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A new pillared lithium bismuth phosphate, $LiBi_{7.37}P_3O_{19}$, with elliptical channels

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The structure of a new lithium bismuth phosphate, $LiBi_{7.37}P_3O_{19}$, consists of infinite OBi_4 edge-sharing tetrahedral chains in the *ac* plane, which form Bi_2O_2 layers parallel to the *b* axis. They are sandwiched between PO_4 tetrahedral and Bi polyhedral layers. The PO_4–Bi–PO_4 layers are bridged by columns formed by one Bi polyhedron flanked on each side by LiO_4 tetrahedra. This bridging Bi atom lies on a twofold axis, special position 4*e* of the *C*2/*c* space group. This arrangement creates pillared open elliptical channels parallel to [010].

Comment

The discovery of the oxygen ion conductor $Bi_4V_2O_{11}$ (Abraham *et al.*, 1988) initiated an intensive sequence of research on compounds in complex phase space formed by Bi–Pb–transition metal phosphates, arsenates and vanadates (Steinfink *et al.*, 2005; Steinfink & Lynch, 2004; Arumugam *et al.*, 2007; Giraud *et al.*, 2003; Cousin *et al.*, 2002; Roussel *et al.*, 2002). The structural motif of many of these compounds is related to the δ-Bi_2O_3 and CaF_2 structures, where the metals occupy the Bi or Ca sites and O atoms form irregular polyhedra around them. The structures usually consist of edge-sharing OBi_4 tetrahedra that articulate into chains and planes, which are linked by PO_4 tetrahedra and transition metal octahedra into a three-dimensional network (Abraham *et al.*, 2002). The polyhedra are distorted by the presence of nonbonding $6s^2$ electrons on Bi. Aliovalent metal substitutions give rise to oxygen vacancies, thus opening pathways for the transport of ions (Giraud *et al.*, 2003). Many structures are pseudocentrosymmetric because the metal ions are in nearly centrosymmetric sites, but oxygen ions frequently destroy this arrangement. The compositions are nonstoichiometric, subject to extensive formations of solid solutions, twinning, and the formation of commensurate and incommensurate superstructures. Only two lithium bismuth phosphates, *viz.* $LiBi_4O_5(PO_4)$ and $Li_3Bi_2(PO_4)_3$, have been reported, characterized only by X-ray powder diffraction (Berul, 1971). Recently, the crystal structure of $Bi_{4.25}(PO_4)_2O_{3.375}$ was reported, which also displays a CaF_2-related structure (Muktha & Guru Row, 2006). It appeared to us that this structure might be able to intercalate lithium ions and we prepared a mixture of Li_2CO_3, Bi_2O_3 and $NH_4H_2PO_4$. Green–yellow single crystals were found in the annealed reaction mixture formed from these precursors and were used for the crystal structure determination. We report here the crystal structure of a new lithium bismuth phosphate.

The structure, viewed parallel to [010], is shown in Fig. 1. It displays the formation of infinite Bi_2O_2 chains perpendicular to [010], formed by the edge-sharing OBi_4 tetrahedra that are observed in so many of these structures (Abraham *et al.*, 2002). The Bi_2O_2 chains in the *ac* plane form layers parallel to the *b* axis and are sandwiched between PO_4 tetrahedral and Bi6 and Bi7 polyhedral layers. The PO_4–Bi–PO_4 layers are bridged by columns formed by Bi8 polyhedra flanked on each side by LiO_4 tetrahedra. This arrangement creates pillared, open, elliptical channels parallel to [010] (Fig. 2). Atoms Bi6 and Bi7 are in rectangular-pyramidal coordination to O atoms at distances ranging from 2.04 (1) to 2.75 (3) Å. The coordination polyhedron formed by eight O atoms around atom Bi8

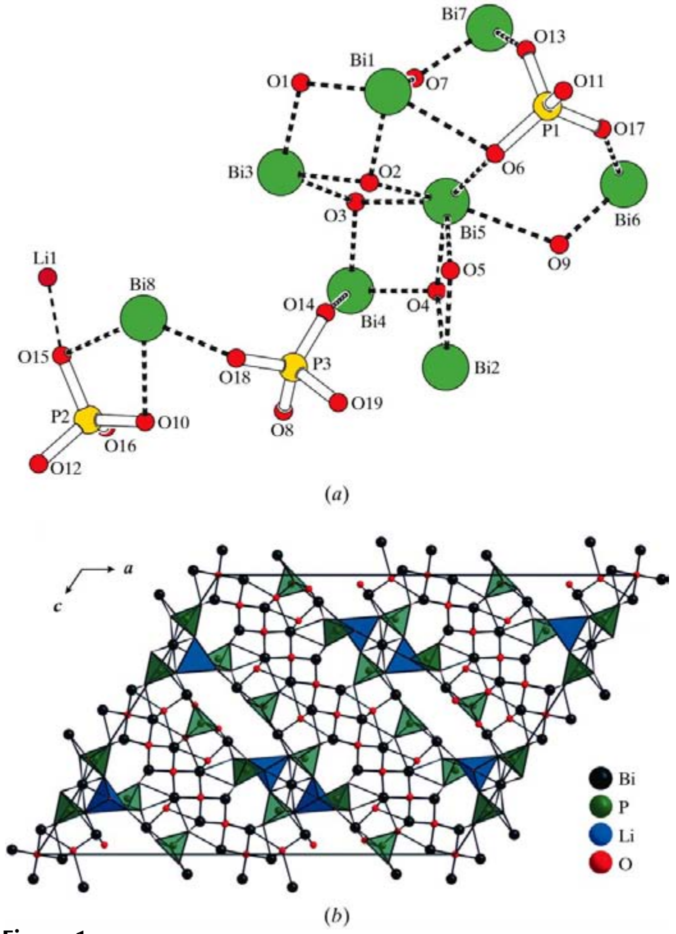

Figure 1
(*a*) A view of the asymmetric unit of $LiBi_{7.3}P_3O_{19}$, parallel to the *b* axis, showing the atomic labeling scheme. (*b*) The complete unit cell.

