

TlSrPS₄, the first strontium quaternary thiophosphate

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(S-P) = 0.003$ Å; R factor = 0.033; wR factor = 0.084; data-to-parameter ratio = 22.8.

The new thallium(I) strontium(II) thiophosphate TlSrPS₄ is isostructural with TIPbPS₄ and exhibits a layered structure. Each layer is composed of [(SrS₆(TlS₆)]_n zigzag chains, which consist of irregular trigonal prisms centred alternately by Tl and Sr atoms. Adjacent [TlS₆] and [SrS₆] prisms share common triangular faces to form one-dimensional chains parallel to [001]. These chains are connected along [010] by sharing edges of rectangular faces in such a way that the apical edges of the prisms point alternately up and down, forming parallel zigzag layers. The layers are stacked perpendicular to the crystallographic a axis and are held together by [PS₄] tetrahedra.

Related literature

Background information on related structures can be found in Belkhal, El Azhari, Bensch & Depmeier (2006), Carrillo-Cabrera *et al.* (1995) and Becker *et al.* (1987).

For related literature, see: Belkhal *et al.* (2005); Belkhal, El Azhari, Wu *et al.* (2006); Hadenfeldt & Hoedel (1996); Horn & Sterzel (1973); Johri *et al.* (1970); Shannon (1976).

Experimental

Crystal data

TlSrPS₄ Orthorhombic, $Pnma$
 $M_r = 451.20$ $a = 12.2985$ (8) Å

$b = 6.6003$ (6) Å
 $c = 8.7957$ (6) Å
 $V = 713.98$ (9) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 31.28$ mm⁻¹
 $T = 293$ (2) K
 $0.08 \times 0.07 \times 0.06$ mm

Data collection

Stoe IPDS diffractometer
Absorption correction: numerical
(*X-SHAPE*; Stoe & Cie, 1998)
 $T_{\min} = 0.018$, $T_{\max} = 0.111$

6570 measured reflections
935 independent reflections
780 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.099$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.084$
 $S = 1.02$
935 reflections

41 parameters
 $\Delta\rho_{\max} = 1.46$ e Å⁻³
 $\Delta\rho_{\min} = -2.30$ e Å⁻³

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *BS* (Version 1.51; Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2039).

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Comment

In our effort to extend the range of quaternary *ortho*-thiophosphate, AMPS₄ (A = K, Rb, Cs, Tl and M: divalent metal) (Belkhal *et al.*, 2005 and 2006a), the new compound TlSrPS₄ was obtained. Neither the structure nor the properties of strontium quaternary thiophosphates have been known until now. The title compound crystallizes in the centrosymmetric space group *Pnma* and is isostructural with TIPbPS₄ (Belkhal *et al.*, 2006b) and is closely related to those of the other thallium tetrathiophosphate namely TlEuPS₄ (Carrillo-Cabrera *et al.*, 1995) and TlSnPS₄ (Becker *et al.*, 1987).

The asymmetric unit of the title compound is plotted on Fig. 1. The structure of TlSrPS₄ has a pseudo two-dimensional character. Looking down the *c* axis (Fig. 2), one can see layers of [(SrS₆)(TlS₆)_n] separated by P⁵⁺ cations. These geometric parameters are in agreement with values reported in the literature for TIPbPS₄ (Belkhal *et al.*, 2006b) or TlEuPS₄ (Carrillo-Cabrera *et al.*, 1995).

