Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

The layered gallium borophosphate $Ga[B_2P_2O_7(OH)_5]$ refined from X-ray powder data

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Key indicators

Powder X-ray study
T = 295 K
Mean σ(O–B) = 0.009 Å
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.

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

The crystal structure of $Ga[B_2P_2O_7(OH)_5]$, 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 $Fe[B_2P_2O_7(OH)_5]$ 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*. $NaGa[BP_2O_7(OH)_3]$ (Huang *et al.*, 2001) and $KGa[BP_2O_7(OH)_3]$ (Li *et al.*, 2002), and the ammonium gallium borophosphate $(NH_4)Ga[BP_2O_8(OH)]$ (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 {$Fe[B_2P_2O_7(OH)_5]$ (Boy *et al.*, 1998), $Al[B_2P_2O_7(OH)_5(H_2O)]$ (Kniep *et al.*, 2002) and $Cr_2(BP_3O_{12})$ (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 $Fe[B_2P_2O_7(OH)_5]$ and is closely related to $Al[B_2P_2O_7(OH)_5(H_2O)]$.

$Ga[B_2P_2O_7(OH)_5]$ 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

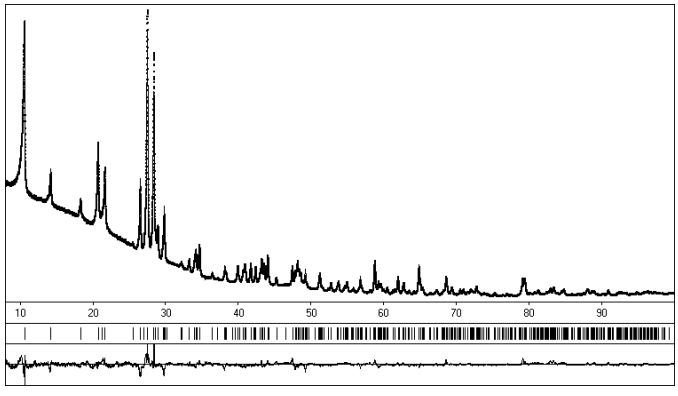

Figure 1
A Rietveld refinement plot for $Ga[B_2P_2O_7(OH)_5]$, showing the observed and difference profiles. The reflection positions are shown above the difference profile.

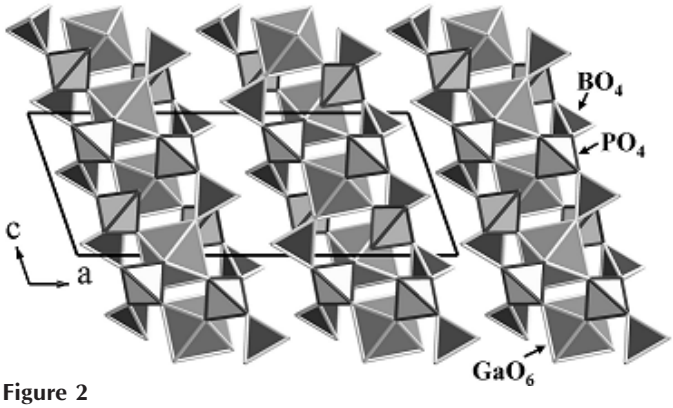

Figure 2
The crystal structure of $Ga[B_2P_2O_7(OH)_5]$ in polyhedral representation, viewed down the *b* axis.

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 $Ga[B_2P_2O_7(OH)_5]$ 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 $[-BO_4-PO_4-BO_4-PO_4-]$ 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

$Ga[B_2P_2O_7(OH)_5]$ 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 endothermal 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 molecules. It was confirmed that the elimination of all water molecules occurs at nearly the same temperature.

Crystal data

$Ga[B_2P_2O_7(OH)_5]$	D_x = 2.976 Mg m^{-3}
M_r = 350.32	Cu $K\alpha_1$ radiation
Monoclinic, *C*2/*c*	μ = 9.56 mm^{-1}
a = 17.6404 (3) Å	*T* = 295 K
b = 6.70735 (8) Å	White
c = 6.99525 (8) Å	Specimen shape: Plate
β = 109.157 (1)°	25 × 25 × 1 mm
V = 781.85 (2) Å^3	Particle morphology: thin sheet
Z = 4	

Data collection

Stoe STADI-P diffractometer	397 independent reflections
Debye–Scherrer scans	θ_{max} = 49.5°
Specimen mounting: packed powder pellet	$h = 0 \rightarrow 17$
	$k = 0 \rightarrow 6$
Specimen mounted in transmission mode	$l = -6 \rightarrow 6$
	$2\theta_{min}$ = 3, $2\theta_{max}$ = 100°
Absorption correction: none	Increment in 2θ = 0.005°
396 measured reflections	

Refinement

Refinement on I_{net}	H-atom parameters not refined
R_p = 0.146	$(\Delta/\sigma)_{max}$ = 0.001
R_{wp} = 0.069	Preferred orientation was refined (*CSD*; Pecharsky *et al.*, 1987), $I_{corr} = I_{obs}/[1 + (\tau^2 - 1)\cdot\sin^2\varphi]^{1/2}$ axis [100], τ = 1.869 (1)
R_{exp} = 0.025	
397 reflections	
36 parameters	

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···O6^{iv}	2.783 (5)	O5···O5^{viii}	2.447 (5)
O1···O6^{v}	2.892 (6)	O5···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 isotypic iron compound $Fe[B_2P_2O_7(OH)_5]$ (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).

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