# A new bismuth iron oxyphosphate, $Bi_6(Bi_{0.32}Fe_{0.68})(PO_4)_4O_4$

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Iron was inserted into the known crystal structure of the bismuth phosphate oxide $Bi_{6.67}(PO_4)_4O_4$ to ascertain its location in the vacancies associated with the bismuth ion located at the origin of the unit cell. Single-crystal X-ray diffraction refinements converged to a model of composition $Bi_6(Bi_{0.32}Fe_{0.68})(PO_4)_4O_4$ (hexabismuth iron tetraphosphate tetraoxide), in which Bi and Fe are displaced from the origin giving rise to a random distribution over the $2i$ sites instead of $1a$, the origin of space group $P\bar{1}$. The isotropic displacement parameter for Bi/Fe has a reasonable value in this model. This structure establishes for the first time that Fe substitutes in the Bi-deficient site in this series of materials and that Fe and Bi are disordered around the center of symmetry. These results enhance understanding of the crystal chemistry of these main group phosphates that are of interest in ion transport.

## Comment

Recently, the crystal structure of a pillared lithium bismuth phosphate, $LiBi_{7.37}P_3O_{19}$, was described in which Li is incorporated in an interstitial tetrahedral site by four O atoms (Arumugam *et al.*, 2007). Preliminary experiments indicated that no $Li^+$ transport occurs in this compound. We attempted to substitute $Fe^{2+}$ into the structure, hoping that any charge deficiency would be balanced by additional introduction of Li into the structure. The synthesis of a putative $Li_2Bi_{7.37-x}Fe_xP_3O_{19}$ from stoichiometric mixtures in the ratio 3:8:6:5 of $Li_2CO_3$, $NH_4H_2PO_4$, $Bi_2O_3$ and metallic Fe, respectively, by the standard ceramic technique led to single crystals that were eventually identified as isostructural with $Bi_{6.67}(PO_4)_4O_4$ (Ketatni *et al.*, 1998; Giraud *et al.*, 2000). The single-crystal X-ray diffraction refinement of the crystal structure of $Bi_{6.67}(PO_4)_4O_4$ (Ketatni *et al.*, 1998) showed that the site occupancy of the Bi4 atom at the origin was less than unity, 0.67 (6), and the equivalent isotropic displacement parameter was large, 3.44 (6) $Å^2$ ($U_{eq} = 0.044$ $Å^2$). The authors also

reported the unit-cell parameters of phases containing Li, Na, K, Sr, Cd, Ca and Pb, where the substituents were placed into the site containing the vacancy, *viz.* $Bi_{6.5}A_{0.5}^+$ and $Bi_6M^{2+}$. Giraud *et al.*, (2000) investigated several of these phases, including $PbBi_6(PO_4)_4O_4$, using Rietveld refinement of X-ray diffraction data and reported that Pb completely replaced Bi at the origin. However, its isotropic displacement parameter was large.

A single crystal was selected from the product and X-ray fluorescence spectroscopy showed the presence of iron. We decided, therefore, to subject this crystal to a complete structure determination to clarify the location of Fe and to see whether the anomalously large displacement parameter of the occupant atom at the origin position could be due to disorder. We report the result here.

The crystal structure of $Bi_{6.67}(PO_4)_4O_4$ has previously been described by Ketatni *et al.* (1998) and Giraud *et al.* (2000). Using the reported atomic parameters, our absorption-corrected intensities and anisotropic displacement parameters except for O atoms, and placing Fe1 together with Bi4 into the (0, 0, 0) position with the sum of the site occupancies for these two atoms restrained to 0.5, the least-squares refinements converged to $R_1 = 0.093$. However, in this final result the restraint failed (disagreeable restraint), the isotropic displacement parameter for Fe1/Bi4 became large, $U_{eq} = 0.060$ (4) $Å^2$, and the displacement parameters for P1 and P2 were nonpositive definite. Difference electron densities also indicated that these atoms were displaced from the origin. The atomic positions for Fe1 and Bi4 were permitted to vary in the next cycles of refinement, but the isotropic displacement parameters were restrained to remain equal; $R_1$ converged to 0.0364 with a Bi4 occupancy of 0.155 (6) and an Fe1 occupancy of 0.347 (15), leading to the stoichiometry $Bi_{6.32}Fe_{0.68}P_4O_{20}$ or $Bi_6(Bi_{0.32}Fe_{0.68})(PO_4)_4O_4$. Fig. 1 shows the unit cell with Fe1 displaced slightly from the origin; atom Bi4 that shares a nearby site has been omitted for the sake of clarity. The
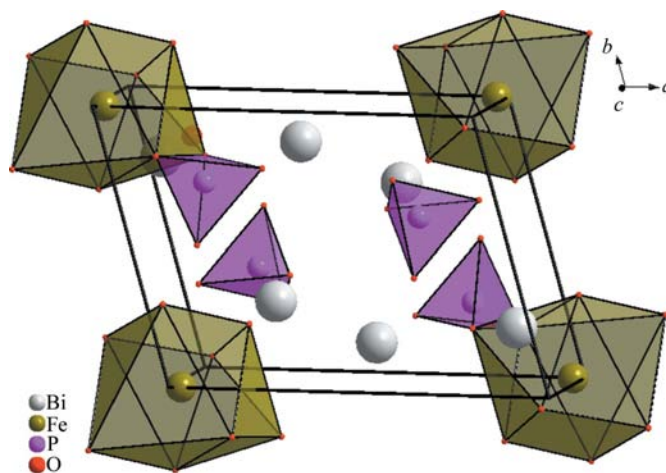


