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Reinvestigation of the $Pb_2[B_5O_9]Br$ structure based on single-crystal data

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(O–B) = 0.019 Å
R factor = 0.034
wR factor = 0.080
Data-to-parameter ratio = 29.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title pentaborate, $[Pb_2(B_5O_9)Br]$ (dilead pentaborate bromide), known from powder data, has been refined based on single-crystal data (R = 0.034) and is discussed in terms of intercrossing anionic and cationic frameworks.

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Comment

The mineral family of hilgardite includes three polymorphs with the common formula $Ca_2[B_5O_9]Cl\cdot H_2O$ (triclinic phases hilgardite-1A and parahilgardite, and monoclinic hilgardite-4M), tyretskite $Ca_2[B_5O_9]OH\cdot H_2O$ (Strunz & Nickel, 2001), that seems to be isotypic with hilgardite-1A (Ghose, 1985), and kurgantaite $CaSr[B_5O_9]Cl\cdot H_2O$ (Pekov *et al.*, 2001). Sr occupies one of two independent Ca positions of hilgardite-1A in the crystal structure of kurgantaite (Ferro, Pushcharovskii *et al.*, 2000). Several synthetic compounds of composition $M_2^{2+}[B_5O_9]X$ (M = Ca, Sr, Ba, Eu, Pb and X = Cl, Br) have been obtained during attempts to prepare boracite-type structures (Fouassier *et al.*, 1971; Peters & Baglio, 1970). The crystal structure investigation of the calcium ($Ca_2[B_5O_9]Br$; Lloyd *et al.*, 1973) and europium ($Eu_2[B_5O_9]Cl$; Machida *et al.*, 1981) members of this group revealed their orthorhombic symmetry (space group $Pnn2$) and a close relationship to the hilgardite structure type. Zeolite-like construction and piezoelectric properties have been noted earlier for hilgardites (Ghose & Wan, 1979; Ghose, 1982; Wan & Ghose, 1983). According to Ghose & Wan (1979), hilgardite was successfully tested for second harmonic generation and gives piezoelectric signals comparable to quartz. Blue emission at about 430 and 435 nm was established for $Eu_2[B_5O_9]Br$ and $Eu_2[B_5O_9]Cl$ (Machida *et al.*, 1981), noting that their Eu^{2+} activated alkaline earth analogues are efficient phosphors.

The crystal structure of an orthorhombic synthetic Ba variety in the hilgardite structure group, $Ba_2[B_5O_9]Cl\cdot 0.5H_2O$, was reported by Ferro, Merlino *et al.* (2000) and two more Pb-

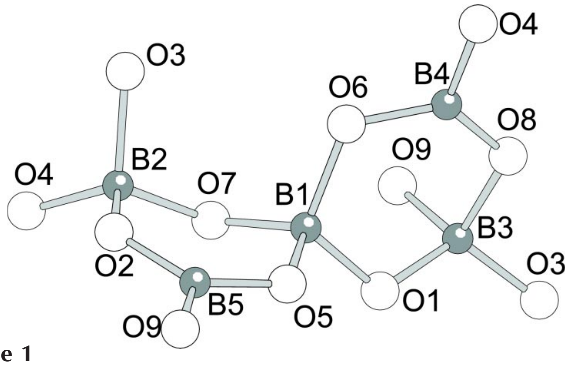

Figure 1
The basic $[B_5O_{12}]$ fragment of the anionic framework.

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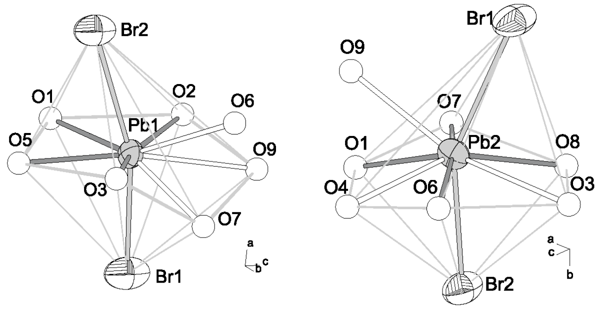

Figure 2
Coordination around Pb1 (*a*) and Pb2 (*b*). Short bonds are dark. Displacement ellipsoids are drawn at the 90% probability level.

