

$\theta/\theta$  powder scans  
Absorption correction:  
none

$2\theta_{\min} = 20$ ,  $2\theta_{\max} = 120^\circ$   
Wavelength of incident radiation:  
1.54178 Å

### Refinement

Refinement on powder data  
points  
 $R_p = 0.072$   
 $R_{wp} = 0.101$   
 $\chi^2 = 5.04$   
200 reflections  
24 parameters  
 $w = 1/\sigma^2(y)$

$(\Delta/\sigma)_{\max} < 0.01$   
 $\Delta\rho_{\max} = 0.9 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.5 \text{ e } \text{Å}^{-3}$   
Atomic scattering factors  
from *International Tables*  
for *X-ray Crystallography* (1974, Vol. IV, Table  
2.2B)

Table 3. Fractional atomic coordinates and isotropic displacement parameters ( $\text{Å}^2$ ) for (II)

	x	y	z	$U_{\text{iso}}$
Be(1)	1/4	0	1/2	0.005 (3)
As(1)	1/4	1/2	0	0.0046 (3)
O(1)	0.13390 (31)	0.4066 (4)	0.14093 (32)	0.009 (2)
Li(1)	0.1772 (11)	0.1772 (11)	0.1772 (11)	0.017 (5)
Cl(1)	0	0	0	0.018 (1)

Table 4. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ ) for (II)

Be(1)—O(1 <sup>i</sup> )	1.6174 (24)	Li(1)—O(1)	1.946 (6)
As(1)—O(1)	1.6895 (29)	Li(1)—Cl(1)	2.528 (16)
O(1 <sup>i</sup> )—Be(1)—O(1 <sup>ii</sup> )	107.97 (9)	Be(1 <sup>vi</sup> )—O(1)—Li(1)	120.12 (17)
O(1 <sup>i</sup> )—Be(1)—O(1 <sup>iii</sup> )	112.51 (19)	As(1)—O(1)—Li(1)	116.36 (13)
O(1)—As(1)—O(1 <sup>iv</sup> )	108.69 (9)	O(1)—Li(1)—O(1 <sup>i</sup> )	107.4 (5)
O(1)—As(1)—O(1 <sup>v</sup> )	111.05 (18)	O(1)—Li(1)—Cl(1)	111.5 (5)
Be(1 <sup>vi</sup> )—O(1)—As(1)	123.43 (19)	Li(1)—Cl(1)—Li(1 <sup>vii</sup> )	109.471

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

Both crystal structures were optimized by X-ray Rietveld refinements (Rietveld, 1969), following a similar procedure to that described by Gier, Harrison & Stucky (1991). Starting unit-cell parameters were obtained by unit-cell powder refinements and starting atomic coordinates were obtained from the structure of  $\text{Li}_4\text{Br}(\text{BePO}_4)_3$  (Gier, Harrison & Stucky, 1991), with Cl substituting Br and As replacing P in the  $\text{Li}_4\text{Cl}(\text{BeAsO}_4)_3$  phase. The Rietveld refinements progressed smoothly in each case, with the usual profile parameters (scale factor, zero-point error, pseudo-Voigt peak-width variation parameters, six-term Fourier-cosine series background coefficients and unit-cell parameters) treated as least-squares variables in the usual fashion. All atom positions and isotropic displacement factors were refined. No corrections for preferred orientation, extinction or absorption were applied.

Program(s) used to refine structures: *GSAS* (Larson & Von Dreele, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976), with local modifications.

We thank the National Science Foundation and Office of Naval Research for partial financial support.

