Crystal structure of cesium lead tetrathiophosphate, $CsPbPS_4$

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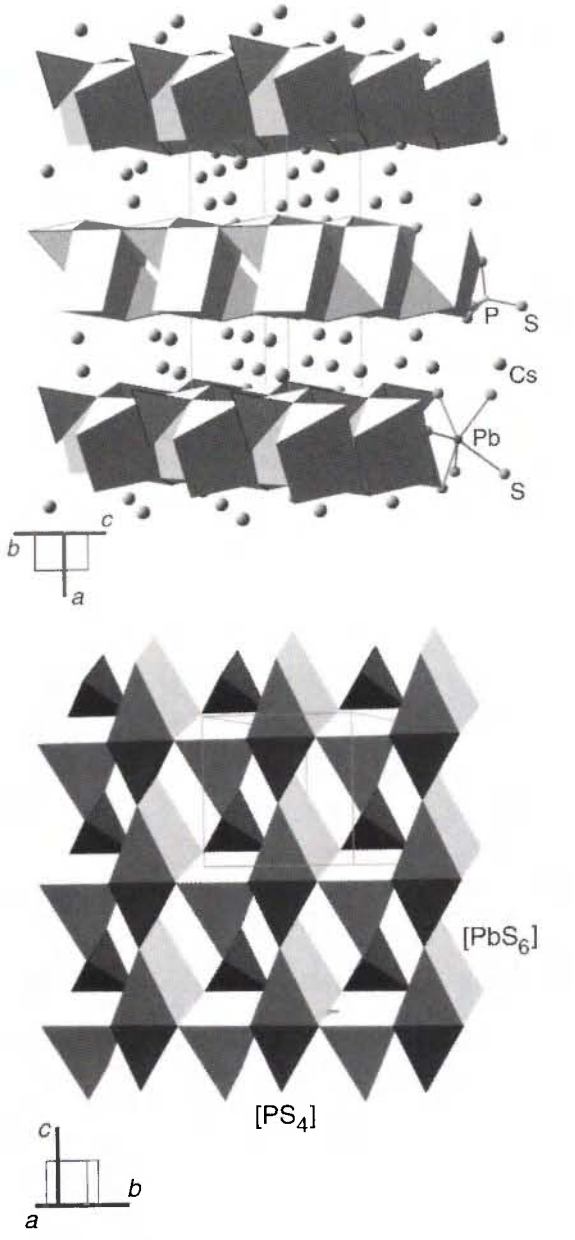

Abstract

$CsPPbS_4$, orthorhombic, *Pnma* (no. 62), $a = 18.185(1)$ Å, $b = 6.8085(5)$ Å, $c = 6.3518(5)$ Å, $V = 786.4$ Å^3, $Z = 4$, $R_{gt}(F) = 0.039$, $wR_{ref}(F^2) = 0.101$, $T = 293$ K.

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Source of material

Cs_2S_3 was prepared from a stoichiometric mixture of the elements (Cs – 99.5%, Strem; S – 99.99%, Heraeus) in liquid ammonia under argon atmosphere. $CsPbPS_4$ was prepared by the reaction of Cs_2S_3, Pb (99.9%, Aldrich), P_2S_5 (99.99%, Alfa), and S in an 1:1:1:6 molar ratio. The reaction mixture was thoroughly combined in a nitrogen-filled glove-box and loaded into a glass tube (Duran), which was evacuated (1×10^{-3} mbar) and flame sealed. The ampoule was placed in a computer-controlled furnace and heated to 773 K, then kept at this temperature for 6 days, and afterwards cooled to 373 K at the rate of 2 K/h, then turned off the furnace. To remove unreacted $Cs_xP_yS_z$ the solidified melt was washed with dimethylformamide and acetone. The product consisted of transparent yellow crystals which are stable in air and moisture. A semiquantitative EDX analysis indicated the presence of all four elements (Cs, Pb, P and S) in an approximate atomic ratio of 1:1:1:4.

Discussion

In the course of our ongoing work on alkali metal thiophosphates we have prepared $CsPbPS_4$. The title compound has a structure similar to that of the previously reported $KPbPS_4$ [1] and is closely related to those of the other alkali metal ortho-chalcophosphates studied to date, namely $KEuPS_4$ [2], $KEuPSe_4$ [3,4], and $CsPbPSe_4$ [5].

The structure of $CsPbPS_4$ consists of two-dimensional $[PbPS_4]_n^{n-}$ layers perpendicular to [100]. These layers are separated by Cs^+ cations (figure, top). Similar to $KPbPS_4$, each layer is made up of trigonal $[PbS_6]$ prisms and tetrahedral $[PS_4]$ groups (figure, bottom). Pb is surrounded by six S atoms in an irregular trigonal prismatic arrangement. Two adjacent prisms share an edge of rectangular faces to form a one-dimensional $[PbS_6]$ chain. The apical edges of the prisms of these chains point alternately up and down along [010]. These parallel zigzag chains are joined by $[PS_4]$ tetrahedra along [001] by sharing edges with the rectangles of the trigonal prisms to form two-dimensional $[PbPS_4]_n^{n-}$ layers. In this way, each $[PbS_6]$ trigonal prism is connected to four $[PS_4]$ tetrahedra. With two of the tetrahedra it shares a common edge while with two others it is only corner-linked (figure, bottom). The Pb—S distances found in $CsPbPS_4$ range from 2.910(3) Å to 3.208(2) Å and compare very well with those reported for $KPbPS_4$ [1]. The $[PbPS_4]_n^{n-}$ layers are separated by Cs^+ ions which have an irregular sevenfold coordination and the Cs—S distances range from 3.469(3) Å to 4.012(3) Å. This environment of Cs atom has already been observed in $CsPbPSe_4$ [5]. The size of the alkali metal cation is small compared with the distance between adjacent $[PbPS_4]_n^{n-}$ layers. This is probably the reason for the large and strongly anisotropic displacement parameters. The average P—S distance within the PS_4 unit (2.045(3) Å) is in good agreement with the P—S distances found in related phases.

Table 1. Data collection and handling.

Crystal:	transparent yellow prism, size 0.07 × 0.10 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	271.69 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	60.7°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7958, 1230
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1035
$N(param)_{refined}$:	41
Programs:	SHELXS-97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	4c	0.01524(3)	¼	0.70901(7)	0.0218(3)	0.0659(4)	0.0260(3)	0	0.0001(2)	0
P	4c	0.0955(1)	¼	0.2180(4)	0.013(1)	0.020(1)	0.023(1)	0	0.0015(8)	0
S(1)	4c	0.1539(1)	¼	0.9462(4)	0.015(1)	0.029(1)	0.028(1)	0	0.0055(8)	0
S(2)	4c	0.9840(2)	¼	0.1584(5)	0.011(1)	0.074(2)	0.029(1)	0	0.0023(9)	0
S(3)	8d	0.1184(1)	0.0058(3)	0.3940(3)	0.030(1)	0.0208(8)	0.0329(9)	–0.0018(6)	–0.0022(7)	0.0053(7)
Cs	4c	0.29577(4)	¼	0.4300(2)	0.0210(4)	0.0299(4)	0.0869(7)	0	–0.0138(4)	0

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