The layers are composed of wedge-like irregular trigonal prisms alternately centred by Tl and Sr atoms. Adjacent prisms TlS₆ and SrS₆ share edges of rectangular faces in such a way that edges of the prisms point alternately up and down forming one-dimensional parallel zigzag chains along [010] (Fig. 3). These zigzag chains are joined together by sharing the triangular faces along [001], in such way that the TlS₆ prism of one chain shares triangular face with SrS₆ prism of the other chain. Thus, the layers formed are connected by [PS₄] tetrahedra along [100]. The P—S bonds, within the [PS₄] tetrahedra, are almost equidistant from 2.031 (3) to 2.044 (2) Å. The average of these distances is in good agreement with those found in TIPbPS₄ [Belkhal *et al.*, 2006b] or TlEuPS₄ (Carrillo-Cabrera *et al.*, 1995). The Tl—S bond lengths found in TlSrPS₄ range from 3.268 (1) to 3.397 (3) Å and compare very well with those reported for TIPbPS₄ (Belkhal *et al.*, 2006b). Whereas the Sr—S distances (2.984 (3) to 3.095 (2) Å) are smaller than those found in the strontium ternary compound Sr₂P₂S₆ (Hadenfeldt & Hoedel, 1996) (3.058 (2)–3.200 (1) Å). This reduction is the result of the increase in the covalent character of the Sr—S bond in TlSrPS₄. The same behavior was observed for the Pb—S distances between TIPbPS₄ (Belkhal *et al.*, 2006b) and Pb₂P₂S₆ (Hadenfeldt & Hoedel, 1996). The average Tl—S and Sr—S distances in TlSrPS₄ match well with the sum of the ionic radii (Shannon, 1976).

Experimental

TlSrPS₄ was prepared from a stoichiometric mixture of P₂S₅ (99,99%, Alfa), SrS (99,9%, ABCR), S (99,99%, Heraeus) and Tl₂S. The latter was prepared by thermal decomposition of Tl₂CS₃ (Horn & Sterzel, 1973; Johri *et al.*, 1970) in argon atmosphere under reduced pressure at T_{max} = 523 K. The reaction mixture was thoroughly mixed in a N₂-filled glove box and loaded into a quartz ampoule. After evacuation to 10⁻³ mbar the ampoule was flame-sealed and placed in a computer controlled furnace. The sample was heated to 1200 K, kept at this temperature for 5 days, cooled to 400 K at a rate of 4.8 °K/h, then turned off the furnace. After washing with ether transparent orange platelets were obtained. The compound is slightly air

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and moisture sensitive. An EDX analysis indicated the presence of all four elements (Tl, Sr, P, S) in an approximate atomic ratio of 1:1:1:4. The EDX analysis was performed using a Philips ESEM XL 30 scanning electron microscope equipped with an EDAX analyser.

Figures

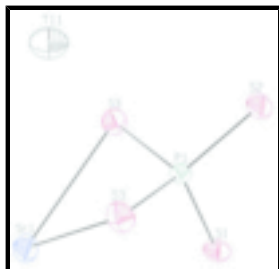


Fig. 1. The asymmetric unit of the title compound, with anisotropic displacement parameters drawn at the 50% probability level.

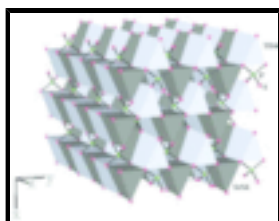


Fig. 2. Extended structure of TlSrPS₄ projected along [001].

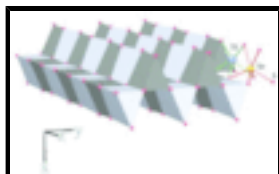


Fig. 3. Projection along [001], showing the puckered layer of condensed chains of SrS₆ and TlS₆ trigonal prisms.

Thallium strontium tetrathiosphosphate

Crystal data

TlSrPS₄

$M_r = 451.20$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 12.2985$ (8) Å

$b = 6.6003$ (6) Å

$c = 8.7957$ (6) Å

$V = 713.98$ (9) Å³

$Z = 4$

$F_{000} = 792$

$D_x = 4.198$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 935 reflections