Lists of raw X-ray powder data and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71662 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1052]

### References

- Beagley, B., Henderson, C. M. B. & Taylor, D. (1982). *Mineral. Mag.* **46**, 459–464.  
Felsche, J. & Luger, S. (1987). *Thermochim. Acta*, **118**, 35–55.  
Gier, T. E., Harrison, W. T. A. & Stucky, G. D. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 1169–1171.  
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
Larson, A. C. & Von Dreele, R. B. (1990). *GSAS User's Guide*. Los Alamos National Laboratory, New Mexico, USA.  
Moran, K. L., Gier, T. E., Harrison, W. T. A., Stucky, G. D., Eckert, H., Eichele, K. & Wasylishen, R. E. (1994). *J. Am. Chem. Soc.* In the press.  
Nenoff, T. M., Harrison, W. T. A., Gier, T. E. & Stucky, G. D. (1991). *J. Am. Chem. Soc.* **113**, 378–379.  
Pauling, L. (1930). *Z. Kristallogr.* **74**, 213–225.  
Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.  
Stein, A., Ozin, G. & Stucky, G. D. (1990). *J. Am. Chem. Soc.* **112**, 904–905.  
Stucky, G. D., Srdanov, V. I., Harrison, W. T. A., Gier, T. E., Keder, N. L., Moran, K. L., Haug, K. & Metiu, H. I. (1992). *Supramolecular Architecture*, *Am. Chem. Soc. Symp. Ser.* 499, edited by T. E. Bein, pp. 294–313. Washington: American Chemical Society.  
Taylor, D. & Henderson, C. M. B. (1978). *Phys. Chem. Miner.* **2**, 325–336.

*Acta Cryst.* (1994). **C50**, 473–476

## Synthesis and Structures of Two Isostructural Phosphites, $\text{Al}_2(\text{HPO}_3)_3$ and $\text{Ga}_2(\text{HPO}_3)_3$

RUSSELL E. MORRIS, MARTIN P. ATTFIELD  
AND ANTHONY K. CHEETHAM

Materials Department, University of California,  
Santa Barbara, CA 93106, USA

(Received 22 May 1992; accepted 31 August 1993)

### Abstract

Aluminium hydrogen phosphite,  $\text{Al}_2(\text{HPO}_3)_3$ , and gallium hydrogen phosphite,  $\text{Ga}_2(\text{HPO}_3)_3$ , were prepared hydrothermally in Teflon-lined steel autoclaves at 473 K. The compounds are isostructural with  $\text{Fe}_2(\text{HPO}_3)_3$ . The structures consist of very distorted  $\text{MO}_6$  octahedra which share faces to form a dimeric  $\text{M}_2\text{O}_9$  unit. These dimers are interlinked by the phosphite groups, which link three different dimers into a three-dimensional arrangement having small proton-lined channels running parallel to the  $c$  axis.

### Comment

Aluminium and gallium phosphates have received much attention in recent years because of their capacity to form framework structures with topologies similar to those of

the zeolites (Wilson, Lok, Messina, Cannan & Flanigen, 1982; Flanigen, Lok, Patton & Wilson, 1986). In contrast, however, the phosphites of these elements have not been studied in any great detail. Phosphites of other metal atoms, notably Zn and the rare earths, have indicated that interesting and novel structures can be produced using hydrothermal methods. These include a number of structures containing channels and cavities (Ortiz-Avila, Squattrino, Shieh & Clearfield, 1989), and layer structures (Durand, Loukili, Tijani, Rafiq & Cot, 1988). Here we report two new phosphites that are isostructural with Fe<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub> (Sghyar, Durand, Cot & Rafiq, 1991) and have similar structural features to those of Ga<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O (Morris, Harrison, Wilkinson, Nicol & Cheetham, 1992).

The title compounds were prepared in a 23 ml Teflon-lined steel autoclave from reaction mixtures containing MCl<sub>3</sub>·xH<sub>2</sub>O (0.6 g) and H<sub>3</sub>PO<sub>3</sub> (0.8 g) in 15 ml of water (*M* = Al or Ga). The autoclaves were heated for 2 days at 473 K and then left to cool slowly to room temperature. From the reaction mixture containing the Al compound, colorless hexagonal crystals of Al<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>, (I), were recovered, while Ga<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>, (II), was recovered as a white microcrystalline powder.