**Figure 1**
A view of the crystal structure of $Bi_6(Bi_{0.32}Fe_{0.68})(PO_4)_4O_4$ along [001]. The disordered Bi4 site near the origin has been omitted for clarity.
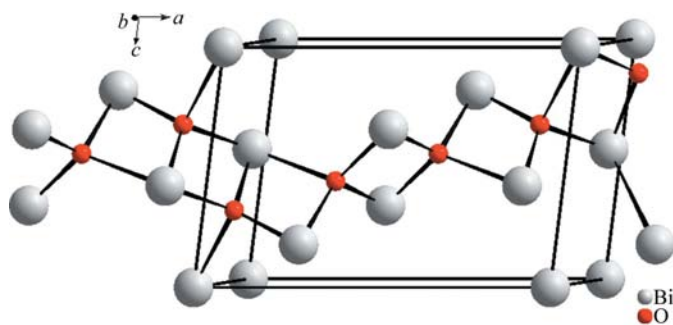
# inorganic compounds



**Figure 2**
A view of the zigzag $Bi_2O_2$ infinite chains in the *ac* plane.

coordination polyhedron around this site consists of eight O atoms in a distorted cubic arrangement. The two crystallographically distinct $PO_4$ tetrahedra are isolated but share an edge with the oxygen coordination polyhedron around the origin. The $Bi_2O_2$ chains that are so characteristic of these structures (Colmont *et al.*, 2008; Arumugam *et al.*, 2008; Abraham *et al.*, 2002) are present here as well. A corrugated chain of $Bi_2O_2$ exists in the *ac* plane (Fig. 2). The substitution of isovalent and aliovalent ions occurs in the Bi4 site containing the vacancies in the parent compound. If this site is completely occupied by Bi or a mixture of cations, it is likely that small oxygen variations in the stoichiometry required for charge balance occur among these O atoms.

## Experimental

The title compound, $Bi_6(Bi_{0.32}Fe_{0.68})(PO_4)_4O_4$, was synthesized by the ceramic method by reacting a mixture of analytical grade $Li_2CO_3$, $NH_4H_2PO_4$ and $Bi_2O_3$ and metallic Fe in the molar ratio 3:8:6:5. Prior to use, $Bi_2O_3$ was dried in air at 873 K for 24 h in order to remove any moisture or carbonates associated with it. The mixture was initially heated in air at 468 K for 2 h to decompose $NH_4H_2PO_4$ and finally at 973 K for 12 h in alumina crucibles. The intermediate product was then ground and reheated in air at 1100 K for 1 h in a gold boat and further heated to 1173 K and annealed at that temperature for about 14 h. Green–yellow single crystals of this pure phase were obtained by cooling the reaction mixture from 1173 to 1073 K at a rate of 5 K h$^{-1}$ and then furnace-cooling to room temperature. The phase purity was determined from the powder diffraction pattern and was nearly 100%. A few very weak reflections barely visible above background were not indexed with the single-crystal lattice parameters.

### Crystal data

| | |
|---|---|
| $Bi_6(Bi_{0.32}Fe_{0.68})(PO_4)_4O_4$ | $\gamma = 106.95\,(3)°$ |
| $M_r = 1801.1$ | $V = 414.2\,(2)$ Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z = 1$ |
| $a = 9.2097\,(18)$ Å | Mo $K\alpha$ radiation |
| $b = 7.5214\,(15)$ Å | $\mu = 67.86$ mm$^{-1}$ |
| $c = 6.9033\,(14)$ Å | $T = 293\,(2)$ K |
| $\alpha = 112.48\,(3)°$ | $0.03 \times 0.01 \times 0.01$ mm |
| $\beta = 93.71\,(3)°$ | |

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Bi1—O4 | 2.083 (9) | Bi3—O2$^{iii}$ | 3.067 (10) |
| Bi1—O9$^{i}$ | 2.965 (9) | Bi4—O1$^{iv}$ | 2.291 (11) |
| Bi2—O4$^{ii}$ | 2.227 (9) | Bi4—O4$^{v}$ | 2.999 (11) |
| Bi2—O5 | 2.760 (9) | Fe1—O2$^{vi}$ | 2.332 (16) |
| Bi3—O7$^{ii}$ | 2.177 (8) | Fe1—O3$^{iv}$ | 2.779 (15) |

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

### Data collection

| | |
|---|---|
| Nonius KappaCCD diffractometer | 6043 measured reflections |
| Absorption correction: numerical (*EUHEDRAL*; Spek, 2006; de Meulenaer & Tompa, 1965) | 1855 independent reflections |
| | 1600 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.053$, $T_{max} = 0.403$ | $R_{int} = 0.081$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | 96 parameters |
| $wR(F^2) = 0.097$ | 1 restraint |
| $S = 1.11$ | $\Delta\rho_{max} = 4.10$ e Å$^{-3}$ |
| 1600 reflections | $\Delta\rho_{min} = -2.90$ e Å$^{-3}$ |

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

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