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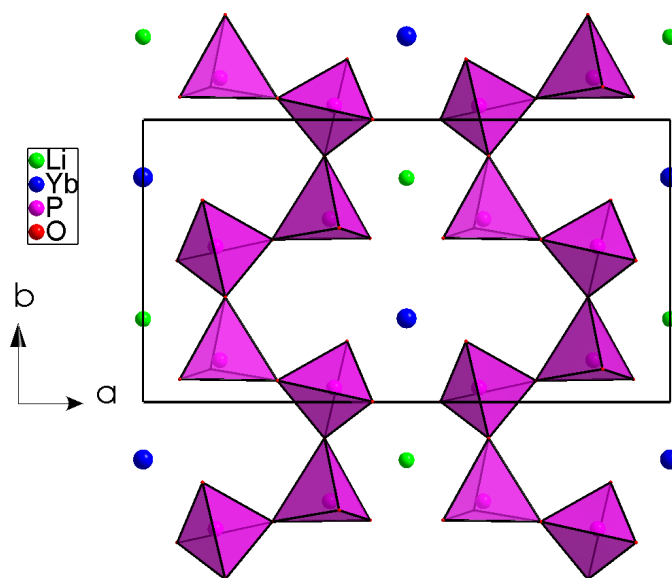
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The structure of the lithium ytterbium polyphosphate LiYb(PO<sub>3</sub>)<sub>4</sub> is described. It consists of a three-dimensional framework made up of spiral (PO<sub>3</sub>)<sub>n</sub> chains linked by YbO<sub>8</sub> polyhedra. The Li<sup>+</sup> cations reside in the tunnels delimited by the framework. The structure is compared with that of some other compounds like LiNd(PO<sub>3</sub>)<sub>4</sub>, NaNd(PO<sub>3</sub>)<sub>4</sub>, KNd(PO<sub>3</sub>)<sub>4</sub>, RbNdP<sub>4</sub>O<sub>12</sub> and Yb(PO<sub>3</sub>)<sub>3</sub>.

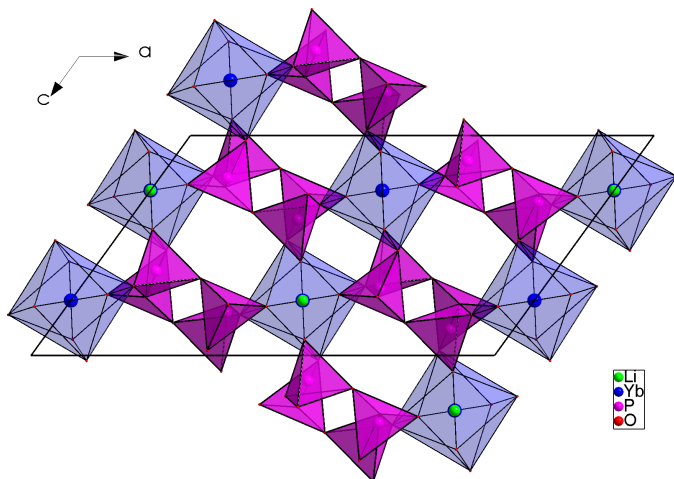
Received 6 July 2004  
Accepted 14 July 2004  
Online 24 July 2004**Key indicators**Single-crystal X-ray study  
*T* = 293 K  
Mean  $\sigma$ (P–O) = 0.003 Å  
*R* factor = 0.018  
*wR* factor = 0.047  
Data-to-parameter ratio = 11.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**Comment**

Mixed polyphosphates involving both alkaline and lanthanide cations are of particular importance because of the laser properties they may exhibit (Yamada *et al.*, 1974). In order to discover new materials with interesting optical properties, we have undertaken the study of the Li<sub>2</sub>O–Yb<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> system and have isolated the title compound, LiYb(PO<sub>3</sub>)<sub>4</sub>.

