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Structure determination of a new misfit layer compound $(PbS)_{1.18}(TiS_2)_2$*

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Abstract

$(PbS)_{1.18}(TiS_2)_2$ is a misfit layer compound in which two types of slabs, PbS and $2(TiS_2)$, alternate along the c direction. The $|TiS_2|$ blocks (about 11.39 Å thick) are interleaved by $|PbS|$ layers, thus leading to a value for c of 17.46 Å. The misfit between the two slab types occurs along the a direction; the parameter values being $a(PbS) = 5.761$ Å and $a(TiS_2) = 3.390$ Å respectively. This yields a ratio of approximately 1.699, which is irrational but close to 5/3. The common in-plane b parameter is equal to 5.873 Å. The PbS unit consists of a {001} slice (half an edge thick) of an NaCl-type f.c.c. cell.

1. Introduction

A great deal of interest has recently been devoted to the so-called misfit layer compounds with a general formulation close to MTS_3 ($M \equiv Sn$, Pb, Bi and a rare-earth element; $T \equiv Ti$, V, Cr, Nb, Ta) [1, 2]. Their structure consists of an alternating sequence along the c axis of $|MS|$ and $|TS_2|$ slabs. Each of these sublattices is characterized by a and b in-plane parameters. The two b values, b_1 (MS) and b_2 (TS_2), are identical but the ratio between the two a values is irrational ($1.65 < a_1/a_2 < 1.80$). The corresponding c parameters are equal in length or the length of one c is twice the other along the stacking direction. The misfit results in chemical formulations $(MS)_nTS_2$ with $1.08 < n < 1.23$.

The $|MS|$ part consists of a double $|MS|$ layer which is actually a {001} slice (half an edge thick) of an f.c.c. NaCl type. The $|TS_2|$ part shows a different geometry which depends on the nature of T.

(1) For $T \equiv Ti$, V, Cr, the $|TS_2|$ slabs are made of edge-sharing $|TS_6|$ octahedra as in TiS_2. This is observed for example in $(SnS)_{1.20}TiS_2$ [3], $(PbS)_{1.18}TiS_2$ [4] or $(LaS)_{1.20}CrS_2$ [5]. A monoclinic symmetry usually characterizes the $|TS_2|$ slab in this case.

(2) For $T \equiv Nb$, Ta, the $|TS_2|$ layer is built up from trigonal prisms as in $2H\text{-}NbS_2$ or $2H\text{-}TaS_2$. An orthorhombic symmetry is generally observed in this case as illustrated by $(PbS)_{1.14}NbS_2$ [6].

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*Dedicated to Professor W. Bronger and Professor Ch. J. Raub on the occasions of their 60th birthdays.

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Obviously, one could expect to prepare a new series of phases by changing the 1/1 sequence stacking of the slabs. The present paper is concerned with the preparation of a phase in which two successive $|TiS_2|$ slabs are separated by a $|PbS|$ part.

2. Experimental details

The elements Pb, Ti, S were mixed in the proportions 1:2:5 and heated in a quartz tube, sealed under vacuum, at 850–900 °C (gradient approx. 50 °C) for ten days. The product of the reaction was ground and reheated at the same temperature, for one week, in the presence of a small amount of iodine (less than 5 mg cm^{-3}) to favour crystallization. Platelet-shaped single crystals were obtained under these conditions.

Preliminary classical X-ray investigations on a single crystal indicated a monoclinic symmetry. A least-squares refinement of the unit cell parameters was performed on the diffraction pattern obtained with an INEL curved detector, calibrated with silicon (λCu $K\alpha_1 = 1.540598$ Å). The unit cell constants, along with the X-ray indexed pattern, are given in Table 1.

Chemical analyses were carried out with an electron microprobe (TRACOR model: dispersive energy) mounted on a scanning electron microscope. This gives semiquantitative results which are reported in Table 2.

3. Structure determination

A platelet-shaped single crystal ($0.025 \times 0.12 \times 0.20$ mm^3) was mounted on a NONIUS-CAD4 diffractometer. Details of the data collection are shown in Table 3. The intensities were corrected for polarization and Lorentz effects. At the final stage of refinement (before an anisotropic thermal parameter refinement), an absorption correction using the DIFABS program [7] was applied.

Two separate sets of reflections belonging to the $|PbS|$ and $|TiS_2|$ parts of the structure were recorded from the same crystal. The unit cells of both parts are C-centred monoclinic with corresponding b and c axes parallel and equal in length, the c axes being perpendicular to the layers. The corresponding a axes are also parallel but differ in length; the ratio, a_1:$a_2 = 1.699$, is irrational. The β_1 and β_2 angles are identical.

