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Crystal structure of synthetic $PbTlAs_3S_6$

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Abstract. The crystal structure of a new synthetic sulfosalt $PbTlAs_3S_6$ has been determined. The space group is *Fdd*2 with $a = 47.453(2)$, $b = 15.476(7)$, $c = 5.847(2)$ Å, $Z = 16$. The structure was determined by Patterson methods and refined with anisotropic temperature factors and anomalous dispersion correction to a final *R*-value of 0.063 for 1105 observed reflections.

The Pb atom is coordinated by seven S atoms (mean Pb – S = 3.074 Å). The coordination polyhedra form $^{2}_{\infty}[PbS_3]$ layers parallel to the (100) crystal face. The Tl atom is coordinated by seven S atoms (mean Tl – S = 2.300 Å). The coordination polyhedra form $^{1}_{\infty}[TlS_5]$ double chains parallel to the *c*-axis. The As atoms are bonded to three S atoms forming a trigonal pyramid with the As atom at the apex. The pyramids are connected to form $[As_6S_{12}]$ groups which contain a two membered ring.

1. Introduction

A new synthetic sulfosalt, $PbTlAs_3S_6$, was prepared by hydrothermal synthesis in the system $Tl_2S - PbS - As_2S_3$ by A. Edenharter (Nowacki et al., 1982). $PbTlAs_3S_6$ crystallizes in the form of platy orthorhombic prismatic crystals of dark-red colour. According to the classification of sulfosalts proposed by W. Nowacki (1969), synthetic $PbTlAs_3S_6$ with S:As = 2 belongs to the group IV.a_2.

2. Experimental

A synthetic crystal of $PbTlAs_3S_6$ of lath-like shape, elongated along the *c*-axis as illustrated in Figure 1, was selected for X-ray investigations. The distances of the planes to the center of the cyrstal measured with the microscope, were:

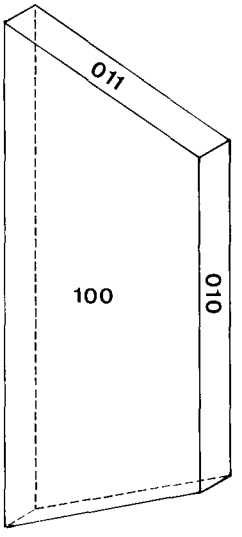

Fig. 1. Shape of the crystal used for the X-ray investigation

$d_{100}=d_{\bar{1}00}=0.0109$ mm, $d_{010}=d_{0\bar{1}0}=0.0584$ mm and $d_{011}=d_{01\bar{1}}=0.1022$ mm. The crystal was mounted on a fiber of Lindemann glass of diameter 0.06 mm with nail polish. The determination of the lattice parameters and the intensity measurements were made with the NONIUS CAD4 diffractometer and Ni-filtered Cu$K\alpha$-radiation. 23 reflections determined with the NONIUS peak hunting procedure in the range $20° < 2\theta < 45°$ were carefully centered. Accurate cell parameters were calculated with a least-squares procedure which led to the orthorhombic cell constants $a=47.453(2)$, $b=15.476(7)$ and $c=5.847(2)$ Å. Systematic extinctions hkl, $h+k=2n+1$,$k+l=2n+1$, $l+h=2n+1$; $0kl$, $k+l=4n+1$, $4n+2$, $4n+3$ and $h0l$, $h+l=4n+1$, $4n+2$, $4n+3$ indicated the space group $Fdd2$.

The intensities of 1230 independent reflections in the range $7° \leqslant 2\theta \leqslant 145°$ were measured by the $\omega-2\theta$ scan technique. Every 200 reflections the orientation of the crystal, and every 4.2 h the intensity of the $(0.14.\overline{24})$ reflection, were checked. 112 reflections were regarded as unobserved: 105 had $I<2.5\sigma(I)$ and 7 were weak, with indices not in agreement with the $Fdd2$ space group extinctions. These weak reflections were probably caused by double reflection because they were not observed on Weissenberg photographs. The standard deviation was calculated as: $\sigma^2(I)=P+m^2(B_1+B_2)$, where P is the peak scan and B_1, B_2 are the background measurements for $\frac{1}{2m}$ of the time of the peak scan. The intensities were corrected for Lorentz-polarization effects.

