Lead zinc borate, PbZn₂(BO₃)₂

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PbZn₂(BO₃)₂ crystallizes in the space group $Pccn$, with the Pb cation at a site with imposed twofold symmetry. The compound represents a new structure type in which ZnBO₃ layers are bridged by Pb²⁺ cations, giving rise to a three-dimensional framework. Channels parallel to the [010] direction accommodate the stereochemically active lone pairs of the Pb²⁺ cations.

Comment

Borates have attracted much attention because they have important practical applications in second harmonic generation (SHG). For example, β-BaB₂O₄, LiB₃O₅ and YCa₄(BO₃)₃O are all well known non-linear optical (NLO) crystals (Becker, 1998). So far, many investigations have been carried out on the alkali and alkali-earth metal borates, while borates incorporating other main group elements together with transition metal elements are relatively less explored. The title compound, PbZn₂(BO₃)₂, was previously reported by Petzold (1966), who presented its powder X-ray diffraction pattern. However, its crystal structure remains as yet undetermined. In the course of our investigation of novel borate NLO materials, we have unexpectedly obtained single crystals of PbZn₂(BO₃)₂. Our X-ray structural analysis has established that PbZn₂(BO₃)₂ crystallizes in a new unique structure type (Pearson symbol $oP44$), not observed for any of the known borates. We report here its crystal structure.

PbZn₂(BO₃)₂ is characterized by a complex three-dimensional network consisting of Pb²⁺ cations, tetrahedral Zn²⁺ centers and BO₃³⁻ anions. We have chosen a description emphasizing the substructures to help visualize the crystal structure. In this sense, the structure can be considered as being built upon two-dimensional sheets in the following way (Fig. 1). Within the (100) plane, the fundamental building units of BO₃ triangles and ZnO₄ tetrahedra are linked together by sharing common vertices to generate a two-dimensional ZnBO₃ layer. Applying the c-glide symmetry operation to this layer produces the neighboring equivalent layers along the [100] direction. These layers are further bridged by the Pb²⁺ ions, resulting in the formation of the final three-dimensional

framework. This framework contains V-shaped open channels running parallel to the [010] direction that are filled by the Pb²⁺ $6s^2$ lone pairs.

All atoms occupy general positions, except Pb, which lies on a twofold axis, giving two sets of short bond lengths [Pb—O2 = 2.273 (5) Å and Pb—O1 = 2.515 (5) Å; Table 1]. The Pb atom is also weakly bonded to four more O atoms at distances of 3.301 (6)–3.652 (8) Å. Bond-valence-sum (BVS) calculations (Brown & Altermatt, 1985) produced a value of 1.97 for the four shorter Pb—O bonds, which indicates that the longer distances need not be included in the coordination environment of Pb. All the short Pb—O distances fall within the same hemisphere around the Pb atom, leaving room for the $6s^2$ lone pair of Pb²⁺ in the opposite direction (Fig. 2). A similar highly distorted Pb²⁺ coordination geometry has also been observed in Pb₆B₁₀O₂₁, with four short Pb—O distances of 2.30 (2)–2.48 (2) Å (Krogh-Moe & Wold-Hansen, 1973). In contrast, the ZnO₄ and BO₃ groups in the title compound are only slightly distorted. The B—O distances lie within a narrow range of 1.371 (9)–1.384 (10) Å, with an average of 1.376 Å, which is consistent with the value reported in Li₃In(BO₃)₂ [1.371 (1) Å; Penin et al., 2001]. The Zn—O distances of
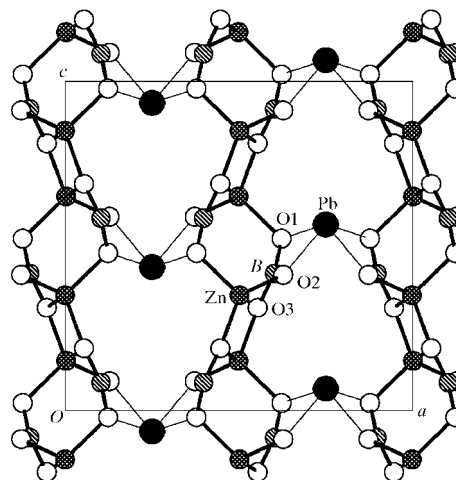

Figure 1
The crystal structure of PbZn₂(BO₃)₂ projected along the [010] direction, where black circles, doubly shaded circles, singly shaded circles and open circles represent Pb, Zn, B and O atoms, respectively. The Pb—O contacts [2.273 (5) and 2.515 (5) Å] are drawn with thin solid lines.
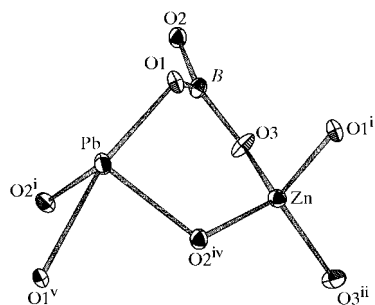

Figure 2
The local coordination geometries of Pb, Zn and B in PbZn₂(BO₃)₂, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, z$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x, y + 1, z$; (v) $-x + \frac{3}{2}, -y + \frac{3}{2}, z$.]

1.941 (5)–1.958 (5) Å (average 1.950 Å) are also very reasonable when compared with the range 1.926 (6)–1.977 (6) Å [average 1.95 (2) Å] in $BaZn_2(BO_3)_2$ and 1.95 (3)–2.03 (4) Å [average 1.98 (3) Å] in $Ba_2Zn(BO_3)_2$, all featuring tetrahedrally coordinated Zn^{2+} (Smith & Keszler, 1992; Smith & Koliha, 1994). Bond valence analysis gave values of 2.06 for Zn and 2.96 for B, in good agreement with their expected formal valences.