The structure determination of this so-called composite crystal [8] has been separated into three parts:

(1) the $|PbS|$ part excluding reflections with $h_1 = 0$ or 5, as they are common with those of the $|TiS_2|$ part;

(2) the $|TiS_2|$ part excluding reflections with $h_2 = 0$ or 3, for the same reasons as above;

(3) the common part, *i.e.* the relative position (y and z coordinates) of $|PbS|$ and $|TiS_2|$ sublattices using the common *okl* reflections.

TABLE 1

X-ray powder diffraction pattern for "$PbTi_2S_5$" (least-square refinements are conducted for separate |PbS| and |TiS_2| parts)

h k l	Type	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
0 0 3	c	5.808	5.810	44
0 0 4	c	4.355	4.357	82
1 1 1	a	3.954	3.960	3
1 1 $\bar{2}$	a	3.789	3.782	9
1 1 2	a	3.661	3.655	7
0 0 5	c	3.485	3.486	99
1 1 $\bar{3}$	a	3.431	3.427	8
1 1 3	a	3.291	3.287	5
0 2 0	c	2.9284	2.9309	25
1 1 4	a		2.9254	
1 1 0	b		2.9344	
0 0 6	c	2.9049	2.9049	100
2 0 0	a	2.8793	2.8807	15
1 1 1	b		2.8788	
0 2 1	c	2.8619	2.8609	12
2 0 1	a	2.8437	2.8422	13
0 2 $\bar{2}$	c	2.8312	2.8326	7
0 2 $\bar{3}$	c	2.6858	2.6859	9
1 1 3	b	2.5906	2.5865	10
0 2 $\bar{4}$	c	2.5069	2.5064	16
0 0 7	c	2.4905	2.4899	32
0 2 $\bar{5}$	c	2.3168	2.3166	11
0 2 5	c	2.1760	2.1766	20
1 1 $\bar{7}$	a	2.1700	2.1725	1
2 2 0	a	2.0532	2.0545	16
2 2 $\bar{1}$	a		2.0510	
2 0 6	a	2.0454	2.0455	3
1 1 $\bar{8}$	a	1.9604	1.9611	14
0 2 $\bar{7}$	c		1.9597	
0 0 9	c	1.9370	1.9366	13
0 2 8	c	1.6975	1.6979	9
3 1 $\bar{4}$	a	1.6943	1.6953	9
1 3 $\bar{1}$	b		1.6938	
1 3 0	b		1.6928	
2 0 0	b		1.6948	
0 0 11	c	1.5848	1.5845	9
0 2 9	c	1.5704	1.5707	10
0 4 1	c	1.4526	1.4526	49
0 0 12	c		1.4524	

a, |PbS|; b, |TiS_2|; c, common.
|PbS| part: $a=5.761(2)$ Å, $b=5.873(1)$ Å, $c=17.464(3)$ Å, $\alpha=93.62(2)°$; |TiS_2| part: $a=3.390(1)$ Å, $b=5.873(1)$ Å, $c=17.464(3)$ Å, $\alpha=93.62(2)°$.

3.1. *Refinement of the |PbS| part*

Positions for the Pb and S atoms were determined from the Patterson map. The |PbS| structural part was refined in the $C2/m$ space group and

TABLE 2

Chemical analysis averaged on three distinct crystals: corrected atomic fraction

	Pb	Ti	S
Experimental	14.2	23.9	61.9
Theoretical for $(PbS)_{1.18}(TiS_2)_2$	14.1	23.9	62.0

yielded reliability factors $R=0.064$, $R_w=0.082$ for 258 reflections ($I \geqslant 3\ \sigma I$), restricted to the range $0 \leqslant \sin\ \theta.\ \lambda^{-1} \leqslant 0.65$. Furthermore, reflections with the weakest intensities ($F_0 \leqslant 1/10\ F_0^{\max}$, $|F_0| \leqslant 4$) were disregarded. Indeed, X-ray photographic films showed diffuse lines (in addition to Bragg spots) indicating a relative disorder probably related to stacking faults, such as the following.

(1) A shift of building blocks in either the *a* and/or *b* directions (translational disorder).

(2) A misorientation of blocks at their juxtaposition plane (*a*, *b* plane); for example, there are two orientations (differing by 90°) for the pseudohexagonal $|TS_2|$ layer deposited on the |MS| layer (see Kuypers *et al.* [9] for a detailed study of stacking disorder).

A refinement of the structure with anisotropic U values did not yield better results and even some U components of the sulphur atom became negative. The coordinates and isotropic thermal factors are given in Table 4.