The absorption correction was made before the structure refinement. The linear absorption coefficient for $PbTlAs_3S_6$ and Cu$K\alpha$ radiation is $\mu = 793.86\,cm^{-1}$ (Ibers and Hamilton, 1974). With the known shape and dimensions of the crystal and its orientation on the diffractometer, the absorption corrections were calculated using the analytical method of Howells (1950) with the program ABSKOR (Engel, 1977). The reflections for which the transmission factor was lower than 0.04 (13 of the observed reflections) were later excluded from the refinement procedure, since we considered them to be effected by the total or nearly total absorption of the primary beam in the crystal. There were 1105 unique observed reflections left for the final refinement of the structure.

The calculated density is $d_x = 5.13\,gcm^{-3}$ for 16 formula units $PbTlAs_3S_6$ per unit cell.

3. Structure determination and refinement

The absolute scale factor and the overall temperature factor were determined from a Wilson plot (program NORMSF of the X-Ray 76 system, Stewart et al., 1976). The statistical distribution of the normalized E-values showed good agreement with the theoretical values given in brackets for the acentric structure:

$\langle E \rangle$	0.887	(0.886)
$\langle E^2 \rangle$	1.000	(1.000)
$\langle E^2 - 1 \rangle$	0.717	(0.736)

The coordinates of the two heavy atoms in the asymmetric unit were found from a three-dimensional Patterson synthesis which was calculated with the program FOURR of the X-Ray 76 system.

The F_o-Fourier synthesis calculated with the two heavy atoms clearly showed three additional peaks which were assigned to the three As atoms. From the second F_o-Fourier synthesis calculated with all metal atoms the remaining six S atoms could be located. The initial atomic coordinates were refined with individual isotropic temperature factors, using the least-squares full-matrix refinement program CRYLSQ of the X-Ray 76 system. The initial R-value of 0.25 dropped to 0.20 only. At that stage the absorption correction was applied and the structure was further refined using the least-squares block-diagonal refinement program SFLSX of the KRIPROG system (Engel, 1978) which finaly decreased the R value to 0.063 for all 1105 observed reflections using anisotropic temperature factors and anomalous dispersion factors taken from the International Tables Vol. IV (Ibers and Hamilton, 1974). The drawings were made using the program PLOT of the

Table 1. The final atomic coordinates and anisotropic temperature factors with standard deviation for $PbTlAs_3S_6$. $[T=\exp-(h^2\beta_{11}+k^2\beta_{22}+\ldots+2kl\beta_{23})]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Pb	0.12226(0)	0.02562(0)	0.00000	0.00019(0)	0.00149(5)	0.0086(4)	0.00001(3)	0.00003(9)	−0.0003(3)
Tl	0.03043(4)	0.2955(1)	0.1861(4)	0.00033(1)	0.00263(7)	0.0153(6)	−0.00021(4)	0.0004(1)	−0.0017(3)
As(1)	0.03380(8)	0.0117(3)	0.1151(8)	0.00016(1)	0.0013(1)	0.010(1)	−0.00004(7)	−0.0001(2)	−0.0004(7)
As(2)	0.07577(7)	0.0967(2)	0.5565(8)	0.00015(1)	0.0010(1)	0.009(1)	0.00011(7)	−0.0003(2)	0.0001(7)
As(3)	0.08313(8)	0.3028(2)	0.7667(8)	0.00019(1)	0.0011(1)	0.009(1)	0.00006(7)	0.0003(2)	−0.0013(7)
S(1)	0.0807(2)	0.1424(6)	0.195(2)	0.00022(3)	0.0019(3)	0.009(3)	−0.0001(2)	0.0000(5)	−0.001(1)
S(2)	0.0813(2)	0.3843(5)	0.452(2)	0.00019(3)	0.0016(3)	0.010(3)	0.0000(2)	−0.0002(5)	0.002(1)
S(3)	0.0045(2)	0.3938(5)	0.612(2)	0.00017(3)	0.0011(3)	0.017(3)	−0.0001(1)	−0.0000(5)	−0.002(2)
S(4)	0.0468(2)	0.2067(5)	0.674(2)	0.00016(3)	0.0013(3)	0.012(3)	0.0001(1)	0.0004(5)	0.000(1)
S(5)	0.1214(2)	0.2201(5)	0.702(2)	0.00019(3)	0.0013(3)	0.010(3)	−0.0001(1)	−0.0002(5)	−0.001(1)
S(6)	0.0402(2)	0.4968(6)	0.996(2)	0.00030(4)	0.0017(3)	0.013(3)	−0.0004(2)	−0.0009(6)	0.001(2)

