuer Informationsinfrastructur, Termann-von-Helmholtz Platz 1, 76344 Eggenstein, Leopoldshafen, CrysDATA@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de.

AUTHOR INFORMATION

Corresponding Author

*E-mail: elbel@geol.msu.ru. Tel: +7(495) 9394926.

Notes

The authors declare no competing financial interest.

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