The structures of Al<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub> and Ga<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub> are isostructural with that of Fe<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub> (Sghyar, Durand, Cot & Rafiq, 1991), and contain highly distorted octahedra of O atoms around the metal atom arising from two MO<sub>6</sub> units sharing a common face to form dimeric M<sub>2</sub>O<sub>9</sub> groups. This distortion manifests itself as a squeezing of the O(2)—M—O(2) bond angles to values of 76.10 (4)° (*M* = Al) and 74.4 (1)° (*M* = Ga), coupled with small M—O(2)—M angles of 89.25 (5)° and 91.3 (1)° (*M* = Al and Ga, respectively). The bond distances for both compounds are similar to those seen for Fe<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>. The dimers are linked into a three-dimensional framework by means of the phosphite groups, which share their three O atoms with three separate dimeric units. This occurs in such a way as to produce columns of alternating

dimer-phosphite linkages that are joined to form small channels (of approximate diameter 3 Å) parallel to the *c* axis. These channels are lined by the phosphite protons. A view of the structure is shown in Fig. 1. The structures of the title compounds show similarities to that of Ga<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O (Morris, Harrison, Wilkinson, Nicol & Cheetham, 1992) and to those of the selenites of aluminium, Al<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Al<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (Morris, Harrison, Stucky & Cheetham, 1991; Harrison, Stucky, Morris & Cheetham, 1992). The selenite has a similar trigonal pyramidal coordination polyhedron to that of the phosphite, with a lone pair of electrons replacing the phosphite proton. All four structures show the same MO<sub>6</sub>—phosphite—MO<sub>6</sub> linking unit, the differences in the structures being accounted for by the presence of the water molecules in Ga<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O and the two selenites, preventing the formation of the dimeric M<sub>2</sub>O<sub>9</sub> units that occur in the title compounds.

## Experimental Compound (I)

### Crystal data

Al<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>  
*M<sub>r</sub>* = 293.3  
 Hexagonal  
*P*6<sub>3</sub>/*m*  
*a* = 7.858 (1) Å  
*c* = 7.086 (1) Å  
*V* = 378.99 Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 2.575 Mg m<sup>-3</sup>

Mo *K*α radiation  
*λ* = 0.71069 Å  
 Cell parameters from 25 reflections  
*θ* = 7.79–12.38°  
*μ* = 1.0249 mm<sup>-1</sup>  
*T* = 293 K  
 Hexagonal prism  
 0.2 × 0.2 × 0.2 mm  
 Colorless

### Data collection

Enraf-Nonius CAD-4F diffractometer  
*ω*-2*θ* scans  
 Absorption correction: *ψ*-scan  
*T<sub>min</sub>* = 0.96, *T<sub>max</sub>* = 1.0  
 3406 measured reflections  
 596 independent reflections

398 observed reflections  
 [*I* > 3σ(*I*)]  
*θ<sub>max</sub>* = 35°  
*h* = -12 → 12  
*k* = -1 → 12  
*l* = -11 → 11  
 3 standard reflections  
 frequency: 60 min  
 intensity variation: none

### Refinement

Refinement on *F*  
*R* = 0.0177  
*wR* = 0.0185  
 398 reflections  
 29 parameters  
 All H-atom parameters refined  
 Calculated weights based on Tukey-Prince algorithm (using Chebyshev polynomial)

(*Δ*/σ)<sub>max</sub> = 0.01  
*Δρ<sub>max</sub>* = 0.3 e Å<sup>-3</sup>  
*Δρ<sub>min</sub>* = -0.3 e Å<sup>-3</sup>  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