Table 2. Interatomic distances in $PbTlAs_3S_6$

Pb	$-S(5)_5$	2.796(10) Å	Tl	$-S(3)_1$	3.169(10) Å
	$-S(1)_1$	2.907(9)		$-S(2)_1$	3.184(9)
	$-S(2)_3$	2.938(8)		$-S(4)_1$	3.262(11)
	$-S(2)_5$	3.011(9)		$-S(6)_2$	3.341(9)
	$-S(1)_5$	3.056(9)		$-S(1)_1$	3.363(9)
	$-S(5)_6$	3.330(10)		$-S(4)_2$	3.385(11)
	$-S(5)_2$	3.478(8)		$-S(3)_4$	3.394(8)
mean		3.074 Å	mean		3.300 Å
As(1)	$-S(6)_3$	2.260(12) Å	As(2)	$-S(1)_1$	2.242(11) Å
	$-S(3)_3$	2.294(9)		$-S(4)_1$	2.293(9)
	$-S(3)_4$	2.332(9)		$-S(6)_3$	2.315(10)
mean		2.295 Å	mean		2.283 Å
As(3)	$-S(2)_1$	2.234(11) Å			
	$-S(5)_1$	2.253(9)			
	$-S(4)_1$	2.339(9)			
mean		2.275 Å			

Symmetry code

1: x, y, z 2: $x, y, z-1$ 3: $x, y-\frac{1}{2}, z-\frac{1}{2}$

4: $\bar{x}, \frac{1}{2}-y, z-\frac{1}{2}$ 5: $\frac{1}{4}-x, y-\frac{1}{4}, z-\frac{1}{4}$ 6: $\frac{1}{4}-x, y-\frac{1}{4}, z-1\frac{1}{4}$

KRIPROG system. Lists of structure factors and additional data may be obtained from the authors upon request.

4. Description of the structure

The final atomic coordinates and the thermal parameters are given in Table 1. Tables 2 and 3 present the interatomic distances and bond angles.

The Pb and Tl atoms were assigned to the two heavy-atom positions according to their different metal-S distances as reported by Edenharter (1976).

The Pb atom is coordinated by seven S atoms which form an almost regular trigonal prism defined by six atoms, with one additional atom beyond one prism face. The Pb atom is situated close to this prism face. This results in five shorter Pb – S distances of 2.80 – 3.06 Å and two longer distances of 3.33 and 3.48 Å. A similar coordination of Pb atoms was found in other sulphosalts, e.g. hutchinsonite (Takéuchi et al., 1965), baumhauerite (Engel and Nowacki, 1969), bournonite and seligmannite (Edenharter et al., 1970), jordanite (Ito and Nowacki, 1974), $Tl_8Pb_4Sb_{21}As_{19}S_{68}$ (Nagl, 1979). The Tl atom is coordinated by 7 + 2 S atoms. The seven closer S atoms form a deformed polyhedron similar to the Pb coordination polyhedron. The Tl atom is situated near to the center of the prism defined by six S atoms.

