

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

The layered gallium borophosphate $\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ refined from X-ray powder data

Shao-Yu Mao, Jin-Xiao Mi, Liev G. Akselrud, Ya-Xi Huang, Jing-Tai Zhao and Rüdiger Kniep

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

Shao-Yu Mao,^{a*} Jin-Xiao Mi,^a
Liev G. Akselrud,^b Ya-Xi Huang,^c
Jing-Tai Zhao^d and
Rüdiger Kniep^c

^aCollege of Chemistry and Chemical
Engineering, Xiamen University, Xiamen
361005, People's Republic of China,

^bDepartment of Inorganic Chemistry, Lviv State
University, UA-79602 Lviv, Ukraine,

^cMax-Planck-Institut für Chemische Physik fester
Stoffe, Nöthnitzer Straße 40, D-01187 Dresden,
Germany, and ^dState Key Laboratory of High
Performance Ceramics and Superfine
Microstructure, Chinese Academy of Sciences,
Shanghai Institute of Ceramics, 1295 Dingxi
Road, Shanghai 200050, People's Republic of
China

Correspondence e-mail:
symao@jingxian.xmu.edu.cn

Key indicators

Powder X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{O}-\text{B}) = 0.009\text{ \AA}$
 R factor = 0.146
 wR factor = 0.069
Data-to-parameter ratio = 11.0

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

The layered gallium borophosphate $\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ refined from X-ray powder data

The crystal structure of $\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$, obtained by mild hydrothermal synthesis, has been refined from X-ray powder diffraction data using the Rietveld method. It is isotypic with the iron borophosphate $\text{Fe}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ and has a two-dimensional layered structure.

Comment

In the past few years, borophosphates have attracted much attention from chemists and materials scientists as potential microporous materials. In our systematic investigations on gallium borophosphates, two alkali metal gallium borophosphates, *viz.* $\text{NaGa}[\text{BP}_2\text{O}_7(\text{OH})_3]$ (Huang *et al.*, 2001) and $\text{KGa}[\text{BP}_2\text{O}_7(\text{OH})_3]$ (Li *et al.*, 2002), and the ammonium gallium borophosphate $(\text{NH}_4)\text{Ga}[\text{BP}_2\text{O}_8(\text{OH})]$ (Mi *et al.*, 2002) have been investigated. Gallium borophosphates without additional alkali metal or ammonium ions have not been reported up to now, although three compounds $\{\text{Fe}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ (Boy *et al.*, 1998), $\text{Al}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5(\text{H}_2\text{O})]$ (Kniep *et al.*, 2002) and $\text{Cr}_2(\text{BP}_3\text{O}_{12})$ (Mi *et al.*, 2000) $\}$ were structurally characterized for the crystal-chemically related trivalent Fe, Al and Cr cations. We report here the first gallium borophosphate without an additional cation. The crystal structure of the title compound is isotypic with $\text{Fe}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ and is closely related to $\text{Al}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5(\text{H}_2\text{O})]$.

$\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ has a two-dimensional layered structure and the crystals clearly show micaceous aggregate thin plates under the microscope. Because of its micaceous character, it is difficult to find suitable crystals for single-crystal X-ray diffraction. The crystal structure was therefore refined from X-ray powder diffraction data (Fig. 1). The Ga—O bond

Received 27 October 2004
Accepted 10 November 2004
Online 30 November 2004

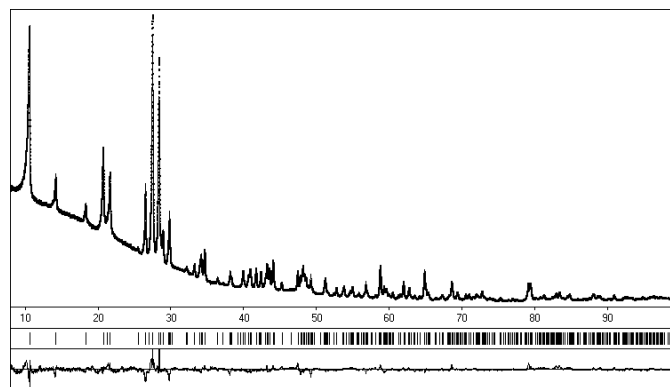


Figure 1

A Rietveld refinement plot for $\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$, showing the observed and difference profiles. The reflection positions are shown above the difference profile.