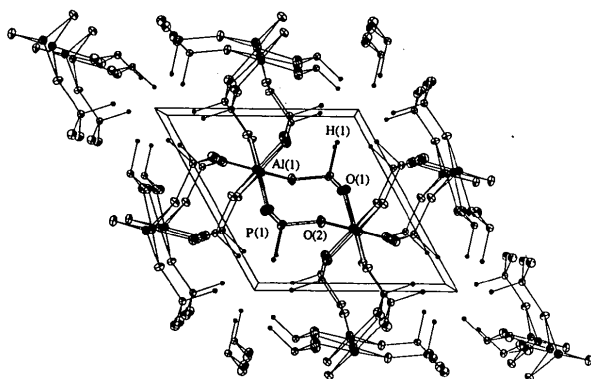


Fig. 1. The structure of Al<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub> viewed in the [0001] direction showing the proton-lined channels. Displacement ellipsoids are shown at 50% probability. H atoms are shown as spheres of arbitrary radii.

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for compound (I)

$U_{\text{eq}} = (U_1U_2U_3)^{1/3}$ , where  $U_i$  are the principle axes of the displacement ellipsoid.  $U_{\text{iso}}$  is given for H(1)

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Al(1)	1/3	2/3	-0.05487 (8)	0.0089
P(1)	0.04922 (6)	0.68905 (6)	1/4	0.0071
O(1)	0.1657 (1)	0.7232 (1)	0.0711 (1)	0.0117
O(2)	-0.1360 (2)	0.4828 (2)	1/4	0.0094
H(1)	0.187 (4)	0.178 (4)	1/4	0.018 (6)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for compound (I)

Al(1)—O(1)	1.8205 (8)	Al(1)—O(2 <sup>v</sup> )	1.9683 (9)
Al(1)—O(1 <sup>i</sup> )	1.8206 (8)	P(1)—O(1)	1.5072 (8)
Al(1)—O(1 <sup>ii</sup> )	1.8205 (8)	P(1)—O(1 <sup>vi</sup> )	1.5072 (8)
Al(1)—O(2 <sup>iii</sup> )	1.9683 (9)	P(1)—O(2)	1.545 (1)
Al(1)—O(2 <sup>iv</sup> )	1.9684 (9)	P(1)—H(1 <sup>ii</sup> )	1.27 (3)
O(1)—Al(1)—O(1 <sup>i</sup> )	98.03 (4)	O(2 <sup>v</sup> )—Al(1)—O(1 <sup>ii</sup> )	91.65 (4)
O(1)—Al(1)—O(1 <sup>ii</sup> )	98.02 (4)	O(2 <sup>iii</sup> )—Al(1)—O(2 <sup>iv</sup> )	76.10 (4)
O(1 <sup>i</sup> )—Al(1)—O(1 <sup>ii</sup> )	98.03 (4)	O(2 <sup>iii</sup> )—Al(1)—O(2 <sup>v</sup> )	76.09 (4)
O(2 <sup>iii</sup> )—Al(1)—O(1)	92.28 (4)	O(2 <sup>iv</sup> )—Al(1)—O(2 <sup>v</sup> )	76.10 (4)
O(2 <sup>iii</sup> )—Al(1)—O(1 <sup>i</sup> )	91.65 (4)	O(1)—P(1)—O(1 <sup>vi</sup> )	114.54 (7)
O(2 <sup>iii</sup> )—Al(1)—O(1 <sup>ii</sup> )	164.72 (4)	O(2)—P(1)—O(1)	110.88 (4)
O(2 <sup>iv</sup> )—Al(1)—O(1)	91.65 (4)	O(2)—P(1)—O(1 <sup>vi</sup> )	110.88 (4)
O(2 <sup>iv</sup> )—Al(1)—O(1 <sup>i</sup> )	164.72 (4)	H(1 <sup>ii</sup> )—P(1)—O(1)	106.4 (6)
O(2 <sup>iv</sup> )—Al(1)—O(1 <sup>ii</sup> )	92.27 (4)	H(1 <sup>ii</sup> )—P(1)—O(1 <sup>vi</sup> )	106.4 (6)
O(2 <sup>v</sup> )—Al(1)—O(1)	164.72 (4)	H(1 <sup>ii</sup> )—P(1)—O(2)	107.3 (12)
O(2 <sup>v</sup> )—Al(1)—O(1 <sup>i</sup> )	92.27 (4)		