Table 3. Bond angles in $PbTlAs_3S_6$

$S(5)_5$	– Pb –	$S(1)_1$	83.9(3)°	$S(3)_1$	– Tl –	$S(2)_1$	72.8(2)°
$S(5)_5$		$S(2)_3$	86.2(3)	$S(3)_1$		$S(4)_1$	66.8(3)
$S(5)_5$		$S(2)_5$	73.9(3)	$S(3)_1$		$S(6)_2$	82.4(2)
$S(5)_5$		$S(1)_5$	79.3(3)	$S(3)_1$		$S(1)_1$	127.0(2)
$S(5)_5$		$S(5)_6$	145.1(5)	$S(3)_1$		$S(4)_2$	168.5(4)
$S(5)_5$		$S(5)_2$	137.8(3)	$S(3)_1$		$S(3)_4$	108.9(2)
$S(1)_1$		$S(2)_3$	93.0(3)	$S(2)_1$		$S(4)_1$	64.8(2)
$S(1)_1$		$S(2)_5$	89.7(3)	$S(2)_1$		$S(6)_2$	69.8(3)
$S(1)_1$		$S(1)_5$	163.0(4)	$S(2)_1$		$S(1)_1$	76.0(2)
$S(1)_1$		$S(5)_6$	126.8(2)	$S(2)_1$		$S(4)_2$	115.6(2)
$S(1)_1$		$S(5)_2$	69.5(3)	$S(2)_1$		$S(3)_4$	143.6(2)
$S(2)_3$		$S(2)_5$	159.5(3)	$S(4)_1$		$S(6)_2$	130.6(3)
$S(2)_3$		$S(1)_5$	88.3(2)	$S(4)_1$		$S(1)_1$	61.3(2)
$S(2)_3$		$S(5)_6$	77.0(2)	$S(4)_1$		$S(4)_2$	123.2(3)
$S(2)_3$		$S(5)_2$	126.0(3)	$S(4)_1$		$S(3)_4$	82.2(2)
$S(2)_5$		$S(1)_5$	83.4(2)	$S(6)_2$		$S(1)_1$	124.3(3)
$S(2)_5$		$S(5)_6$	117.0(2)	$S(6)_2$		$S(4)_2$	93.0(2)
$S(2)_5$		$S(5)_2$	73.8(2)	$S(6)_2$		$S(3)_4$	146.2(3)
$S(1)_5$		$S(5)_6$	70.0(2)	$S(1)_1$		$S(4)_2$	64.1(2)
$S(1)_5$		$S(5)_2$	122.7(3)	$S(1)_1$		$S(3)_4$	74.9(2)
$S(5)_6$		$S(5)_2$	75.1(2)	$S(4)_2$		$S(3)_4$	69.5(2)
$S(6)_3$	– As(1) –	$S(3)_3$	90.4(4)°	$S(1)_1$	– As(2) –	$S(4)_1$	96.4(4)°
$S(6)_3$		$S(3)_4$	100.1(4)	$S(1)_1$		$S(6)_3$	98.2(4)
$S(3)_3$		$S(3)_4$	91.5(3)	$S(4)_1$		$S(6)_3$	96.0(3)
mean			94.0 °	mean			96.9 °

$S(2)_1$	– As(3) –	$S(5)_1$	102.3(4)°
$S(2)_1$		$S(4)_1$	98.1(4)
$S(5)_1$		$S(4)_1$	101.1(3)
mean			100.5 °

Therefore there is a more uniform distribution of the Tl – S distances in the range 3.17 – 3.39 Å. The two additional S atoms are at distances of 3.67 and 3.88 Å. Considering that there is a short Tl – As distance of 3.50 Å, we describe the Tl coordination polyhedron only by the seven nearest S atoms. The As atoms are each bonded to three nearest S atoms forming a trigonal pyramid with the As atom at the apex, as usually found in sulphosalts. The mean As – S distance is 2.28 Å and the mean S – As – S angle is 97.1°, close to the values given by Edenharter (1976). The Pb coordination polyhedra form $^2_\infty[PbS_3]$ layers parallel to the (100) crystal face with each polyhedron sharing two faces and three vertices with its neighbours, as shown in Figure 2. The layers are interconnected by $^1_\infty[TlS_5]$-double chains, shown in Figure 3, which extend in the [001] direction. The Tl polyhedra share 4 vertices with their neighbours. The Pb layers and Tl chains are further interconnected by finite $[As_6S_{12}]$ groups, shown in Figure 4. Remarkably the $[As_6S_{12}]$ group

