

Bismuth(V) iron(III) tris(phosphate) oxide

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$\text{Bi}_{0.4}^{\text{V}}\text{Fe}_3^{\text{III}}\text{O}(\text{PO}_4)_3$ crystallizes with two Fe atoms (one on an inversion centre and one on a mirror plane) displaying octahedral geometry and a third Fe atom (on a mirror plane) with trigonal bipyramidal coordination. Fe atoms are seen in oxygen-bridged chains. Bi^{V} atoms are found in the interstitial sites between these chains. Bi shows sevenfold coordination, with Bi—O distances between 2.357 (7) and 2.529 (6) Å.

Comment

There have been numerous studies of oxyphosphate structures (Tordjman *et al.*, 1974; Abraham *et al.*, 1994; Mizrahi *et al.*, 1997). In particular, compounds of the type $A^{\text{I}}B^{\text{IV}}\text{OPO}_4$ have been of interest because of their non-linear optical properties (Voloshina *et al.*, 1985; Harrison *et al.*, 1990; Thomas *et al.*, 1990). Structures of the form $A_xB_y\text{O}(\text{XO}_4)_3$, where X is P or Si, A is a mono- or bivalent cation, and B is a trivalent cation, have not appeared widely in the literature. Among those known are $\text{CaLa}_4\text{O}(\text{SiO}_4)_3$ (Schroeder & Mathew, 1978), seen in the hexagonal space group $P6_3/m$, and $\text{Pb}_4\text{BiO}(\text{PO}_4)_3$ (Moore *et al.*, 1982) and $\text{K}_2\text{Bi}_3\text{O}(\text{PO}_4)_3$ (Debreuille-Gresse *et al.*, 1986), both of which crystallize in the orthorhombic space group $Pnma$.

We have also noted that the natural mineral piemontite, $\text{Ca}_2\text{Al}_2M(\text{SiO}_4)_3\text{OH}$ (M is Fe or Mn; Dollase, 1969; Bonazzi *et al.*, 1992), seen in space group $P2_1/m$, resembles compounds of the type $A_xB_y\text{O}(\text{XO}_4)_3$. This structure is characterized by two sites of high coordination occupied by Ca and three octahedral sites occupied by Al and Fe/Mn.

We have prepared a new member of the oxyphosphate family, the title compound, $\text{Bi}_{0.4}^{\text{V}}\text{Fe}_3^{\text{III}}\text{O}(\text{PO}_4)_3$, and determined its single-crystal X-ray structure. Unlike the other known oxyphosphates, this structure crystallizes in the monoclinic space group $P2_1/m$.

Fig. 1 gives a projection view of the structure. The three Fe sites are situated on symmetry elements. Fe1 is found on a centre of symmetry with octahedral geometry [average Fe1—O 2.030 (5) Å]. Fe2 and Fe3 are seen on a mirror plane perpendicular to the b cell edge. Fe2 is octahedrally coordi-

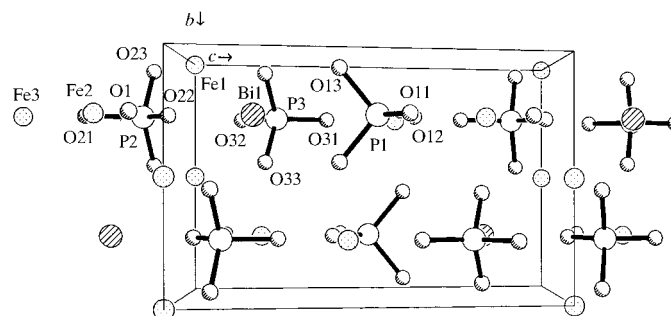


Figure 1
A projection view of $\text{Bi}_{0.4}^{\text{V}}\text{Fe}_3^{\text{III}}\text{O}(\text{PO}_4)_3$ in the (100) plane.

nated [average Fe2—O 2.016 (6) Å], while Fe3 is found to have a trigonal-bipyramidal coordination geometry [average Fe3—O 1.939 (7) Å] (Fig. 2). The environment of Fe3 is different from that of the corresponding atom in $\text{CaLa}_4\text{O}(\text{SiO}_4)_3$, which shows a deformed octahedral geometry.

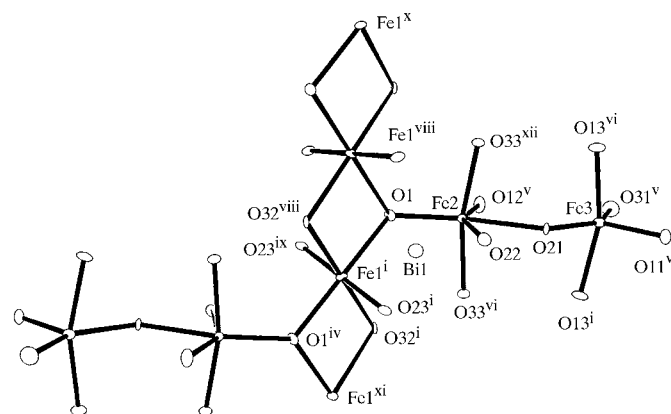


Figure 2
A view of the polymeric Fe array and the bridging O atoms in $\text{Bi}_{0.4}^{\text{V}}\text{Fe}_3^{\text{III}}\text{O}(\text{PO}_4)_3$. Displacement ellipsoids are shown at the 50% probability level [symmetry codes (i), (iv), (v) and (vi) are as in Table 1; (viii) $1+x, y, z$; (ix) $1+x, \frac{1}{2}-y, z$; (x) $1+x, -\frac{1}{2}-y, z$; (xi) $1+x, 1+y, z$; (xii) $1-x, y-\frac{1}{2}, -z$].