3.2. *Refinement of the $|TiS_2|$ part*

The positions for Ti and S atoms were determined from the Patterson map. Refinement of the $|TiS_2|$ part conducted in the $C2_1/m$ space group converged to reliability factors $R=0.116$, $R_w=0.137$ for 101 reflections $I \geqslant 3\ \sigma I$; the weakest reflections ($F_0 < 1/8\ F_0^{\max}$, $|F_0| \leqslant 5$) being rejected. It was not realistic to refine with anisotropic thermal factors as values for isotropic ones (Ti atom) were already negative. Although the R values are not very satisfactory, no significant feature appears in the Fourier difference synthesis. It is undeniable that the presence of diffuse lines giving evidence of disorder alters the measurement of intensities and thus the quality of refinement. Thus, no major significance should be attached to the large range of values of B temperature factors. The coordinates and thermal parameters are given in Table 5.

3.3. *Refinement of the common part*

The relative positions (y and z parameters) of both structural parts have to be deduced from the refinement of the *okl* reflections only. Because of the incommensurate character along the a direction, it is impossible to relate the x coordinates. Refinements were performed in the space group $C2/m$; the variables being the y and z coordinates of the |PbS| sublattice with

TABLE 3

Crystal data and details of the data collection details

	PbS part	TiS$_2$ part
Crystal system	monoclinic, S.G. $C2/m$	monoclinic, S.G. $C2_1/m$
Unit cell parameters (celdim program)	$a = 5.755(9)$ Å $b = 5.869(6)$ Å $c = 17.35(5)$ Å $\alpha = 93.74(5)°$	$a = 3.396(6)$ Å $b = 5.866(7)$ Å $c = 17.41(3)$ Å $\alpha = 93.60(6)°$
Data collection		
Radiation	Mo Kα, $\lambda = 0.7107$ Å	Mo Kα, $\lambda = 0.7107$ Å
Monochromator	Graphite	Graphite
θ range; min., max. (°)	2, 30	2, 35
θ–2θ scan	$\Delta\omega = 1.20 + 0.35 \tan\theta$	$\Delta\omega = 1.20 + 0.35 \tan\theta$
Min. and max. absorption correction factors	0.630, 1.479	0.606, 1.315

Refinement

PbS		TiS$_2$ part		Common part	
No. of reflections ($I \geqslant 3\sigma I$) ($h \neq 0, 5$)	258	No. of reflections ($I > 3\sigma I$) ($h \neq 0, 3$)	101	No. of reflections ($I > 2\sigma I$, (okl)) issued from the TiS$_2$ part	83
No. of refined parameters	7	No. of refined parameters	10	No. of refined parameters	16
Final agreement factors		Final agreement factors		Final agreement factors	
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.064	$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.116	$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.148
$R_w = [\Sigma(w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.082	$R_w = [\Sigma(w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.137	$R_w = [\Sigma(w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.180
With $w = 1$ for all reflections		With $w = 1$ for all reflections		With $w = 1$ for all reflections	
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$	5.72	$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$	3.8	$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$	10.3
Highest residual peak in final Fourier difference	± 1.87 e$^-$ Å^{-3}	Highest residual peak in final Fourier difference	± 1.05 e$^-$ Å^{-3}		

TABLE 4

Coordinates and thermal parameters: |PbS| part

Site	x	y	z	B(Å^2)
Pb (4i)	0	0.7671(5)	0.0904(2)	1.20(3)
S (4i)	1/2	0.768(4)	0.072(1)	3.6(4)

TABLE 5

Coordinates and thermal parameters: $|\mathrm{TiS}_2|$ part

Site	x	y	z	B(Å^2)
Ti (2e)	1/4	0.217(2)	0.3355(6)	−0.9(5)
S1 (2e)	3/4	0.042(9)	0.256(3)	8(1)
S2 (2e)	3/4	0.416(6)	0.423(2)	5.5(7)

TABLE 6

Coordinates and thermal parameters: common part

	(a)				(b)			
	x	y	z	B(Å^2)	x	y	z	B(Å^2)
Pb	–	0.766(2)	0.091(1)	0.3(2)	–	0.766(2)	0.091(1)	0.3(1)
S	–	0.767	0.072	5.0(4)	–	0.782(18)	0.055(7)	4.0(3)
Ti	–	0.217	0.336	2.2(8)	–	0.219(5)	0.336(2)	2.4(7)
S1	–	0.042	0.256	−0.4(6)	–	0.041(5)	0.254(2)	0.1(6)
S2	–	0.416	0.423	2.0(1)	–	0.390(7)	0.416(2)	1.3(7)