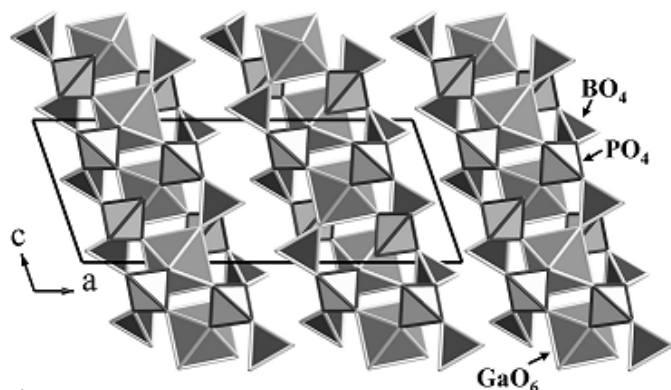


Figure 2
The crystal structure of $\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ in polyhedral representation, viewed down the b axis.

distances range from 1.840 (3) to 2.035 (4) Å in the GaO_6 octahedra, and those of P—O from 1.532 (4) to 1.594 (4) Å in the PO_4 tetrahedra. Although the average B—O bond distance of the title compound (1.450 Å) is reasonable in comparison with its Fe and Al analogues (Fe 1.471 Å and Al 1.470 Å), the individual bond lengths show considerable scatter, caused by the limitation of the X-ray powder data refinement and the lower precision of the determined positions of the light atoms.

The crystal structure of $\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ is characterized by sandwich-type ‘tetrahedra–octahedra–tetrahedra’ layers parallel to (100) (Fig. 2) which are connected by hydrogen bonds (Table 2). Atom O1 is part of the OH group attached to the phosphate tetrahedron, whereas atoms O5 and O6 belong to OH functions of the borate group. The PO_4 and BO_4 tetrahedra share one O-atom corner with each other, forming an infinite zigzag single chain of $[-\text{BO}_4-\text{PO}_4-\text{BO}_4-\text{PO}_4-]$ units along the c axis. One set of GaO_6 octahedra connect with two infinite single chains by sharing O-atom corners. These two chains are connected again through another two sets of GaO_6 octahedra to two other chains shifted by a period of $a/2$. This construction leads to the puckered shape of the layer parallel to (100). Each GaO_6 octahedron shares O-atom corners with four PO_4 and two BO_4 tetrahedra in the layer; each PO_4 tetrahedron shares O-atom corners with two GaO_6 octahedra and two BO_4 tetrahedra, while each BO_4 shares vertices with one GaO_6 and two PO_4 besides the terminal OH group.

Experimental

$\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ was synthesized under mild hydrothermal conditions. The reaction was carried out with mixtures of GaCl_3 (0.523 g gallium metal dissolved in 2.5 ml 37% HCl), 1.237 g H_3BO_3 and 2.5 ml 85% H_3PO_4 in a Ga:B:P molar ratio of 1.5:4:7. The container was about 50% full of solution. The autoclave was placed in an oven with subsequent heating at 443 K for 7 d. All starting materials were of analytical grade and used without further purification. The formula was confirmed by chemical analysis (ICP) with a Ga:B:P:H ratio of 1:1.88:1.97:5.36. TG/DTA analysis showed an endothermic peak at 636 K associated with about 12.1% weight loss. This is consistent with the theoretical value of 12.9% for loss of two and a half water mol-

ecules. It was confirmed that the elimination of all water molecules occurs at nearly the same temperature.

Crystal data

$\text{Ga}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$
 $M_r = 350.32$
Monoclinic, $C2/c$
 $a = 17.6404$ (3) Å
 $b = 6.70735$ (8) Å
 $c = 6.99525$ (8) Å
 $\beta = 109.157$ (1)°
 $V = 781.85$ (2) Å³
 $Z = 4$

$D_x = 2.976$ Mg m⁻³
Cu $K\alpha_1$ radiation
 $\mu = 9.56$ mm⁻¹
 $T = 295$ K
White
Specimen shape: Plate
25 × 25 × 1 mm
Particle morphology: thin sheet

Data collection

Stoe STADI-P diffractometer
Debye–Scherrer scans
Specimen mounting: packed powder pellet
Specimen mounted in transmission mode
Absorption correction: none
396 measured reflections

397 independent reflections
 $\theta_{\text{max}} = 49.5^\circ$
 $h = 0 \rightarrow 17$
 $k = 0 \rightarrow 6$
 $l = -6 \rightarrow 6$
 $2\theta_{\text{min}} = 3$, $2\theta_{\text{max}} = 100^\circ$
Increment in $2\theta = 0.005^\circ$

Refinement

Refinement on I_{net}
 $R_p = 0.146$
 $R_{\text{wp}} = 0.069$
 $R_{\text{exp}} = 0.025$
397 reflections
36 parameters

H-atom parameters not refined
(Δ/σ)_{max} = 0.001
Preferred orientation was refined (CSD; Pecharsky *et al.*, 1987),
 $I_{\text{corr}} = I_{\text{obs}}/[1 + (\tau^2 - 1) \cdot \sin^2\varphi]^{1/2}$
axis [100], $\tau = 1.869$ (1)

Table 1

Selected geometric parameters (Å, °).

