

CsLa(PO₃)₄

Tongqing Sun,* Guangqiu Shen,
Xiaoqing Wang, Ruji Wang,
Jingzhi Wei and Dezhong Shen

Department of Chemistry, Tsinghua University,
Beijing 100084, People's Republic of China

Correspondence e-mail:
suntq98@mails.tsinghua.edu.cn

Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{P}-\text{O}) = 0.005 \text{ \AA}$

R factor = 0.022

wR factor = 0.049

Data-to-parameter ratio = 12.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, caesium lanthanum tetrametaphosphate, CsLa(PO₃)₄, was grown using the flux method and its structure determined by single-crystal X-ray diffraction methods. This compound is isostructural with CsNd(PO₃)₄. The structure is built up from infinite helical chains, (PO₃)_{*n*}, which are connected by isolated LaO₈ dodecahedra and irregularly shaped Cs polyhedra. These chains are formed by corner-sharing of PO₄ tetrahedra and run along the *b* axis.

Comment

Tetrametaphosphates with space group *P*2₁ corresponding to the general formula *M*^ILn(PO₃)₄ are well known (Chinn & Hong, 1975; Malinowski & Streck, 1987; Xue & Zhang, 1998), because not only are the Ln–O polyhedra in the structure isolated from each other, which markedly reduces the concentration quenching when Ln³⁺ is the laser-activated ion, but also the space group is non-centrosymmetric, which may allow non-linear optical processes (*e.g.* second-harmonic generation) as well as linear electro-optical modulation to be carried out. The compounds *M*^I = K and Ln = Nd (Hong, 1975), Er (Krutik *et al.*, 1980) and La (Lin *et al.*, 1983), and *M*^I = Cs and Ln = Nd (Koizumi & Nakano, 1978), Tb (Palkina, Maksimova, Kuznetsov & Chibiskova, 1978) and Pr (Palkina, Maksimova & Kuznetsov, 1978) have been obtained and have a monoclinic structure, space group *P*2₁. Hassen *et al.* (1984)

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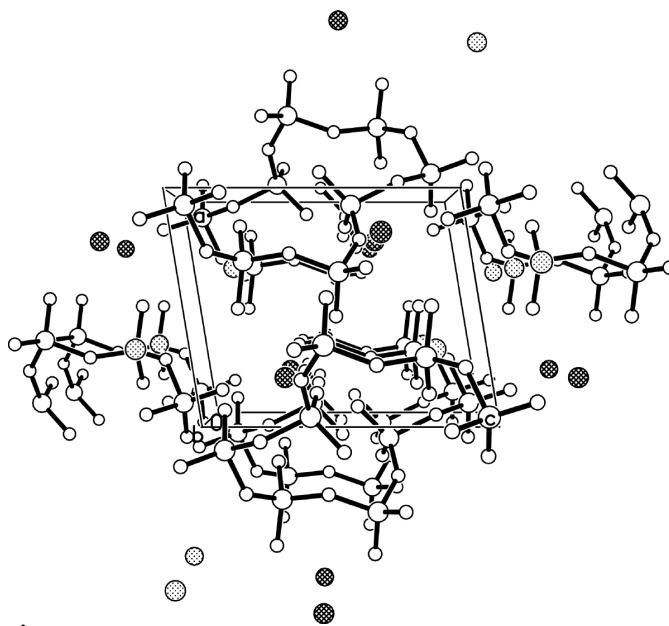


Figure 1

A view of the molecular packing in CsLa(PO₃)₄ along the [010] direction. Large open circles represent P atoms and small circles represent O atoms, while circles with a regular dot pattern depict Cs and cross-hatched circles depict La atoms.

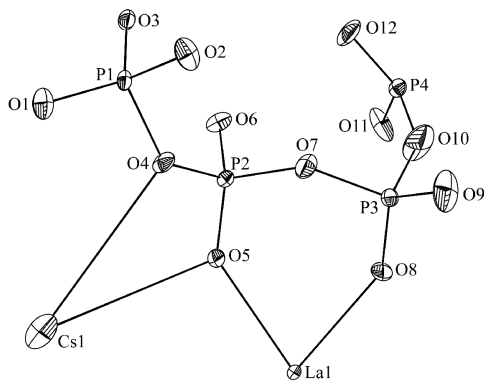


Figure 2
The asymmetric unit of $\text{CsLa}(\text{PO}_3)_4$, showing 50% probability displacement ellipsoids.

investigated the phase diagram of the CsPO_3 – LaP_3O_9 system, and the result showed the existence of the compound $\text{CsLa}(\text{PO}_3)_4$. In the present work, we report its crystal growth and structure.

