

produced a comparable  $T_{\max}/T_{\min}$  ratio. The structure was solved by Patterson methods and *DIRDIF92* (Beurskens *et al.*, 1992). The position of the H atom was deduced from difference Fourier maps. Structure refinement was performed using *TEXSAN* (Molecular Structure Corporation, 1992). Graphics were produced using *ORTEPII* (Johnson, 1976) and *CHARON* (Lauher, 1989). All computations were performed on an IRIS INDIGO.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## KYP<sub>4</sub>O<sub>12</sub>

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## Abstract

Potassium yttrium cyclotetraphosphate is isostructural with RbNdP<sub>4</sub>O<sub>12</sub>. The structure is built up from P<sub>4</sub>O<sub>12</sub><sup>4-</sup> cyclotetraphosphate anions linked by YO<sub>8</sub> polyhedra to form a three-dimensional framework, which delimits intersecting tunnels in which the K<sup>+</sup> ions are located. The P<sub>4</sub>O<sub>12</sub> ring anion is centrosymmetric.

## Comment

The cyclotetraphosphates corresponding to the general formula  $M^I\text{LnP}_4\text{O}_{12}$  are well known (Hong, 1975*a,b*; Koizumi, 1976*a*; Koizumi & Nakano, 1978; Averbuch-Pouchot & Durif, 1983; Durif, Averbuch-Pouchot & Guitel, 1983). The compounds obtained for  $M^I = \text{K}$  and  $\text{Ln} = \text{Sm}$ ,  $M^I = \text{Rb}$  and  $\text{Ln} = \text{Nd}$ , and  $M^I = \text{NH}_4$  and  $\text{Ln} = \text{Pr}$  and  $\text{Nd}$ , are isostructural (Ferid, Ariguib & Trabelsi, 1987; Koizumi & Nakano, 1977; Masse, Guitel & Durif, 1977). The title compound is isostructural with the compounds of this series. In the present work we report its chemical preparation and structural investigation.

This structure contains the centrosymmetrical cyclotetraphosphate ring anion P<sub>4</sub>O<sub>12</sub><sup>4-</sup>. As shown in the projection onto the *ab* plane, the P<sub>4</sub>O<sub>12</sub> rings form layers perpendicular to the *c* axis at  $z = 0$  and  $1/2$ . The YO<sub>8</sub> polyhedra interconnect the P<sub>4</sub>O<sub>12</sub> rings to form a three-dimensional framework. This disposition creates intersecting tunnels in which the K atoms reside. All the K<sup>+</sup> and Y<sup>3+</sup> ions are located on twofold axes in the  $z = 1/4$  and  $z = 3/4$  planes. The coordination around the Y atom forms a lozenge antiprism which shares its two lozenge faces with two neighbouring KO<sub>10</sub> polyhedra. The YO<sub>8</sub> polyhedra are isolated from one another since they do not share any O atoms. This type of isolation appears responsible for the good fluorescence properties shown in lanthanide compounds, such as those of the series  $M^I\text{NdP}_4\text{O}_{12}$  ( $M^I = \text{Li}$ ,  $\text{Na}$  and  $\text{K}$ ) (Otsuka, Miyazawa, Yamada, Iwasaki & Nakano, 1977; Chinn & Hong, 1975; Tsujimoto, Fukuda & Fukai, 1977; Tofield, Weber, Damen & Liao, 1975). The shortest Y...Y distance [5.978(1) Å] has a value between those of the corresponding Nd...Nd distances in NaNdP<sub>4</sub>O<sub>12</sub> (5.719 Å) (Koizumi, 1976*b*) and RbNdP<sub>4</sub>O<sub>12</sub> (6.129 Å). The structures of KYP<sub>2</sub>O<sub>7</sub> (Hamady, Zid & Jouini, 1994) and the related compound RbYP<sub>2</sub>O<sub>7</sub> (Akrim, Zambon, Metin & Cousseins, 1993) display shorter Y...Y distances of 5.423 and 5.30 Å, respectively. In the KO<sub>10</sub> polyhedron, the K—O distances exhibit a

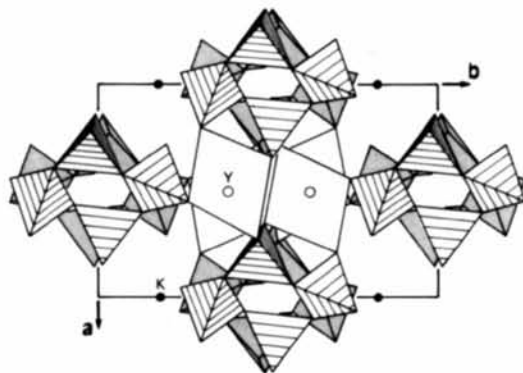


Fig. 1. The KYP<sub>4</sub>O<sub>12</sub> structure projected along the *c* axis showing the P<sub>4</sub>O<sub>12</sub> rings.

wide range (2.73–3.37 Å). The average value of 3.06 Å is slightly lower than that of 3.15 Å found for the analogous coordination of Rb in RbNdP<sub>4</sub>O<sub>12</sub> (range 2.86–3.52 Å).