Ga1—O2 ⁱ	1.840 (3)	P1—O2 ^{vii}	1.545 (4)
Ga1—O2 ⁱⁱ	1.840 (3)	P1—O3 ^{viii}	1.560 (5)
Ga1—O1	1.978 (4)	P1—O4 ^{ix}	1.593 (4)
Ga1—O1 ⁱⁱⁱ	1.978 (4)	B1—O5 ^v	1.372 (10)
Ga1—O6 ^{iv}	2.035 (4)	B1—O3	1.386 (9)
Ga1—O6 ^v	2.035 (4)	B1—O4 ^v	1.482 (8)
P1—O1 ^{vi}	1.532 (4)	B1—O6 ^v	1.559 (9)
O1 ^{vi} —P1—O2 ^{vii}	116.2 (2)	O5 ^v —B1—O3	121.6 (6)
O1 ^{vi} —P1—O3 ^{viii}	109.8 (2)	O5 ^v —B1—O4 ^v	104.6 (6)
O1 ^{vi} —P1—O4 ^{ix}	104.2 (2)	O5 ^v —B1—O6 ^v	103.7 (5)
O2 ^{vii} —P1—O3 ^{viii}	109.5 (2)	O3—B1—O4 ^v	114.6 (6)
O2 ^{vii} —P1—O4 ^{ix}	109.0 (2)	O3—B1—O6 ^v	109.1 (6)
O3 ^{viii} —P1—O4 ^{ix}	107.8 (2)	O4 ^v —B1—O6 ^v	100.8 (5)

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

Table 2

Hydrogen-bonding $D \cdots A$ distances (Å).

O1 \cdots O6 ^{iv}	2.783 (5)	O5 \cdots O5 ^{viii}	2.447 (5)
O1 \cdots O6 ^v	2.892 (6)	O5 \cdots O5 ^{iv}	2.704 (6)

Symmetry codes: (iv) $1-x, y, \frac{3}{2}-z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (viii) $1-x, 1-y, 1-z$.

The crystal structure was refined with the atomic coordinates of the isotopic iron compound $\text{Fe}[\text{B}_2\text{P}_2\text{O}_7(\text{OH})_5]$ (Boy *et al.*, 1998) as starting parameters. All atoms were refined with isotropic displacement parameters.

Data collection: *WinXPOW* (Stoe & Cie, 1999); cell refinement: *CSD* (Akselrud *et al.*, 1989); data reduction: *CSD*; program(s) used to refine structure: *CSD*; molecular graphics: *DIAMOND* (Brandenburg, 1996–2001).

This project was supported by the National Natural Science Foundation of China (No. 40472027), and the Natural Science Foundation of Fujian (No. E0410003). We thank R. Niewa and Ms S. Müller (thermal analysis), and Ms U. Schmidt (chemical analysis).

References

- Akselrud, L. G., Grin, Y. N., Zavalii, P. Y. & Pecharsky, V. K (1989). *Z. Kristallogr. Suppl.* **2**, 155–158.
- Boy, I., Hauf, C. & Kniep, R. (1998). *Z. Naturforsch. Teil B*, **53**, 631–633.
- Brandenburg, K. (1996–2001). *DIAMOND*. Version 2.1a. Crystal Impact GbR, Bonn, Germany.
- Huang, Y.-X., Mao, S.-Y., Mi, J.-X., Wei, Z.-B., Zhao, J.-T. & Kniep, R. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 15–16.
- Kniep, R., Koch, D. & Borrmann, H. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 187–188.
- Li, M.-R., Mao, S.-Y., Huang, Y.-X., Mi, J.-X., Wei, Z.-B., Zhao, J.-T. & Kniep, R. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 165–166.
- Mi, J.-X., Huang, Y.-X., Mao, S.-Y., Borrmann, H., Zhao, J.-T. & Kniep, R. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 167–168.
- Mi, J.-X., Zhao, J.-T., Mao, S.-Y., Huang, Y.-X., Engelhardt, H. & Kniep, R. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 201–202.
- Pecharsky, V. K., Akselrud, L. G. & Zavalii P. Y. (1987). *Kristallografiya*, **32**, 874–877.
- Stoe & Cie (1999). *WinXPOW*. Version 106. Stoe & Cie GmbH, Darmstadt, Germany.