$\theta = 2.9$ – 27.9°

$\mu = 31.28$ mm⁻¹

$T = 293$ (2) K

Platelet, orange

$0.08 \times 0.07 \times 0.06$ mm

Data collection

Stoe IPDS
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

935 independent reflections

780 reflections with $I > 2\sigma(I)$

$R_{int} = 0.099$

$T = 293(2)$ K $\theta_{\max} = 27.9^\circ$
 φ scans $\theta_{\min} = 2.9^\circ$
 Absorption correction: numerical
 (X-SHAPE; Stoe & Cie, 1998) $h = -15 \rightarrow 16$
 $T_{\min} = 0.018$, $T_{\max} = 0.111$ $k = -8 \rightarrow 8$
 6570 measured reflections $l = -11 \rightarrow 11$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 $w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 3.1599P]$
 Least-squares matrix: full where $P = (F_o^2 + 2F_c^2)/3$
 $R[F^2 > 2\sigma(F^2)] = 0.033$ $(\Delta/\sigma)_{\max} = 0.001$
 $wR(F^2) = 0.084$ $\Delta\rho_{\max} = 1.46 \text{ e } \text{\AA}^{-3}$
 $S = 1.03$ $\Delta\rho_{\min} = -2.29 \text{ e } \text{\AA}^{-3}$
 935 reflections Extinction correction: SHELXL97 (Sheldrick, 1997)
 41 parameters Extinction coefficient: 0.0033 (3)
 Primary atom site location: structure-invariant direct methods

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Tl1	0.3980 (1)	0.7500	0.6257 (1)	0.031 (1)
Sr1	0.6395 (1)	0.2500	0.8923 (1)	0.016 (1)
P1	0.3468 (2)	0.2500	0.8764 (2)	0.012 (1)
S1	0.4445 (2)	0.2500	0.6903 (3)	0.020 (1)
S2	0.4310 (2)	0.2500	1.0761 (2)	0.018 (1)
S3	0.2472 (1)	0.0025 (2)	0.8659 (2)	0.018 (1)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tl(1)	0.035 (1)	0.036 (1)	0.022 (1)	0.000	-0.003 (1)	0.000
Sr(1)	0.015 (1)	0.021 (1)	0.013 (1)	0.000	0.001 (1)	0.000

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P(1)	0.015 (1)	0.008 (1)	0.013 (1)	0.000	-0.001 (1)	0.000
S(1)	0.021 (1)	0.026 (1)	0.013 (1)	0.000	0.002 (1)	0.000
S(2)	0.016 (1)	0.027 (1)	0.011 (1)	0.000	-0.002 (1)	0.000
S(3)	0.020 (1)	0.010 (1)	0.025 (1)	-0.004 (1)	-0.007 (1)	0.002 (1)

Geometric parameters (Å, °)