**Experimental**

The title compound was prepared by a flux method. At room temperature, 4 g of KH<sub>2</sub>PO<sub>4</sub> and 0.5 g of Y<sub>2</sub>O<sub>3</sub> were slowly added to 5 ml of monophosphoric acid (85%). The mixture was then slowly heated to 873 K and kept at this temperature for 24 h. Elongated irregular prisms of KYP<sub>4</sub>O<sub>12</sub> were separated from the excess phosphoric flux by washing the product in boiling water.

*Crystal data*

KYP<sub>4</sub>O<sub>12</sub>  
*M<sub>r</sub>* = 443.89  
 Monoclinic  
*C*2/*c*  
*a* = 7.8067 (6) Å  
*b* = 12.3221 (10) Å  
*c* = 10.4078 (10) Å  
 $\beta$  = 111.174 (7)°  
*V* = 933.59 (14) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 3.158 Mg m<sup>-3</sup>

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 14–16°  
 $\mu$  = 7.47 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism  
 0.10 × 0.05 × 0.02 mm  
 Colourless

*Data collection*

CAD-4 diffractometer  
 $\omega/2\theta$  scans [width (0.80 + 0.35 tan  $\theta$ )°]  
 Absorption correction: none  
 880 measured reflections  
 832 independent reflections  
 778 observed reflections  
 [*I* > 2 $\sigma$ (*I*)]

*R<sub>int</sub>* = 0.0262  
 $\theta_{\max}$  = 24.97°  
*h* = -9 → 8  
*k* = 0 → 14  
*l* = 0 → 12  
 2 standard reflections  
 frequency: 120 min  
 intensity decay: 1%

*Refinement*

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.0264  
*wR*(*F*<sup>2</sup>) = 0.0648  
*S* = 1.138  
 832 reflections  
 83 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 2.2124P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> = 0.093  
 $\Delta\rho_{\max}$  = 0.637 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.624 e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Y	0	0.11940 (4)	1/4	0.0064 (2)
K	0	0.1842 (1)	3/4	0.0384 (5)
P1	0.281 (1)	0.02344 (7)	0.05977 (9)	0.0068 (2)
P2	0.4579 (1)	0.17090 (7)	0.5033 (1)	0.0071 (2)
O(E11)	0.2198 (3)	0.0291 (2)	0.1775 (3)	0.0112 (6)
O(E12)	0.1462 (4)	0.0106 (2)	-0.0827 (3)	0.0115 (6)

O(L1)	0.4017 (4)	0.1288 (2)	0.0663 (3)	0.0121 (6)
O(L2)	0.4317 (3)	0.0709 (2)	0.5897 (3)	0.0100 (6)
O(E21)	0.2880 (3)	0.1992 (2)	0.3863 (3)	0.0108 (6)
O(E22)	0.5560 (4)	0.2572 (2)	0.6020 (3)	0.0123 (6)

Table 2. Selected geometric parameters (Å, °)

Y—O(E22) <sup>i</sup>	2.315 (3)	K—O(E11) <sup>iii</sup>	3.370 (3)
Y—O(E22) <sup>ii</sup>	2.316 (3)	K—O(E11) <sup>x</sup>	3.370 (3)
Y—O(E12) <sup>iii</sup>	2.338 (3)	P1—O(E11)	1.469 (3)
Y—O(E12) <sup>iv</sup>	2.338 (3)	P1—O(E12)	1.484 (3)
Y—O(E11) <sup>v</sup>	2.385 (3)	P1—O(L1)	1.592 (3)
Y—O(E11)	2.385 (3)	P1—O(L2) <sup>xi</sup>	1.602 (3)
Y—O(E21)	2.394 (3)	P2—O(E21)	1.482 (3)
Y—O(E21) <sup>v</sup>	2.394 (3)	P2—O(E22)	1.485 (3)
K—O(E12) <sup>vi</sup>	2.735 (3)	P2—O(L2)	1.582 (3)
K—O(E12) <sup>v</sup>	2.735 (3)	P2—O(L1) <sup>xii</sup>	1.602 (3)
K—O(L1) <sup>vii</sup>	2.914 (3)	P1...P2 <sup>xii</sup>	2.928 (1)
K—O(L1) <sup>i</sup>	2.914 (3)	P1...P2 <sup>xiii</sup>	2.976 (1)
K—O(E21) <sup>viii</sup>	2.917 (3)	Y...Y <sup>iv</sup>	5.978 (1)
K—O(E21) <sup>j</sup>	2.917 (3)	Y...Y <sup>i</sup>	6.165 (1)
K—O(E22) <sup>ix</sup>	3.367 (3)	Y...Y <sup>xiii</sup>	7.293 (1)
K—O(E22) <sup>ix</sup>	3.367 (3)		
O(E11)—P1—O(E12)	120.8 (2)	O(E21)—P2—O(L2)	112.94 (15)
O(E11)—P1—O(L1)	107.0 (2)	O(E22)—P2—O(L2)	107.72 (15)
O(E12)—P1—O(L1)	108.9 (2)	O(E21)—P2—O(L1) <sup>xii</sup>	105.08 (15)
O(E11)—P1—O(L2) <sup>xii</sup>	107.99 (15)	O(E22)—P2—O(L1) <sup>xiii</sup>	106.1 (2)
O(E12)—P1—O(L2) <sup>xi</sup>	108.83 (15)	O(L2)—P2—O(L1) <sup>xii</sup>	104.76 (14)
O(L1)—P1—O(L2) <sup>xii</sup>	101.63 (15)	P1—O(L1)—P2 <sup>xii</sup>	137.4 (2)
O(E21)—P2—O(E22)	119.0 (2)	P2—O(L2)—P1 <sup>xiii</sup>	133.7 (2)