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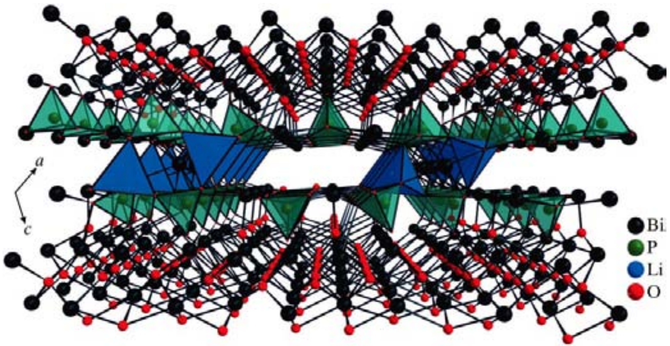

Figure 2
An in-depth view of the structure of $LiBi_{7.3}P_3O_{19}$, parallel to the *b* axis, emphasizing the elliptical channels and Bi_2O_2 layers.

at distances ranging from 2.34 (3) to 2.78 (3) Å can best be described as a distorted bicapped trigonal prism. The bases of the tetrahedra and pyramids form the walls of the channels and the Bi8–Li–O columns form the pillars. The Li ions are part of the columnar pillars and would not be expected to be mobile. However, it is reasonable to expect that ion transport might occur through these channels. Such experiments are in progress. As mentioned above, irregular coordination polyhedra around Bi have been described in related structures and are attributed to the nonbonding $6s^2$ electrons (Giraud *et al.*, 2000).

The displacement parameter for atom Bi8 was anomalously large. Refinement of the site-occupation factor showed that atom Bi8 is present 92% of the time. The anisotropic displacement parameters for Bi are disk-shaped, with the disk nearly perpendicular to [001]. The displacement parameters for atoms O15–O19, all in PO_4 tetrahedra, are larger than those for the other oxygen ions. Similarly, atom P3 has a larger displacement value than the other two P atoms. Atom P3 can be modeled as disordered over closely adjacent sites, but in the final refinement, averaged positional parameters were used. This explains the large displacements of atoms O18 and O19. Atoms O15–O17 are part of the P1 and P2 tetrahedra, and it is likely that these may have a large value of libration (Giraud *et al.*, 2003). The P—O bond lengths range from 1.487 (17) to 1.598 (18) Å and the Li—O bonds range from 1.86 (5) to 2.12 (5) Å, while selected Bi—O bond lengths are shown in Table 1.

Experimental

Lithium bismuth phosphate, $Li_4Bi_{17}P_8O_{152}$, was synthesized by the ceramic method by reacting a mixture of analytical grade Bi_2O_3, $NH_4H_2PO_4$ and Li_2CO_3. The precursors were mixed to yield a putative lithium-containing phase with a Bi:P:Li ratio of 17:8:4. 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 873 K for 12 h in alumina crucibles. The intermediate product was then ground, reheated in air at 1103 K for 1 h in a gold boat, and further heated to 1163 K and annealed at that temperature for about 12 h. Green–yellow single crystals of a new phase were obtained by cooling the reaction mixture from 1163 to 1073 K at a rate of 5 K h^{-1} and then furnace cooling to room temperature. The product was analyzed by inductively coupled plasma optical emission spectroscopy, yielding a Bi:Li ratio of 6.73:1.2 on the basis of three stoichiometric P atoms.

Crystal data

$LiBi_{7.37}P_3O_{19}$
$M_r = 15548.92$
Monoclinic, $C2/c$
$a = 30.796\ (6)$ Å
$b = 5.2836\ (11)$ Å
$c = 24.594\ (5)$ Å
$\beta = 122.87\ (3)^\circ$
$V = 3361.1\ (16)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 77.25$ mm^{-1}
$T = 293\ (2)$ K
0.10 × 0.05 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: numerical (*SADABS*; Sheldrick, 2007)
$T_{min} = 0.022$, $T_{max} = 0.145$
3845 measured reflections
3337 independent reflections
3337 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.134$
$S = 1.17$
3337 reflections
164 parameters
19 restraints
$\Delta\rho_{max} = 8.81$ e Å^{-3}
$\Delta\rho_{min} = -4.55$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Bi1—O1	2.211 (11)	Bi5—O6^{ii}	2.947 (12)
Bi1—O6	2.760 (13)	Bi6—O9	2.044 (15)
Bi2—O4	2.212 (11)	Bi6—O11^{ii}	2.556 (13)
Bi2—O19	2.93 (2)	Bi7—O7	2.055 (16)
Bi3—O1^{i}	2.226 (11)	Bi7—O18^{iii}	3.04 (2)
Bi3—O7^{i}	2.843 (14)	Bi8—O16^{iv}	2.34 (3)
Bi4—O4	2.219 (11)	Bi8—O18	2.33 (2)
Bi4—O14	2.676 (17)	Bi8—O10	2.630 (15)
Bi5—O5	2.214 (11)	Bi8—O15	2.79 (3)

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

Bi8, which is in the special position 4*e*, showed anomalously large displacement parameters and the occupancy factor refinement converged to 0.368 (3). With anisotropic displacement parameters only for Bi, the final *R*1 value was 0.049. The stoichiometry based on the structure determination is $LiBi_{7.3}P_3O_{19}$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3091). Services for accessing these data are described at the back of the journal.

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