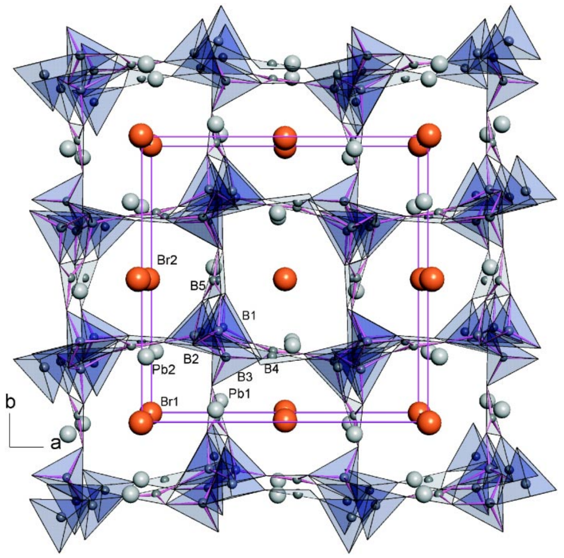

Figure 3
The anionic framework $[B_5O_9]^{3-}$.

containing phases in the hilgardite family, $Pb_2[B_5O_9]OH{\cdot}H_2O$ (monoclinic, $P2_1/n$) (Belokoneva *et al.*, 1998), *viz*. the lead formula analogue of tyretskite and $Na_{0.5}Pb_2[B_5O_9]Cl{\cdot}(OH)_{0.5}$ (orthorhombic, *Pnn*2; Belokoneva *et al.*, 2000), have been synthesized and studied in recent years. The crystal structure of an orthorhombic compound $Pb_2[B_5O_9]Br$ (Fouassier *et al.*, 1971) was solved by Belokoneva *et al.* (2003) based on powder data. The present paper reports the results of an improved refinement of this structure based on single-crystal diffraction data and a discussion of the structure in terms of intercrossing frameworks.

The cell parameters determined from 4734 single-crystal reflections deviate significantly from the reported powder data, the *a* parameter being 0.03 Å smaller and *b* 0.04 Å larger. This is surely due to the pseudotetragonal metrics. In the single-crystal data, errors are induced by the observed twinning. As the first domain dominates by 70%, the resulting lattice constants *a* and *b* will approach the correct values but become too nearly equal. In Rietveld refinements, the pseudotetragonal metrics (overlap of *hkl* and *khl* reflections) will lead to correlations with the profile function that may also influence the *a*–*b* difference. As the *c* axis differs also by 0.01 Å (10σ) between single-crystal and powder work, we decided to use the single-crystal cell constants for the refinement. The difference in bond lengths calculated with both cells has been proved to be less than 0.01 Å.

The precision of bond lengths and angles derived from the single-crystal data is remarkably improved with respect to the powder work. The s.u. values of the Pb—O bonds, for instance, ranging in the latter between 0.03 and 0.08 Å, are between 0.009 and 0.013 Å in the present work. The absolute differences in bond lengths obtained by the different methods are up to 0.08 Å in the Pb—O bonds and 0.10 Å in the B—O bonds. In all cases of large differences, the new values appear more sensible. The discussion of correlations of non-linear optical properties and the coordination geometry of Pb can, therefore, refer to a more reliable basis.

As shown in Fig. 1, three $[BO_4]$ tetrahedra and two $[BO_3]$ triangular groups form a basic fragment $[B_5O_{12}]$ of the anionic framework. This fragment can be interpreted as a combination of two three-membered boron-oxygen rings as found in the structures of the dimorphic minerals inderite and kurnakovite $Mg[B_3O_3(OH)_5]{\cdot}5H_2O$ (Rumanova, 1971). These rings are formed by two $[BO_4]$ tetrahedra and one $[BO_3]$ triangle sharing oxygen vertices. The vertices of the tetrahedra are directed to one side from the plane of the 'inderite' ring (B1/B2/B5) and to different sides from the plane of the 'kurnakovite' ring (B1/B3/B4). The B—O distances in the triangular configuration range from 1.34 (2) to 1.38 (2) Å. The B—O distances in the tetrahedra are, as usual, larger and lie in the range 1.42 (2)–1.52 (2) Å, with the same average value of 1.48 Å for all three independent tetrahedra.

The O^{2-} and Br^- anions form large nine-vertex polyhedra around two independent Pb^{2+} cations, with Pb1—O distances between 2.497 (13) and 3.076 (11) Å, and Pb2—O distances between 2.475 (9) and 3.010 (10) Å. The Pb—Br distances vary between 2.998 (2) and 3.055 (1) Å in the Pb1 polyhedron, and the Pb2—Br bond lengths between 3.056 (1) and 3.153 (2) Å. The average Pb—O(Br) distances coincide for both polyhedra and are 2.81 Å. These polyhedra can be described as distorted bipyramids with a hexagonal basis formed by O atoms and two apical vertices occupied by Br, similar to the Ca environment in $Ca_2[B_5O_9]Br$ (Lloyd *et al.*, 1973). The ninth ligands (O6 at Pb1 and O9 at Pb2) complicate the Pb bipyramids by capping a side plane (Fig. 2). Their Pb—O distances are in the range of Pb—Br bond lengths.