Fe1O_6 edge-sharing octahedra form an infinite chain extending in the b direction, with an $\text{Fe1}\cdots\text{Fe1}$ distance of 3.154 (1) Å. The three corner-sharing polyhedra, Fe1O_6 , Fe2O_6 and Fe3O_5 , form a pentamer in the sequence $\text{Fe3}\cdots\text{Fe2}\cdots\text{Fe1}\cdots\text{Fe2}\cdots\text{Fe3}$ [$\text{Fe1}\cdots\text{Fe2}$ 3.418 (1) Å and $\text{Fe2}\cdots\text{Fe3}$ 3.684 (1) Å]. These pentamers are seen perpendicular to the chain formed by the Fe1O_6 octahedra.

The Bi^{V} atoms are found in the interstitial sites between the chains. Bi shows sevenfold coordination, with Bi—O distances of between 2.357 (7) and 2.529 (6) Å.

Atom O1 is the oxide O atom. It is found on a mirror plane parallel to (010) and situated approximately at the centre of a triangle formed by three Fe³⁺ atoms [Fe1 ($\times 2$) and Fe2; Fe1–O1 1.981 (4) Å and Fe2–O1 1.857 (8) Å]. The Fe–O_{oxide} distances are shorter on average than the Fe–O_{phosphate} distances, as would be predicted from the greater negativity of O²⁻. This phenomenon has also been observed in a comparison of the La–O distances in CaLa₄O(SiO₄)₃.

The P–O distances vary between 1.475 (8) and 1.568 (8) Å, and the O–P–O angles between 101.0 (4) and 113.9 (3)°, all of which are comparable with the values seen in phosphates in general.

Experimental

A large quantity of a powder of stoichiometry BiFe₂(PO₄)₃ was heated to the temperature of fusion (1323 K) in a porcelain crucible. The liquified material was held at this temperature for 24 h to obtain a homogeneous mixture and then subjected to slow cooling (5 K h⁻¹) to 1175 K, followed by cooling at a rate of 20 K h⁻¹ to room temperature. Red crystals of the formula Bi_{0.4}Fe₃^{III}O(PO₄)₃ were obtained.

Crystal data

Bi _{0.4} Fe ₃ O(PO ₄) ₃	$D_x = 3.890 \text{ Mg m}^{-3}$
$M_r = 552.04$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 35 reflections
$a = 7.496$ (1) Å	$\theta = 8.5\text{--}13.2^\circ$
$b = 6.308$ (1) Å	$\mu = 12.579 \text{ mm}^{-1}$
$c = 10.125$ (2) Å	$T = 293$ (2) K
$\beta = 100.11$ (1)°	Chunk, red
$V = 471.32$ (13) Å ³	$0.1 \times 0.1 \times 0.1 \text{ mm}$
$Z = 2$	

Data collection

Syntax P4 four-circle diffractometer	$R_{\text{int}} = 0.088$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 30^\circ$
Absorption correction: ψ scan (XEMP; Siemens, 1990a)	$h = -1 \rightarrow 10$
$T_{\text{min}} = 0.244$, $T_{\text{max}} = 0.284$	$k = -1 \rightarrow 8$
2030 measured reflections	$l = -14 \rightarrow 14$
1468 independent reflections	3 standard reflections every 97 reflections
867 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{\text{max}} = 0.056$
$S = 0.835$	$\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{Å}^{-3}$
1468 reflections	$\Delta\rho_{\text{min}} = -0.72 \text{ e } \text{Å}^{-3}$
115 parameters	

We have identified the heavy-atom occupants of the metallic sites by refining their occupancy factors in a prefinal refinement. This has enabled us to establish the identities of the metals in each location and also to eliminate the possibility of shared sites. The anisotropy of

Table 1

Selected geometric parameters (Å).

Bi1–O22	2.357 (7)	Fe3–O11 ⁱⁱⁱ	1.861 (8)
Bi1–O23 ⁱ	2.423 (6)	Fe3–O31 ^v	1.915 (8)
Bi1–O33 ⁱⁱ	2.442 (6)	Fe3–O21	1.951 (7)
Bi1–O13 ⁱⁱⁱ	2.529 (6)	Fe3–O13 ⁱ	1.984 (6)
Fe1–O1 ⁱⁱⁱ	1.981 (4)	P1–O12	1.506 (8)
Fe1–O23	2.005 (5)	P1–O11	1.514 (8)
Fe1–O32	2.104 (5)	P1–O13	1.532 (6)
Fe1–Fe1 ^{iv}	3.1540 (5)	P2–O22	1.520 (8)
Fe2–O1	1.857 (8)	P2–O23	1.531 (6)
Fe2–O12 ^v	1.932 (8)	P2–O21	1.537 (8)
Fe2–O33 ^{vi}	1.985 (6)	P3–O31	1.475 (8)
Fe2–O21	2.154 (7)	P3–O33	1.520 (6)
Fe2–O22	2.183 (8)	P3–O32	1.568 (8)

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

O1 reflects a disorder of this position about the mirror plane and thus the 'looseness' with which the oxo-O atom is bound in the solid.

Data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1990b).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1270). Services for accessing these data are described at the back of the journal.

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