Tl1—Sr1 ⁱ	4.2645 (9)	Sr1—Tl1 ⁱ	4.2645 (9)
Sr1—S1	2.984 (3)	P1—S1	2.031 (3)
Sr1—S2	3.031 (2)	P1—S2	2.039 (3)
Sr1—S3 ⁱⁱ	3.0406 (18)	P1—S3	2.044 (2)
Sr1—S3 ⁱⁱⁱ	3.0406 (18)	P1—S3 ^{vi}	2.044 (2)
Sr1—S3 ^{iv}	3.0951 (18)	P1—Sr1 ^{vii}	3.476 (2)
Sr1—S3 ^v	3.0951 (18)	S2—Sr1 ⁱⁱⁱ	3.4234 (7)
Sr1—S2 ⁱⁱⁱ	3.4234 (7)	S2—Sr1 ⁱ	3.4234 (7)
Sr1—S2 ⁱ	3.4234 (7)	S3—Sr1 ⁱⁱⁱ	3.0406 (18)
Sr1—P1 ^{iv}	3.476 (2)	S3—Sr1 ^{vii}	3.0951 (18)
Sr1—P1	3.603 (2)		
S1—Sr1—S2	68.77 (6)	S3 ^{iv} —Sr1—P1	113.53 (5)
S1—Sr1—S3 ⁱⁱ	141.70 (4)	S3 ^v —Sr1—P1	113.53 (5)
S2—Sr1—S3 ⁱⁱ	90.84 (5)	S2 ⁱⁱⁱ —Sr1—P1	75.53 (4)
S1—Sr1—S3 ⁱⁱⁱ	141.70 (4)	S2 ⁱ —Sr1—P1	75.53 (4)
S2—Sr1—S3 ⁱⁱⁱ	90.84 (5)	P1 ^{iv} —Sr1—P1	134.94 (4)
S3 ⁱⁱ —Sr1—S3 ⁱⁱⁱ	66.47 (6)	S1—Sr1—Tl1 ⁱ	120.33 (5)
S1—Sr1—S3 ^{iv}	84.67 (5)	S2—Sr1—Tl1 ⁱ	51.57 (4)
S2—Sr1—S3 ^{iv}	138.88 (4)	S3 ⁱⁱ —Sr1—Tl1 ⁱ	49.76 (4)
S3 ⁱⁱ —Sr1—S3 ^{iv}	127.32 (3)	S3 ⁱⁱⁱ —Sr1—Tl1 ⁱ	49.76 (4)
S3 ⁱⁱⁱ —Sr1—S3 ^{iv}	91.588 (16)	S3 ^{iv} —Sr1—Tl1 ⁱ	140.86 (4)
S1—Sr1—S3 ^v	84.67 (5)	S3 ^v —Sr1—Tl1 ⁱ	140.86 (4)
S2—Sr1—S3 ^v	138.88 (4)	S2 ⁱⁱⁱ —Sr1—Tl1 ⁱ	83.79 (4)
S3 ⁱⁱ —Sr1—S3 ^v	91.588 (16)	S2 ⁱ —Sr1—Tl1 ⁱ	83.79 (4)
S3 ⁱⁱⁱ —Sr1—S3 ^v	127.32 (3)	P1 ^{iv} —Sr1—Tl1 ⁱ	139.03 (4)
S3 ^{iv} —Sr1—S3 ^v	63.71 (6)	P1—Sr1—Tl1 ⁱ	86.02 (4)
S1—Sr1—S2 ⁱⁱⁱ	81.08 (4)	S1—P1—S2	113.15 (14)
S2—Sr1—S2 ⁱⁱⁱ	75.08 (4)	S1—P1—S3	108.56 (10)
S3 ⁱⁱ —Sr1—S2 ⁱⁱⁱ	125.99 (5)	S2—P1—S3	110.09 (9)
S3 ⁱⁱⁱ —Sr1—S2 ⁱⁱⁱ	62.02 (5)	S1—P1—S3 ^{vi}	108.56 (10)
S3 ^{iv} —Sr1—S2 ⁱⁱⁱ	70.08 (5)	S2—P1—S3 ^{vi}	110.09 (9)
S3 ^v —Sr1—S2 ⁱⁱⁱ	132.59 (5)	S3—P1—S3 ^{vi}	106.13 (13)
S1—Sr1—S2 ⁱ	81.08 (4)	S1—P1—Sr1 ^{vii}	83.47 (10)
S2—Sr1—S2 ⁱ	75.08 (4)	S2—P1—Sr1 ^{vii}	163.37 (12)
S3 ⁱⁱ —Sr1—S2 ⁱ	62.02 (5)	S3—P1—Sr1 ^{vii}	61.95 (7)