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

Data were corrected for Lorentz and polarization effects. No absorption correction was applied as the crystal dimensions are very small ( $\mu r$  is only 0.21).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Caesium–Lithium Phyllosilicate, Cs<sub>1.33</sub>Li<sub>0.67</sub>Si<sub>2</sub>O<sub>5</sub>

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### Abstract

The crystal structure of a (Cs,Li) phyllosilicate with composition Cs<sub>1.33</sub>Li<sub>0.67</sub>Si<sub>2</sub>O<sub>5</sub> has been characterized by a single-crystal X-ray diffraction study. Its silica sheet is exceedingly tortuous with a four-eight-twelve-membered ring topology and a large variation in bridging-oxygen number density in the sheet, thus differing from the six-membered ring topology of Li phyllosilicate and the four-eight-membered ring topology in Cs and Rb phyllosilicate. The title compound lacks the characteristic sandwich structure of sheet silicates. It resembles a three-dimensional network in which Si atoms are replaced by strictly threefold O-coordinated Li atoms which form flat sheets at  $ca\ y = 0$  and  $y = \frac{1}{2}$  with seven- to twelvefold O-coordinated Cs atoms between the silica–lithium sheets at  $y = \frac{1}{4}$  and  $y = \frac{3}{4}$ . The Cs atoms recur in two types of honeycomb tunnels parallel to the  $b$  axis.

### Comment

As part of a study on alkali phyllosilicates and the effect of sheet tortuosity on <sup>29</sup>Si MASNMR chemical shifts, we have prepared transparent colourless (Cs,Li) phyllosilicate crystals from a Li<sub>2</sub>O.Cs<sub>2</sub>O.4SiO<sub>2</sub> glass. The chemical composition of the crystals is Cs<sub>1.33</sub>Li<sub>0.67</sub>Si<sub>2</sub>O<sub>5</sub>, indicating incongruent precipitation. The crystals are not markedly hygroscopic and none of the special measures needed to prevent Cs phyllosilicate from decomposing is required.

The title compound exhibits a new structure type with extreme tortuosity of the silica sheet (Fig. 1). The individual chains (*i.e.* –Si6'–Si1–Si2–Si3–Si4–Si5–Si6–Si1''–) which make up the sheets are 'sechser chains' according to the Liebau (1985) classification, the overall classification of the silica sheet being an unbranched *sechser* single layer. Each Si atom is bonded with two bridging O atoms, O(*br*), in the chain direction and with one O(*br*) perpendicular to that direction, connecting the individual chains into a sheet. The interchain O(*br*)

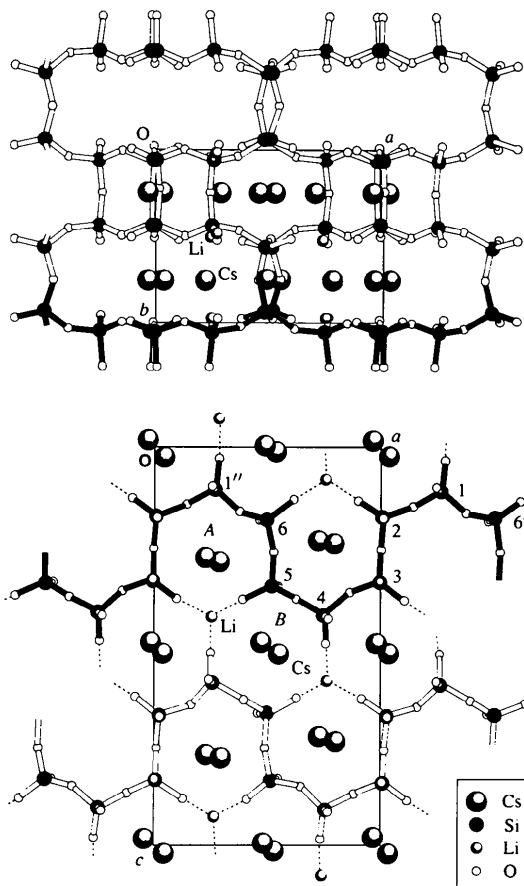


Fig. 1. Projections of the sheet structure of Cs<sub>1.33</sub>Li<sub>0.67</sub>Si<sub>2</sub>O<sub>5</sub>. The *sechser* chain is indicated in black. Top: silica sheet. A similar sheet, generated by the twofold screw axis along  $b$ , completes the unit-cell contents. Bottom: the chicken-wire Li-silicate sheet.