The Pb—O distances in each polyhedron divide into two groups. Rather strong Pb–O bonds, corresponding to the criterion of the sum of ionic radii, lie between 2.497 (13) and 2.686 (9) Å at Pb1, and between 2.475 (10) and 2.695 (11) Å at Pb2 (dark in Fig. 2). O atoms forming these bonds are placed preferentially on one side of the Pb^{2+} cations. For Pb1, the orientation of the short bonds is concentrated on the left side in Fig. 2*a*. For Pb2, an umbrella-like coordination is observed with the short Pb2—Br2 bond as handle (Fig. 2*b*). The oxygen ligands at longer distances [2.798 (10)–3.076 (11) Å from Pb1 and 2.838 (13)–3.010 (10) Å from Pb2] are mainly on the opposite side. Thus, the active lone pairs of the Pb^{2+} ions might be directed towards this side, *i.e.* approximately in the [011]

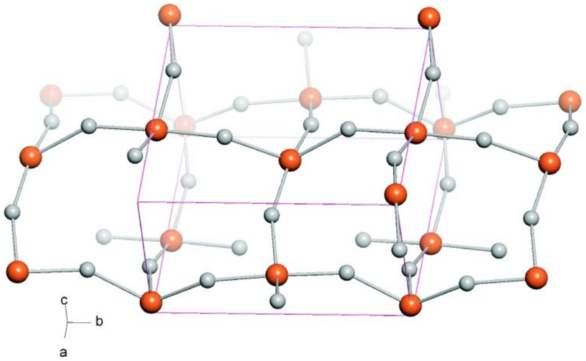

Figure 4
The cationic framework $[Pb_2Br]^{3+}$.

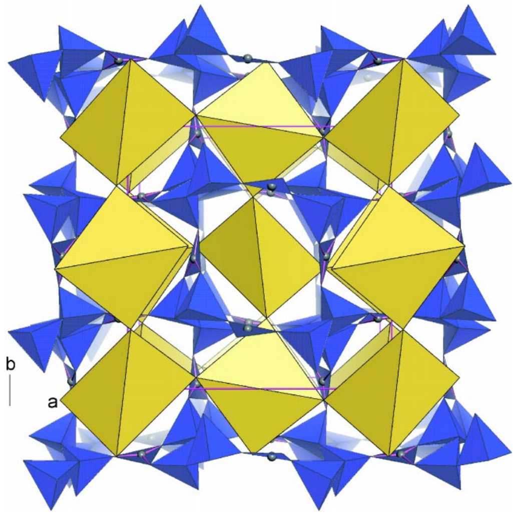

Figure 5
Polyhedral drawing of intercrossing anionic and cationic frameworks.

direction for the Pb1 and the $[0\bar{1}0]$ direction for the Pb2 polyhedron, respectively. The high non-linearity of the compound mentioned by Belokoneva *et al.* (1998) can be related to this asymmetric distribution of the electron density around the Pb atoms.

The crystal structure of $Pb_2[B_5O_9]Br$ can be considered as a combination of two different frameworks: the tetrahedral $[BO_4]$ and trigonal $[BO_3]$ units form a zeolite-like anionic framework of composition $[B_5O_9]^{3-}$ by sharing common vertices, as discussed before. This framework can also be interpreted as formed by polar chains of $[BO_4]$ tetrahedra along the *c* axis that are joined together by $[BO_3]$ triangles along the *a* and *b* axes (Fig. 3). Regarding the Pb—Br substructure only, a second anticristobalite-like cationic $[BrPb_2]^{3+}$ framework can be identified, built from strongly flattened $[BrPb_4]$ tetrahedra sharing vertices (Fig. 4). This is inserted into the large pores of the anionic borate framework (Fig. 5).

Experimental

Transparent colourless very small (maximum 0.1 mm long) crystals of prismatic shape were grown by soft hydrothermal synthesis in the system $PbO—B_2O_3—KBr—H_2O$ [T = 553 K, P = 70 bar (1 bar = 10^5 Pa), t = 20 d, $PbO—B_2O_3—KBr$ ratio = 1:1:1] in 7 ml Cu tubes in a steel autoclave. The presence of Pb and Br in the samples was confirmed by qualitative X-ray spectral analysis (CamScan 4DV + EDA Link AN 1000).