The structure of the title compound is composed of infinite helical chains of corner-shared PO_4 tetrahedra, which are joined to each other by La dodecahedra and Cs polyhedra (shown in Fig. 1). The chains run along the b axis, with eight PO_4 tetrahedra in a repeating unit. $\text{CsLa}(\text{PO}_3)_4$ is isostructural with $\text{CsNd}(\text{PO}_3)_4$, but not with $\text{KLa}(\text{PO}_3)_4$ although they belong to the same space group, $P2_1$. In the latter, the infinite screw $(\text{PO}_3)_n$ chains are repeated after every fourth PO_4 group along the c axis. The average P–O distance in the PO_4 tetrahedra is 1.533 Å, and the average O–P–O angle is 109.2°. Tetrahedral PO_4 groups are distorted from the ideal tetrahedron, and the lengths of P–O bonds taking part in bridging with adjacent PO_4 groups for chain formation are significantly longer than the others. The tetrahedron around P4 has a larger distortion compared with those around other P atoms, with O–P–O angles in the range 97.1 (3)–121.5 (3)°; this feature has also been found in $\text{CsNd}(\text{PO}_3)_4$ (Koizumi & Nakano, 1978). La atoms lie among the helical chains, and are coordinated by O atoms, forming LaO_8 dodecahedra. Eight O atoms come from three helical chains which separately offer one, two and five O atoms. The LaO_8 dodecahedra are isolated from one another since they do not share any O atoms. The lengths of La–O bonds are in the range 2.426 (4)–2.583 (4) Å, and the shortest La···La distance is 6.745 (2) Å. The Cs^+ cations are surrounded by O atoms, except O1 and O7, and the Cs···O distances exhibit a wide range (3.049–3.809 Å). A displacement ellipsoid plot of the asymmetric unit is shown in Fig. 2.

The crystals of the title compound do not dissolve in water or in dilute acid or alkali solutions and have good chemical stability, but they are prone to cleavage under external pressure, which makes them a challenge to cut and polish.

Experimental

Crystals of the title compound were grown by spontaneous nucleation using a vertical cylindrical electric furnace under an ambient air

atmosphere. Starting materials were prepared by melting a mixture of 37.9wt% Cs_2CO_3 (99.0%), 11.3wt% La_2O_3 (99.99%) and 50.8wt% $\text{NH}_4\text{H}_2\text{PO}_4$ (99.0%). The melt was kept at 1173 K for 2 days to homogenize and then cooled to 1136 K rapidly and to 994 K at a rate of 0.5 K h^{-1} . The crucible was removed from the furnace and cooled to room temperature. The flux was washed out by hot water and it was found that the title compound crystallized as colorless transparent irregular prisms.

Crystal data

$\text{CsLa}(\text{PO}_3)_4$
 $M_r = 587.70$
Monoclinic, $P2_1$
 $a = 7.218$ (3) Å
 $b = 9.254$ (3) Å
 $c = 8.864$ (3) Å
 $\beta = 99.377$ (5)°
 $V = 584.2$ (4) Å³
 $Z = 2$

$D_x = 3.341$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 961 reflections
 $\theta = 3.2$ – 28.0°
 $\mu = 7.33$ mm^{-1}
 $T = 293$ (2) K
Prism, colorless
 $0.14 \times 0.06 \times 0.04$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.453$, $T_{\max} = 0.746$
3731 measured reflections

2073 independent reflections
1993 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 28.0^\circ$
 $h = -9 \rightarrow 9$
 $k = -12 \rightarrow 8$
 $l = -10 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.049$
 $S = 1.02$
2073 reflections
164 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 0.0183P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.72$ e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.0191 (8)
Absolute structure: Flack (1983)
Flack parameter = 0.006 (16), 584 Friedel pairs

Table 1

Selected geometric parameters (Å).

La1–O12 ⁱ	2.426 (4)	Cs1–O2 ⁱⁱ	3.186 (4)
La1–O1 ⁱⁱⁱ	2.432 (4)	Cs1–O3 ⁱ	3.193 (4)
La1–O8	2.463 (4)	Cs1–O8 ^{vi}	3.267 (5)
La1–O9 ⁱⁱⁱ	2.472 (5)	Cs1–O9 ^{vi}	3.287 (5)
La1–O3 ⁱ	2.526 (4)	Cs1–O5	3.430 (4)
La1–O5	2.535 (4)	Cs1–O12 ⁱⁱⁱ	3.519 (5)
La1–O11 ^{iv}	2.537 (5)	Cs1–O4	3.591 (4)
La1–O6 ⁱ	2.583 (4)	Cs1–O5 ^v	3.642 (4)
Cs1–O6 ^v	3.049 (4)	Cs1–O11 ^v	3.809 (5)

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

The first eight peaks higher than 0.7 e Å⁻³ on the final difference Fourier map were all located around La1 or Cs1.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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