Both $Zn_3(BO_3)_2$ (Chen et al., 2005) and $BaZn_2(BO_3)_2$ (Smith & Keszler, 1992) are closely related to $PbZn_2(BO_3)_2$ in stoichiometry but differ in structure. In $Zn_3(BO_3)_2$, the BO_3 triangles share common vertices with irregular ZnO_4 tetrahedra to form a three-dimensional framework. The framework contains small unoccupied six-edge and four-edge channels running along the b axis. The structure of $BaZn_2(BO_3)_2$ also consists of a three-dimensional framework of corner-sharing ZnO_4 tetrahedra and BO_3 triangles. However, the channels within this framework host seven-coordinate Ba^{2+} cations. It is the variation in the coordination environments around the metal cations that is mainly responsible for the structural differences between $Zn_3(BO_3)_2$, $BaZn_2(BO_3)_2$ and $PbZn_2(BO_3)_2$.

It is clear from Fig. 1 that two rows of Pb^{2+} cations have their stereochemically active non-bonded electron pairs pointing in the opposite direction, which yields a structure without polarity. To confirm this, SHG measurements were performed on crushed crystals of $PbZn_2(BO_3)_2$ using a modified Kurtz NLO system with a 1064 nm light source (Kurtz & Perry, 1968). No second-harmonic signal at 532 nm was observed, which further supports the description of this new structure type in the centrosymmetric Pccn space group.

Experimental

A powder mixture of PbO (4.520 g, 20.250 mmol), ZnO (1.099 g, 13.500 mmol), Bi_2O_3 (3.146 g, 6.751 mmol) and H_3BO_3 (2.504 g, 40.500 mmol) was transferred to a Pt crucible. The sample was melted at 1023 K for one day, cooled to 823 K at a rate of 2 K h^{-1}, and then cooled to room temperature at a rate of 20 K h^{-1}. Colourless plate-shaped crystals of $PbZn_2(BO_3)_2$ with dimensions of up to 0.6 × 0.6 × 1.0 mm were recovered. They were isolated mechanically from the reaction product for further characterization by single-crystal X-ray diffraction. The X-ray powder diffraction pattern of the ground crystals is in good agreement with that calculated from the single-crystal data. The IR spectrum of $PbZn_2(BO_3)_2$ exhibits three sets of bands characteristic of the planar triangular BO_3 group. They are the out-of-plane bending modes ($v2$) occurring at 761.8 and 719.3 cm^{-1}, the antisymmetric stretch ($v3$) at 1223.6 cm^{-1}, and the in-plane mode ($v4$) at 625.5 cm^{-1}. These values correspond well to those reported in the literature (Thompson et al., 1991).

Crystal data

$PbZn_2(BO_3)_2$	Mo $K\alpha$ radiation
$M_r = 455.55$	Cell parameters from 25
Orthorhombic, Pccn	reflections
$a = 11.1709\ (8)$ Å	$\theta = 20.2–22.5°$
$b = 4.9674\ (7)$ Å	$\mu = 36.61$ mm^{-1}
$c = 10.5987\ (8)$ Å	$T = 290$ K
$V = 588.13\ (10)$ Å^3	Plate, colorless
$Z = 4$	0.1 × 0.06 × 0.02 mm
$D_x = 5.145$ Mg m^{-3}	

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.031$
$2\theta–\omega$ scans	$\theta_{max} = 34.9°$
Absorption correction: ψ scan	$h = 0 \rightarrow 18$
(Kopfmann & Huber, 1968)	$k = 0 \rightarrow 8$
$T_{min} = 0.085$, $T_{max} = 0.473$	$l = 0 \rightarrow 16$
1522 measured reflections	3 standard reflections
1289 independent reflections	every 150 reflections
972 reflections with $I > 2\sigma(I)$	intensity decay: 1.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0998P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.0518P]$
$wR(F^2) = 0.145$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
1289 reflections	$\Delta\rho_{max} = 3.69$ e Å^{-3}
51 parameters	$\Delta\rho_{min} = -3.06$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pb—O2^i	2.273 (5)	Zn—O2^{iv}	1.958 (5)
Pb—O1	2.515 (5)	B—O1	1.371 (9)
Zn—O3^{ii}	1.941 (5)	B—O3	1.372 (9)
Zn—O1^{iii}	1.947 (5)	B—O2	1.384 (10)
Zn—O3	1.953 (6)		
O3^{ii}—Zn—O1^{iii}	113.9 (3)	O3—Zn—O2^{iv}	115.0 (3)
O3^{ii}—Zn—O3	103.34 (19)	O1—B—O3	118.7 (7)
O1^{iii}—Zn—O3	108.2 (3)	O1—B—O2	122.3 (7)
O3^{ii}—Zn—O2^{iv}	108.6 (2)	O3—B—O2	119.0 (7)
O1^{iii}—Zn—O2^{iv}	108.0 (2)		

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, z$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x, y + 1, z$.

The highest residual electronic-density peaks were located 1.54 Å from the Pb atoms.

Data collection, cell refinement and data reduction: Rigaku/AFC Diffractometer Control Software (Rigaku, 1994); structure solution: SHELXS97 (Sheldrick, 1997); structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 1999); software used to prepare material for publication: SHELXL97.

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