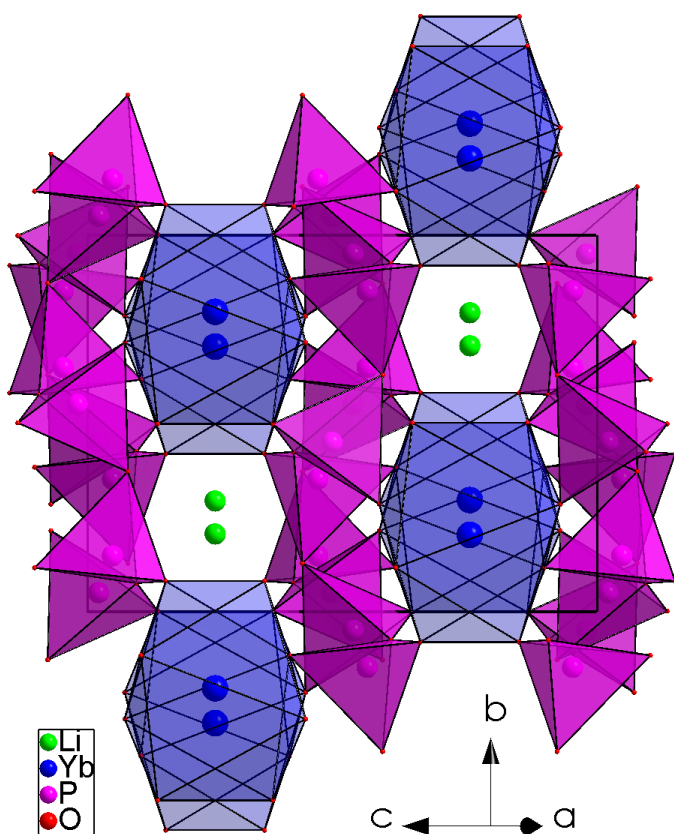
As reported in the literature, polyphosphates with the general formula LiLn(PO<sub>3</sub>)<sub>4</sub> [Ln = La (Ferid *et al.*, 1981), Ce (Rzaigui & Ariguib, 1981), Pr (Ferid *et al.*, 1998), Sm (Ferid *et al.*, 1984) and Er (Liu & Li, 1983)] are isotopic to LiNd(PO<sub>3</sub>)<sub>4</sub> (Hong, 1975*a*), which is the prototype. Although LiYb(PO<sub>3</sub>)<sub>4</sub> and LiNd(PO<sub>3</sub>)<sub>4</sub> crystallize in the monoclinic system (space group *C2/c*) and have similar unit-cell parameters, some details, especially the position of the Li atoms, make their structures distinctive. In fact, while in LiNd(PO<sub>3</sub>)<sub>4</sub> the Li<sup>+</sup> cations are located on the 4(*a*) site, they are clearly found by Fourier difference syntheses at the 4(*e*) site in the present



**Figure 1**  
Projection of the LiYb(PO<sub>3</sub>)<sub>4</sub> structure along the *c* direction, showing the alternation of the (PO<sub>3</sub>)<sub>n</sub> chains with the rows of Li<sup>+</sup> and Yb<sup>3+</sup>. [(PO<sub>3</sub>)<sub>n</sub> chains and cationic rows of Li<sup>+</sup> and Yb<sup>3+</sup> generated by centers of symmetry are not shown.]



**Figure 2**  
Projection of the  $\text{LiYb}(\text{PO}_3)_4$  structure along the  $\mathbf{b}$  direction, showing the association of the  $\text{YbO}_8$  polyhedra with the  $(\text{PO}_3)_n$  chains.



**Figure 3**  
Projection of the  $\text{LiYb}(\text{PO}_3)_4$  structure along the  $[101]$  direction, showing tunnels where  $\text{Li}^+$  cations are located.

structure. In both compounds, the Li atoms are tetra-coordinated, but the geometry of their coordination polyhedra is quite different. In  $\text{LiYb}(\text{PO}_3)_4$  the Li atom is situated within a distorted tetrahedron, with  $\text{O}-\text{Li}-\text{O}$  angles ranging between  $81.8$  (5) and  $127.0$  (1) $^\circ$ , whereas in  $\text{LiNd}(\text{PO}_3)_4$ , it is located at the center of a parallelogram. On the basis of symmetry and bonding considerations, the  $4(e)$  site appears more suitable for the Li atom than the  $4(a)$  site.

In  $\text{LiYb}(\text{PO}_3)_4$ , the  $\text{PO}_4$  tetrahedra share corners to produce infinite helical chains running along the  $\mathbf{b}$  direction.  $(\text{PO}_3)_n$  chains alternate with  $-\text{Yb}^{3+}-\text{Li}^+$  rows (Fig. 1). Their period is four  $\text{PO}_4$  tetrahedra, as in the structures of the polyphosphates  $\text{NaNd}(\text{PO}_3)_4$  (Koizumi, 1976) and  $\text{KNd}(\text{PO}_3)_4$  (Hong, 1975*b*). However, they lie along the  $\mathbf{c}$  direction in  $\text{NaNd}(\text{PO}_3)_4$  and in the  $\mathbf{a}$  direction in  $\text{KNd}(\text{PO}_3)_4$ . The alternation of the polyphosphate anions  $(\text{PO}_3)_4^{4-}$  with the rows of  $\text{Yb}^{3+}$  and  $\text{Li}^+$  cations in  $\text{LiYb}(\text{PO}_3)_4$  resembles that of the  $\text{P}_4\text{O}_{12}$  rings with the rows of  $\text{Nd}^{3+}$  and  $\text{Rb}^+$  cations in the cyclotetraphosphate  $\text{RbNdP}_4\text{O}_{12}$  (Koizumi & Nakano, 1977). On the twofold axes,  $\text{Li}^+$  and  $\text{Yb}^{3+}$  ions are arranged alternately at almost equal spacings (3.496 and 3.528 Å), compared with the quite different spacings of  $\text{Rb}^+$  and  $\text{Nd}^{3+}$  (3.914 and 8.777 Å) in the  $\text{RbNdP}_4\text{O}_{12}$  structure. In the title compound, the Yb atoms are octacoordinated. Each  $\text{YbO}_8$  polyhedron shares its O atoms with four adjacent  $(\text{PO}_3)_n$  chains (Fig. 2). The resulting three-dimensional framework delimits tunnels running along the  $[101]$  direction where  $\text{Li}^+$  cations are located (Fig. 3). The ytterbium coordination polyhedra are isolated from one another, as in  $\text{Yb}(\text{PO}_3)_3$  (Hong, 1974). The structures of  $\text{LiYb}(\text{PO}_3)_4$  and  $\text{Yb}(\text{PO}_3)_3$  display shorter  $\text{Yb}\cdots\text{Yb}$  distances of 5.545 and 5.610 Å, respectively. In  $\text{LiYb}(\text{PO}_3)_4$ , the average values of the  $\text{P1}-\text{O}$ ,  $\text{P2}-\text{O}$ ,  $\text{Li}-\text{O}$  and  $\text{Yb}-\text{O}$  distances are 1.544, 1.540, 1.982 and 2.363 Å, respectively. These values are close to those quoted in the literature (Hong & Pierce, 1974; International Tables for X-ray Crystallography, 1968, Vol. III). Bond-valence-sum values (Brown & Altermatt, 1985) are 4.92, 4.98, 0.99 and 2.81 for P1, P2, Li and Yb, respectively, and are consistent with the cation charges.