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

### Compound (II)

#### Crystal data

$\text{Ga}_2(\text{HPO}_3)_3$

$M_r = 378.9$

Hexagonal

$P6_3/m$

$a = 7.91382 (6) \text{\AA}$

$c = 7.24062 (7) \text{\AA}$

$V = 392.7 \text{\AA}^3$

$Z = 2$

Cu  $K\alpha$  radiation

$\lambda = 1.54178 \text{\AA}$

#### Data collection

High-resolution Scintag  
PAD-X diffractometer

$\theta$ - $\theta$  scans

$\theta_{\text{max}} = 50^\circ$

#### Refinement

$R_p = 0.1119$

$R_{\text{wp}} = 0.1409$

$\chi^2 = 3.52$

24 least-squares parameters

Atomic scattering factors  
from *International Tables*  
for *X-ray Crystallography*  
(1974, Vol. IV)

Table 3. Fractional atomic coordinates and isotropic displacement parameters ( $\text{\AA}^2$ ) for compound (II)

	x	y	z	$U_{\text{iso}}$
Ga(1)	1/3	2/3	-0.0498 (2)	0.0109 (4)
P(1)	0.0450 (3)	0.6925 (3)	1/4	0.0100 (6)
O(1)	0.1614 (4)	0.7329 (4)	0.0727 (4)	0.0023 (9)
O(2)	-0.1327 (6)	0.4759 (2)	1/4	0.0023 (9)
H(1)	0.187	0.178	1/4	0.02

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for compound (II)

Ga(1)—O(1)	1.904 (3)	Ga(1)—O(2 <sup>v</sup> )	2.025 (3)
Ga(1)—O(1 <sup>i</sup> )	1.904 (3)	P(1)—O(1)	1.517 (3)
Ga(1)—O(1 <sup>ii</sup> )	1.904 (3)	P(1)—O(1 <sup>vi</sup> )	1.517 (3)
Ga(1)—O(2 <sup>iii</sup> )	2.025 (3)	P(1)—O(2)	1.583 (5)
Ga(1)—O(2 <sup>iv</sup> )	2.025 (3)		
O(1)—Ga(1)—O(1 <sup>i</sup> )	100.0 (1)	O(2 <sup>v</sup> )—Ga(1)—O(1)	162.1 (1)
O(1)—Ga(1)—O(1 <sup>ii</sup> )	100.0 (1)	O(2 <sup>v</sup> )—Ga(1)—O(1 <sup>i</sup> )	91.0 (1)
O(1 <sup>i</sup> )—Ga(1)—O(1 <sup>ii</sup> )	100.0 (1)	O(2 <sup>v</sup> )—Ga(1)—O(1 <sup>ii</sup> )	91.8 (1)
O(2 <sup>iii</sup> )—Ga(1)—O(1)	91.0 (1)	O(2 <sup>iii</sup> )—Ga(1)—O(2 <sup>iv</sup> )	74.4 (1)
O(2 <sup>iii</sup> )—Ga(1)—O(1 <sup>i</sup> )	91.8 (1)	O(2 <sup>iii</sup> )—Ga(1)—O(2 <sup>v</sup> )	74.4 (1)
O(2 <sup>iii</sup> )—Ga(1)—O(1 <sup>ii</sup> )	162.1 (1)	O(2 <sup>iv</sup> )—Ga(1)—O(2 <sup>v</sup> )	74.4 (1)
O(2 <sup>iv</sup> )—Ga(1)—O(1)	91.8 (1)	O(1)—P(1)—O(1 <sup>vi</sup> )	115.5 (3)
O(2 <sup>iv</sup> )—Ga(1)—O(1 <sup>i</sup> )	162.1 (1)	O(2)—P(1)—O(1)	110.2 (2)
O(2 <sup>iv</sup> )—Ga(1)—O(1 <sup>ii</sup> )	91.0 (1)	O(2)—P(1)—O(1 <sup>vi</sup> )	110.2 (2)