S3 ⁱⁱⁱ —Sr1—S2 ⁱ	125.99 (5)	S3 ^{vi} —P1—Sr1 ^{vii}	61.95 (7)
S3 ^{iv} —Sr1—S2 ⁱ	132.59 (5)	S1—P1—Sr1	55.92 (9)
S3 ^v —Sr1—S2 ⁱ	70.08 (5)	S2—P1—Sr1	57.23 (9)
S2 ⁱⁱⁱ —Sr1—S2 ⁱ	149.15 (8)	S3—P1—Sr1	126.91 (7)
S1—Sr1—P1 ^{iv}	100.63 (6)	S3 ^{vi} —P1—Sr1	126.90 (7)
S2—Sr1—P1 ^{iv}	169.40 (6)	Sr1 ^{vii} —P1—Sr1	139.40 (6)
S3 ⁱⁱ —Sr1—P1 ^{iv}	98.01 (5)	P1—S1—Sr1	89.77 (10)
S3 ⁱⁱⁱ —Sr1—P1 ^{iv}	98.01 (5)	P1—S2—Sr1	88.31 (10)
S3 ^{iv} —Sr1—P1 ^{iv}	35.64 (3)	P1—S2—Sr1 ⁱⁱⁱ	86.63 (5)
S3 ^v —Sr1—P1 ^{iv}	35.64 (3)	Sr1—S2—Sr1 ⁱⁱⁱ	104.92 (4)
S2 ⁱⁱⁱ —Sr1—P1 ^{iv}	103.94 (4)	P1—S2—Sr1 ⁱ	86.63 (5)
S2 ⁱ —Sr1—P1 ^{iv}	103.94 (4)	Sr1—S2—Sr1 ⁱ	104.92 (4)
S1—Sr1—P1	34.31 (6)	Sr1 ⁱⁱⁱ —S2—Sr1 ⁱ	149.15 (8)
S2—Sr1—P1	34.46 (5)	P1—S3—Sr1 ⁱⁱⁱ	97.57 (8)
S3 ⁱⁱ —Sr1—P1	119.03 (5)	P1—S3—Sr1 ^{vii}	82.41 (7)
S3 ⁱⁱⁱ —Sr1—P1	119.03 (5)	Sr1 ⁱⁱⁱ —S3—Sr1 ^{vii}	177.14 (7)

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+1, y+1/2, -z+2$; (iii) $-x+1, -y, -z+2$; (iv) $x+1/2, y, -z+3/2$; (v) $x+1/2, -y+1/2, -z+3/2$; (vi) $x, -y+1/2, z$; (vii) $x-1/2, y, -z+3/2$.

