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$PbGaBO_4$, an orthoborate with a new structure-type

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(Ga–O) = 0.002 Å
R factor = 0.028
wR factor = 0.066
Data-to-parameter ratio = 36.4

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

The crystal structure of a new ternary borate, lead gallium boron tetraoxide, $PbGaBO_4$, has been determined by X-ray diffraction using a single-crystal grown from a PbO flux. The structure consists of infinite [010] chains of edge-sharing GaO_6 octahedra bridged by BO_3 triangles. The Pb^{2+} cations and their stereoactive lone pair occupy the apex of PbO_4 square pyramids. The structure represents a new structure-type for anhydrous orthoborates. Bond-valence analysis reveals the presence of strain within the octahedral chains.

Comment

Inorganic borates continue to be an active area of research with the aim of finding new compounds with interesting optical properties. Previous studies in our laboratory have resulted in the successful structure determinations of two new gallium borate compounds, $MGa_2B_2O_7$ (M = Sr, Ba) (Park & Barbier, 2000). Our current investigation is focused on the PbO–X_2O_3–B_2O_3 systems (X = Al, Ga), which have not yet been explored. The structure of $PbGaBO_4$ represents a new structure-type for the family of anhydrous orthoborates. It is based on a distorted octahedral coordination of Ga, a regular triangular coordination of B and the expected irregular four-fold coordination of divalent Pb with a stereoactive lone pair (Fig. 1). The structure is built of infinite chains of edge-sharing GaO_6 octahedra parallel to the b axis and linked by BO_3 triangles (Figs. 2 and 3). The short B—O bonds (1.37 Å) in the

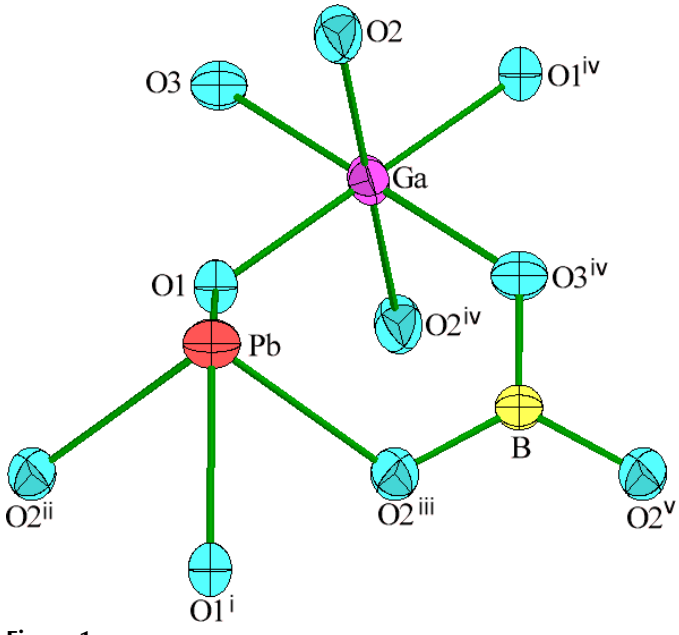

Figure 1
Part of the $PbGaBO_4$ structure. The displacement ellipsoids are drawn at the 90% probability level. The symmetry codes are as in Table 1.

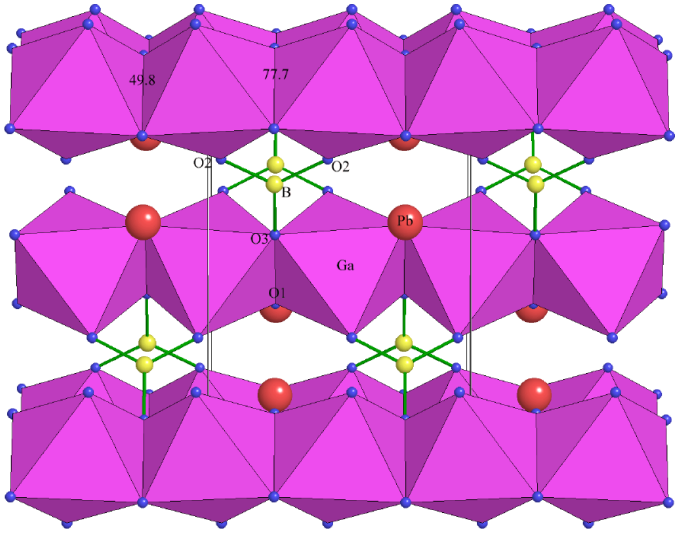

Figure 2
View of the $PbGaBO_4$ structure approximately along the [100] direction. Strong angular distortions are associated with the bridging borate groups.