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

Single-crystal X-ray intensity data were collected on a crystal of  $\text{Al}_2(\text{HPO}_3)_3$  at the Chemical Crystallography Laboratory, Oxford, England. The systematic absences were consistent with space groups  $P6_3$  and  $P6_3/m$ . There was no measurable second-harmonic generation from the compound so the structure was assumed to be centrosymmetric and assigned the space group  $P6_3/m$ . Data reduction was carried out using the program *RC85* (Baird, 1987) and all least-squares and Fourier calculations were carried out using the Oxford *CRYSTALS* program (Watkin, Caruthers & Betteridge, 1985). After structure solution by direct methods (*SHELXS86*; Sheldrick, 1985), the model was developed by difference Fourier techniques. The final cycle of least-squares refinement included anisotropic displacement parameters for Al, P and O, and isotropic displacement parameters for H atoms.

Preliminary X-ray powder diffraction data collected for  $\text{Ga}_2(\text{HPO}_3)_3$  indicated that this phase was isostructural with  $\text{Al}_2(\text{HPO}_3)_3$ . High resolution X-ray powder data were collected on a Scintag PAD-X diffractometer operating in  $\theta$ - $\theta$  geometry ( $\lambda = 1.54178 \text{\AA}$ ) for  $2\theta = 15$ - $100^\circ$ , using a step size of  $0.02^\circ$  to give 4998 data points. Rietveld profile analysis was carried out with the program *GSAS* (Larson & von Dreele, 1987), using the starting model obtained from the structure solution of  $\text{Al}_2(\text{HPO}_3)_3$ . The final cycle of least-squares refinement included scale-factor and detector zero-point corrections, background coefficients, unit-cell parameters and peak shape-width variation terms (pseudo Voigt), as well as positional and isotropic displacement parameters for the Ga, P and O atoms.

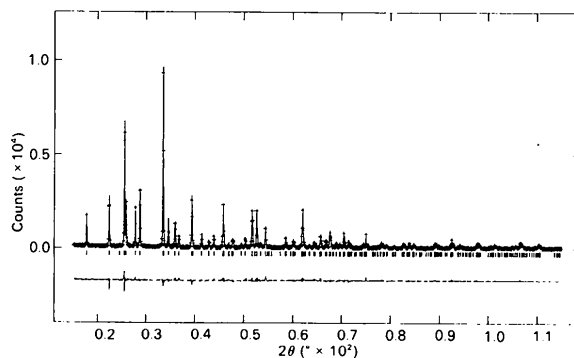


Fig. 2. Final observed (crosses), calculated (line), reflection markers (ticks) and difference profile plots for  $\text{Ga}_2(\text{HPO}_3)_3$ .

The H-atom positional and displacement parameters were left unrefined. Final observed, calculated and difference profile plots are shown in Fig. 2.

MPA would like to acknowledge the University of California for the provision of a scholarship. REM would like to thank the SERC and Blackwell's of Oxford for financial assistance. Some of the work reported here was performed at the Chemical Crystallography Laboratory, University of Oxford, England.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry for Al<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub>, and primary powder diffraction data, H-atom coordinates and complete geometry for Ga<sub>2</sub>(HPO<sub>3</sub>)<sub>3</sub> have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71664 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1025]