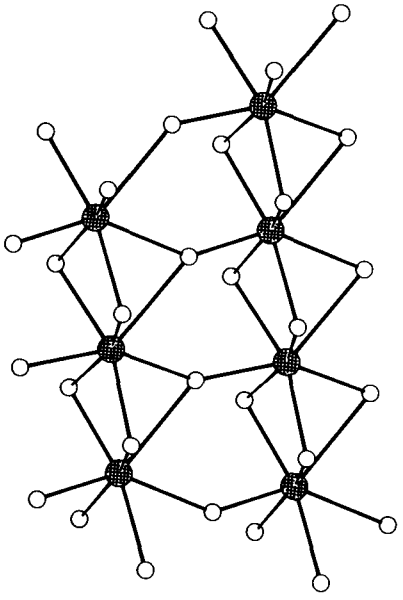

Fig. 2. Cut out of a $^2_\infty[PbS_3]$ layer. Parallel projection along the *a*-axis

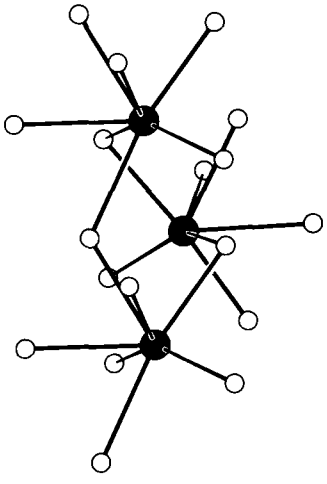

Fig. 3. Cut out of a $^1_\infty[TlS_5]$ double chain. Parallel projection along the *a*-axis

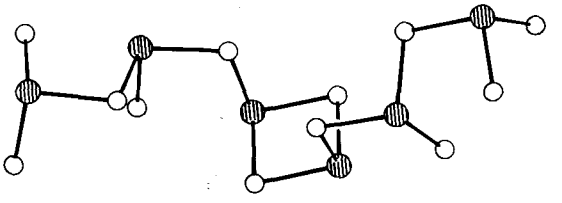

Fig. 4. $[As_6S_{12}]$ group in synthetic $PbTlAs_3S_6$

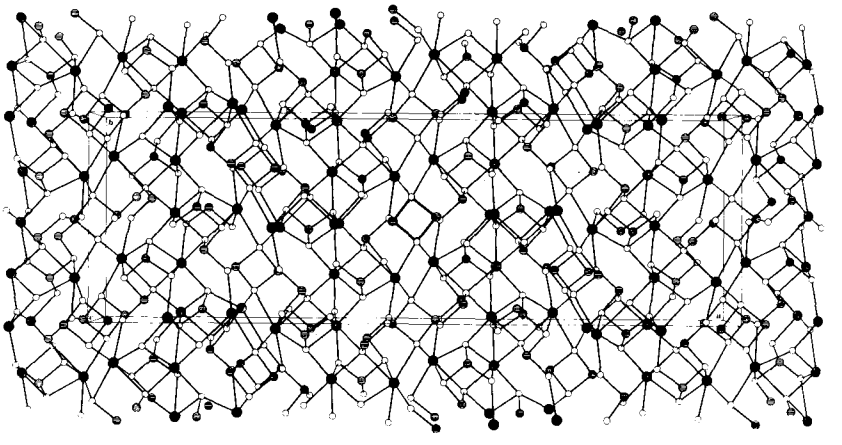

Fig. 5. Central projection of the structure of synthetic $PbTlAs_3S_6$ viewed along the *c*-axis

contains a two-membered ring in cis connection. A two membered ring in trans connection has recently been found by Schäfer (1982) in $BaAs_2S_5$. Short Pb–As distances of 3.56–3.71 Å and Tl–As distance of 3.50 Å which appear in this structure have also been noticed in other sulphosalt structures e.g. hatchite (Marumo and Nowacki, 1967) wallisite (Takéuchi et al., 1968) rebulite (Balić-Žunić et al., 1982).

Five S atoms are each coordinated by 4 metal atoms forming a deformed tetrahedron. S(6) has an almost planar coordination of 3 metal atoms only. A projection of the structure of synthetic $PbTlAs_3S_6$ is shown in Figure 5.

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