Fig. 1

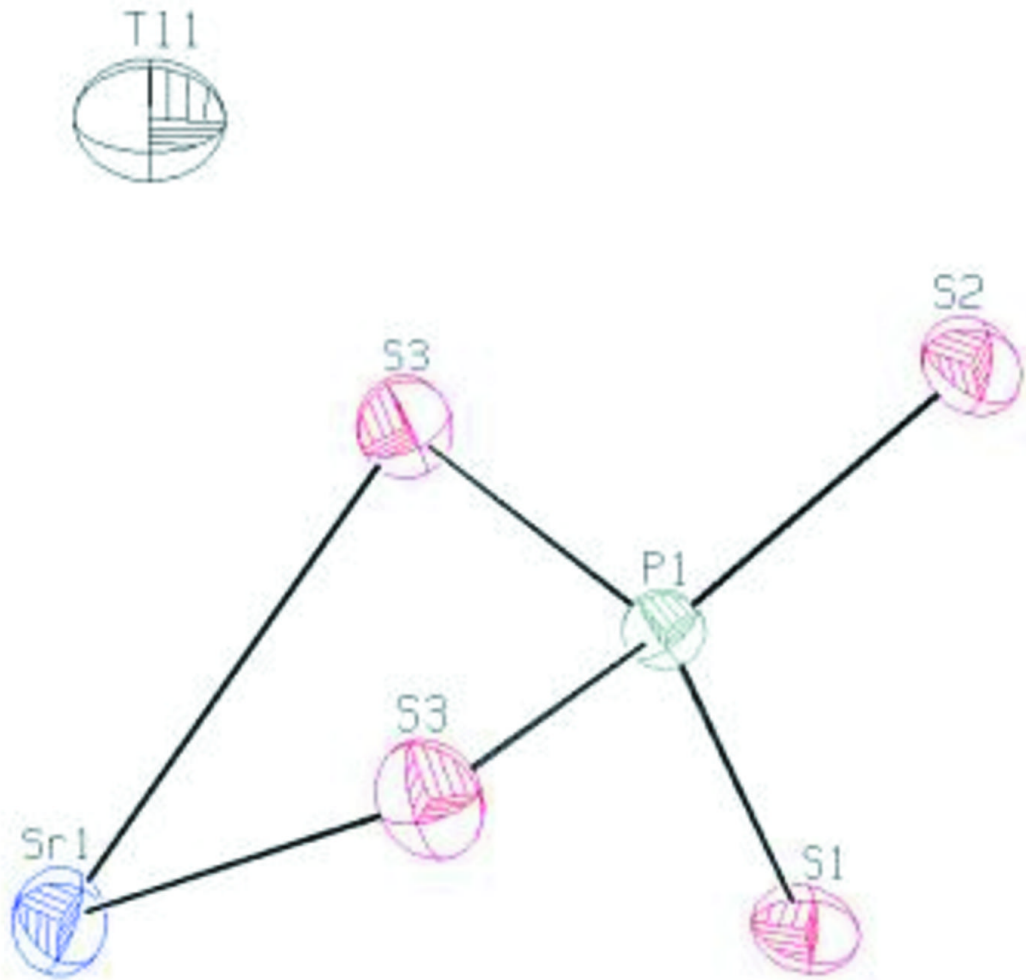


Fig. 2

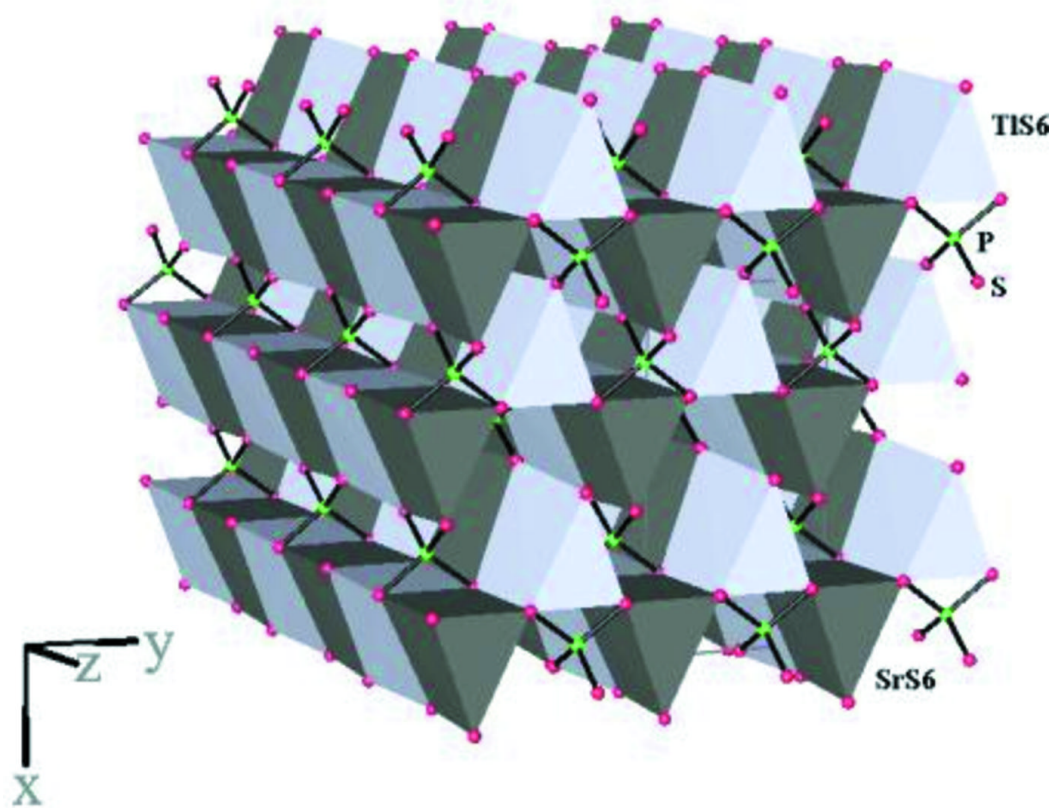


Fig. 3