## References

- Baird, P. D. (1987). *RC85*. Chemical Crystallography Laboratory, Univ. of Oxford, England.
- Durand, J., Loukili, M., Tijani, N., Rafiq, M. & Cot, L. (1988). *Eur. J. Solid State Inorg. Chem.* **25**, 297–303.
- Flanigen, E. M., Lok, B. M., Patton, T. R. & Wilson, S. T. (1986). *Proceedings of the 7th IZ Conference, Tokyo, Japan*, p. 103. New York: Elsevier.
- Harrison, W. T. A., Stucky, G. D., Morris, R. E. & Cheetham, A. K. (1992). *Acta Cryst.* **C48**, 1365–1367.
- Larson, A. C. & von Dreele, R. B. (1987). *GSAS Report No. LA-UR-86-748*. Los Alamos Laboratory, California, USA.
- Morris, R. E., Harrison, W. T. A., Stucky, G. D. & Cheetham, A. K. (1991). *J. Solid State Chem.* **94**, 227–235.
- Morris, R. E., Harrison, W. T. A., Wilkinson, A. P., Nicol, J. M. & Cheetham, A. K. (1992). *Nature (London)*, **359**, 519–522.
- Ortiz-Avila, C. Y., Squattrino, P. J., Shieh, M. & Clearfield, A. (1989). *Inorg. Chem.* **28**, 2608–2615.
- Sghyar, M., Durand, J., Cot, L. & Rafiq, M. (1991). *Acta Cryst.* **C47**, 2515–2517.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
- Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.
- Wilson, S. T., Lok, B. M., Messina, C. A., Cannan, T. R. & Flanigen, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1156.

*Acta Cryst.* (1994). **C50**, 476–482

## X-ray Rietveld Structure Refinement of Ca, Sr and Ba *meta*-Antimonates

BARRY G. DEBOER†

OSRAM SYLVANIA INC, 100 Endicott St,  
Danvers, MA 01923, USA

R. A. YOUNG AND A. SAKTHIVEL‡

School of Physics, Georgia Institute of Technology,  
Atlanta, GA 30332, USA

(Received 12 March 1993; accepted 9 August 1993)

## Abstract

The *meta*-antimonates, MSb<sub>2</sub>O<sub>6</sub>, M = Ca, Sr and Ba, have been prepared, and their crystal structures refined from powder X-ray diffraction data. The interatomic distances have been determined to reasonable accuracy and the preferred space group was found to be *P* $\bar{3}1m$ , not the previously identified *P*312 (a subgroup of *P* $\bar{3}1m$ ). These and other isomorphous AB<sub>2</sub>X<sub>6</sub> materials are now identified as belonging to the Li<sub>2</sub>ZrF<sub>6</sub> (or better, PbSb<sub>2</sub>O<sub>6</sub>) structure type. Powder diffraction data in the JCPDS-PDF format are presented.

## Comment

These isomorphous *meta*-antimonates have the ideal formula MSb<sub>2</sub>O<sub>6</sub>, where M = Ca, Sr or Ba. The Ca and Sr forms are thought to occur as intermediates, and sometimes as by-products, in the synthesis of calcium and strontium halophosphate phosphors activated by antimony. Of the three, only the calcium *meta*-antimonate crystal structure appears to have been studied in any detail; however, that was long ago (Magneli, 1941) and therefore not with modern structure-refinement methods. Our interest originated in a need to accurately account for second-phase calcium *meta*-antimonate contributions to the diffraction pattern of a high antimony content fluorapatite (DeBoer, Sakthivel, Cagle & Young, 1991).

In an admirable effort based on visually estimated intensities in powder photographs, Magneli (1941) studied 12 isomorphous antimonate and arsenate compounds, worked out a detailed structure for lead *meta*-antimonate and suggested atomic parameters for calcium *meta*-antimonate, which served well here

† Present address: OSRAM SYLVANIA INC, Hawes St, Towanda, PA 18848-0504, USA

‡ Present address: Hercules Inc. Research Center, 500 Hercules Road, Wilmington, DE 19808-1599, USA