## Experimental

The synthesis was carried out by a solid-state reaction with the starting materials  $\text{Li}_2\text{CO}_3$  (Fluka, 99%),  $\text{Yb}_2\text{O}_3$  (Prolabo, 99.9%) and  $(\text{NH}_4)_2\text{HPO}_4$  (Fluka, 99%) in a 4:1:15 molar ratio. These ingredients, finely ground, were first heated at 673 K for 5 h and then kept for three weeks at 918 K. A progressive cooling down to 673 K (15 K  $\text{h}^{-1}$ ) followed by a further cooling to room temperature (100 K  $\text{h}^{-1}$ ) led to crystals of  $\text{LiYb}(\text{PO}_3)_4$ .

### Crystal data

$\text{LiYb}(\text{PO}_3)_4$   
 $M_r = 495.86$   
Monoclinic,  $C2/c$   
 $a = 16.194$  (3) Å  
 $b = 7.024$  (1) Å  
 $c = 9.498$  (2) Å  
 $\beta = 125.91$  (1) $^\circ$   
 $V = 875.0$  (3) Å $^3$   
 $Z = 4$

$D_x = 3.764$  Mg  $\text{m}^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 10.0$ – $16.0$  $^\circ$   
 $\mu = 11.49$   $\text{mm}^{-1}$   
 $T = 293$  (2) K  
Prism, colorless  
 $0.18 \times 0.18 \times 0.14$  mm

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.114$ ,  $T_{\max} = 0.189$   
1009 measured reflections  
950 independent reflections  
934 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$   
 $\theta_{\text{max}} = 27.0$  $^\circ$   
 $h = -16 \rightarrow 20$   
 $k = 0 \rightarrow 8$   
 $l = -12 \rightarrow 0$   
2 standard reflections  
frequency: 120 min  
intensity decay: 1%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.047$   
 $S = 1.17$   
 950 reflections  
 84 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 9.6931P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.10 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.36 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0041 (2)

**Table 1**  
 Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Li—O2	1.980 (9)	P1—O6 <sup>v</sup>	1.500 (3)
Li—O6 <sup>i</sup>	1.984 (9)	P1—O4 <sup>vi</sup>	1.590 (3)
Yb—O3 <sup>ii</sup>	2.259 (3)	P1—O5 <sup>vii</sup>	1.595 (3)
Yb—O1	2.314 (3)	P2—O3	1.486 (3)
Yb—O2 <sup>iii</sup>	2.383 (3)	P2—O2	1.487 (3)
Yb—O6 <sup>iv</sup>	2.496 (3)	P2—O5	1.585 (3)
P1—O1	1.491 (3)	P2—O4	1.601 (3)
O1—P1—O6 <sup>v</sup>	118.6 (2)	O3—P2—O2	120.0 (2)
O1—P1—O4 <sup>vi</sup>	106.9 (2)	O3—P2—O5	111.8 (2)
O6 <sup>v</sup> —P1—O4 <sup>vi</sup>	110.7 (2)	O2—P2—O5	108.2 (2)
O1—P1—O5 <sup>vii</sup>	111.8 (2)	O3—P2—O4	109.7 (2)
O6 <sup>v</sup> —P1—O5 <sup>vii</sup>	105.0 (2)	O2—P2—O4	104.3 (2)
O4 <sup>vi</sup> —P1—O5 <sup>vii</sup>	102.7 (2)	O5—P2—O4	100.9 (2)

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

The highest peak in the final difference map is 0.90  $\text{\AA}$  from Yb and the deepest hole is 0.89  $\text{\AA}$  from Yb.

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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