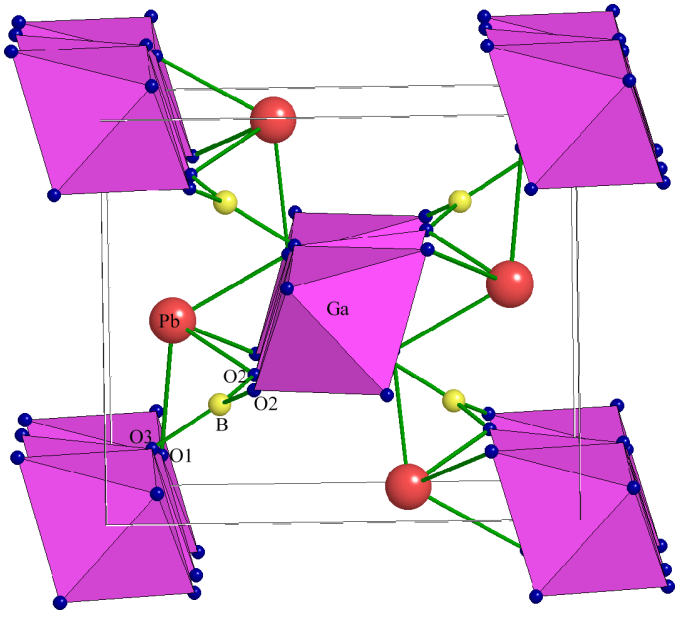

Figure 3
View of the $PbGaBO_4$ structure along the [010] direction. The GaO_6 octahedral chains are linked by the BO_3 triangles.

BO_3 groups bridging adjacent octahedra impose a strong angular distortion along the octahedral chains; the dihedral angle between adjacent octahedra deviate from the ideal angle of 60° and range from 49.8 to 77.7° (Fig. 2). Bond-valence analysis (Brese & O'Keefe, 1991) indicates the presence of structural strain as a result of distortions in the GaO_6 octahedra; the bond-valence sum around O1 is high [$\sigma(s)$ = 2.23] due to two short Ga—O1 bonds (1.889 Å, s = 0.65), whereas the bond-valence sum around O3 is low [$\sigma(s)$ = 1.79] due to two long Ga—O3 bonds (2.076 Å, s = 0.40).

Experimental

Single crystals of $PbGaBO_4$ were grown using a PbO flux. A stoichiometric mixture of PbO, Ga_2O_3 and H_3BO_3 powders with 50 mole% excess PbO (total weight 12.00 g) was melted at 1173 K in a covered Pt crucible and cooled to 773 K (at 3 K h^{-1}). A large quantity of colourless prismatic crystals were recovered after dissolving the PbO flux in dilute aqueous HNO_3.

Crystal data

$PbGaBO_4$
M_r = 351.72
Orthorhombic, *Pnma*
a = 6.9944 (10) Å
b = 5.8925 (8) Å
c = 8.2495 (11) Å
V = 340.00 (8) Å^3
Z = 4
D_x = 6.871 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7743 reflections
θ = 3.8–45.4°
μ = 57.22 mm^{-1}
T = 299 (2) K
Prism, colourless
0.10 × 0.07 × 0.04 mm

Data collection

CCD area detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.016, T_{max} = 0.101
7743 measured reflections
1493 independent reflections
1336 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 45.4°
$h = -14 \rightarrow 11$
$k = -7 \rightarrow 11$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.066
S = 1.14
1493 reflections
41 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.5503P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 5.73 e Å^{-3}
$\Delta\rho_{min}$ = −6.70 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0065 (5)

Table 1
Selected geometric parameters (Å, °).

Pb—O1^{i}	2.316 (4)	Ga—O2^{i}	2.008 (2)
Pb—O2	2.352 (2)	Ga—O3	2.074 (2)
Pb—O2^{ii}	2.352 (2)	Ga—O3^{i}	2.074 (2)
Pb—O1^{iii}	2.365 (3)	B—O3^{iv}	1.372 (6)
Ga—O1	1.888 (2)	B—O2^{v}	1.385 (3)
Ga—O1^{i}	1.888 (2)	B—O2^{i}	1.385 (3)
Ga—O2	2.008 (2)		
O1—Ga—O1^{i}	180.0 (3)	O2^{i}—Ga—O3	91.53 (13)
O1—Ga—O2	93.67 (13)	O1—Ga—O3^{i}	98.35 (11)
O1^{i}—Ga—O2	86.33 (13)	O1^{i}—Ga—O3^{i}	81.65 (11)
O1—Ga—O2^{i}	86.33 (13)	O2—Ga—O3^{i}	91.53 (13)
O1^{i}—Ga—O2^{i}	93.67 (13)	O2^{i}—Ga—O3^{i}	88.47 (13)
O2—Ga—O2^{i}	180.00 (9)	O3—Ga—O3^{i}	180.0
O1—Ga—O3	81.65 (11)	O3^{iv}—B—O2^{v}	120.08 (19)
O1^{i}—Ga—O3	98.35 (11)	O3^{iv}—B—O2^{i}	120.08 (19)
O2—Ga—O3	88.47 (13)	O2^{v}—B—O2^{i}	119.8 (4)

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

The locations of maximum and minimum peaks in the residual electron-density map: highest peak 5.73 e Å^{-3} at 0.0592, 0.1547, 0.3570 (0.56 Å from Pb) and deepest hole −6.70 e Å^{-3} at 0.0553, 0.2500, 0.4608 (0.84 Å from Pb).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XTALDRAW* (Bartelmehs & Downs, 1997); software used to prepare material for publication: *SHELXL*97.

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