Crystal data

$[Pb_2(B_5O_9)Br]$
M_r = 692.34
Orthorhombic, $Pnn2$
a = 11.4935 (19) Å
b = 11.4717 (19) Å
c = 6.5297 (11) Å
V = 860.9 (2) Å^3
Z = 4
D_x = 5.341 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4734 reflections
θ = 3.5–36.0°
μ = 43.73 mm^{-1}
T = 293 (2) K
Column, colourless
0.13 × 0.03 × 0.02 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: numerical (*XPREP* in *SHELXTL*; Sheldrick, 1996).
$T_{\rm min}$ = 0.093, $T_{\rm max}$ = 0.387
7497 measured reflections

2544 independent reflections
2429 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.068
$\theta_{\rm max}$ = 31.0°
$h = -12 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.080$
S = 1.06
2544 reflections
87 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 13.5461P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 1.96 e Å^{-3}
$\Delta\rho_{\rm min}$ = −2.13 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00036 (10)
Absolute structure: Flack (1983), 1059 Friedel pairs
Flack parameter = −0.03 (2)

Table 1
Selected geometric parameters (Å, °).

Pb1—O5$^{\rm i}$	2.497 (13)	B1—O1	1.470 (18)
Pb1—O2$^{\rm i}$	2.534 (12)	B1—O5	1.48 (2)
Pb1—O3	2.659 (11)	B1—O6	1.485 (18)
Pb1—O1$^{\rm i}$	2.686 (9)	B1—O7	1.473 (18)
Pb1—O7$^{\rm ii}$	2.798 (10)	B2—O2	1.468 (19)
Pb1—O9$^{\rm ii}$	2.975 (11)	B2—O3	1.504 (19)
Pb1—Br2$^{\rm i}$	2.9977 (16)	B2—O4	1.450 (19)
Pb1—Br1$^{\rm ii}$	3.0554 (10)	B2—O7$^{\rm ii}$	1.50 (2)
Pb1—O6$^{\rm ii}$	3.076 (11)	B3—O1	1.453 (19)
Pb2—O7	2.475 (10)	B3—O3	1.417 (19)
Pb2—O8$^{\rm iii}$	2.571 (11)	B3—O8	1.516 (19)
Pb2—O1	2.647 (9)	B3—O9	1.52 (2)
Pb2—O6$^{\rm iv}$	2.695 (11)	B4—O4$^{\rm v}$	1.358 (19)
Pb2—O4	2.838 (13)	B4—O6	1.34 (2)
Pb2—O9	2.864 (11)	B4—O8	1.35 (2)
Pb2—O3$^{\rm iii}$	3.010 (10)	B5—O2	1.38 (2)
Pb2—Br2	3.0559 (8)	B5—O5$^{\rm ii}$	1.36 (2)
Pb2—Br1	3.153 (2)	B5—O9$^{\rm vi}$	1.358 (19)
O1—B1—O7	109.5 (11)	O3—B3—O1	115.8 (13)
O1—B1—O5	104.2 (12)	O3—B3—O8	105.0 (12)
O7—B1—O5	110.3 (12)	O1—B3—O8	110.3 (12)
O1—B1—O6	111.4 (12)	O3—B3—O9	114.8 (13)
O7—B1—O6	109.6 (12)	O1—B3—O9	103.7 (11)
O5—B1—O6	111.7 (11)	O8—B3—O9	107.0 (11)
O4—B2—O2	109.9 (13)	O6—B4—O8	121.9 (13)
O4—B2—O7$^{\rm ii}$	110.4 (12)	O6—B4—O4$^{\rm v}$	114.5 (17)
O2—B2—O7$^{\rm ii}$	110.4 (14)	O8—B4—O4$^{\rm v}$	123.4 (16)
O4—B2—O3	108.8 (13)	O5$^{\rm ii}$—B5—O9$^{\rm vi}$	121.1 (15)
O2—B2—O3	110.5 (12)	O5$^{\rm ii}$—B5—O2	120.3 (14)
O7$^{\rm ii}$—B2—O3	106.7 (12)	O9$^{\rm vi}$—B5—O2	118.7 (15)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (ii) $x, y, 1+z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$.

The structure was refined as a pseudomerohedral (110) twin [twin ratio 0.688 (2):0.312 (2)] to residuals wR_2 = 0.0803 (for all 2544 reflections) and R = 0.0344 [for 2429 reflections $>2\sigma(I)$] with anisotropic displacement parameters for Pb and Br atoms. The strong tetragonal pseudosymmetry of the structure and pseudomerohedral twinning of the studied crystal did not allow for refinement of anisotropic displacement parameters for the O and B atoms, in view of the very high scattering power of Pb and Br. A Flack (1983) parameter of $x = -0.03$ (2) confirms the correct choice of the absolute polarity of this crystal. The maximum residual electron density is located 1.70 Å from Pb1 and the minimum 0.64 Å from Pb1. The same atomic labelling scheme has been used as in the powder work of Belokoneva *et al.* (2003), with z parameters inverted. For better comparison, negative z values were retained.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 2000); software used to prepare material for publication: *SHELXL*97.

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