respect to the $|\mathrm{TiS}_2|$ one. However, we constrained the y and z coordinates of Pb and S to get differences identical to those found in the separate refinement of the |PbS| part. In contrast, we used the fractional coordinates of Ti and S atoms (belonging to $|\mathrm{TiS}_2|$) obtained from the separate $|\mathrm{TiS}_2|$ refinement. The relative weight of |PbS| against $2\times|\mathrm{TiS}_2|$ was first fixed in agreement with the mismatch ratio a_1:a_2. Thus, a diffracting weight ratio of 0.59:1 ($|\mathrm{PbS}|$:$|\mathrm{TiS}_2|$) is deduced from the $(\mathrm{PbS})_{1.18}(\mathrm{TiS}_2)_2$ formulation. At this stage of refinement (see Table 6(a)), relatively poor R values were obtained, $R=0.193$, $R_w=0.216$ (for 83 *hkl*, 8 variables). A further refinement, free of any constraint (on the coordinates), was then performed. A noticeable improvement of the goodness of fit was observed. The relative diffracting weight ratio was then changed, step by step. The final refinement (see Table 6(b)) converged to R values of $R=0.148$, $R_w=0.180$ for a ratio 0.56:1 with 83 reflections ($I\geqslant 2\sigma I$, $0<\sin\theta/\lambda<0.7$) and 16 variables. Very small shifts of the atomic coordinates relative to the positions refined in the separate parts are noted but on this occasion the isotropic temperature factors *B* showed greater homogeneous values.

4. Discussion of the structure

Figure 1 shows the projection of the complete structure of $(PbS)_{1.18}(TiS_2)_2$ along the misfit $\vec{a}$ direction. Within the |PbS| part, each Pb atom is coordinated by five S atoms located at the corners of a slightly distorted square pyramid (NaCl structure type). The Pb–S distances are given in Table 7. One Pb–S distance (between Pb and S(e) at opposite sides of the |PbS| "ladder" arrangement) is shorter (2.81 Å) than the other four Pb–S distances in the square basis (Sa, Sb, Sc, Sd) which are 2.895 Å, 2.928 Å, 2.895 Å and 2.976 Å, respectively. Pb atoms protrude from the sulphur planes on both sides

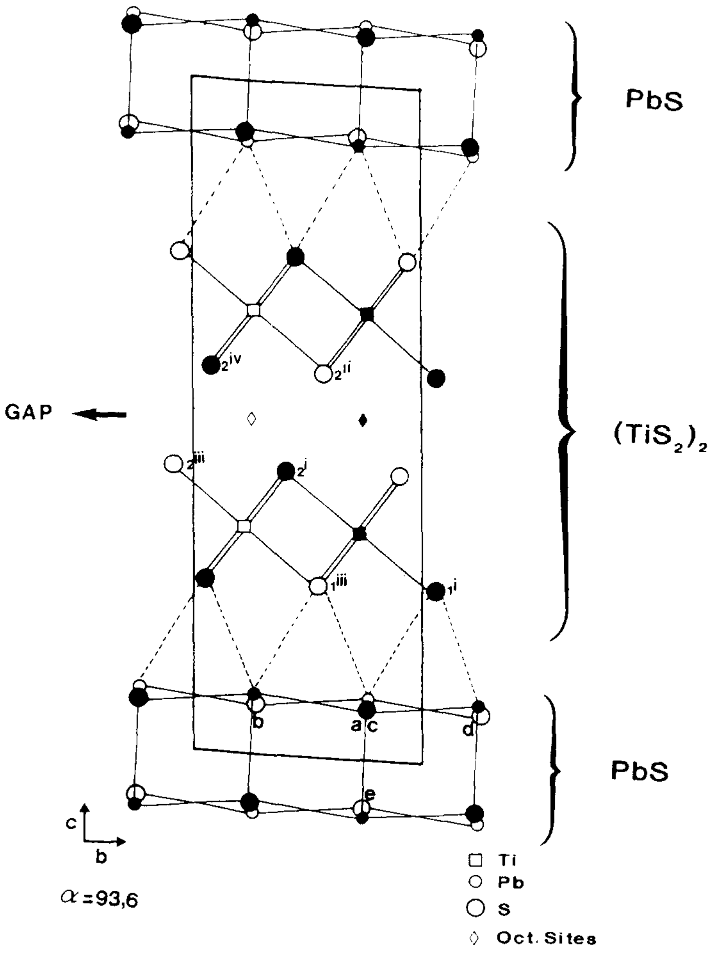

Fig. 1. $(PbS)_{1.18}(TiS_2)_2$ projection along the misfit $\vec{a}$ direction.

TABLE 7

Interatomic distances (Å) for $(PbS)_{1.18}(TiS_2)_2$

PbS		TiS_2		Within the gap	
Pb–S(a)	2.895(1)	Ti–S1^{iii}	2.43(4)	O^c–2×S2^i	2.40
–S(b)	2.928(9)	–S2^{iii}	2.41(3)	–2×S2^{iv}	2.40
–S(c)	2.895(1)	–2×S1^i	2.39(2)	–S2^{iii}	2.30
–S(d)	2.976(9)	–2×S2^i	2.52(2)	–S2^{ii}	2.30
–S(e)	2.81(1)				
$(Pb–S)_{av}$	2.900	$(Ti–S)_{av}$	2.44	$(O–S)_{av}$	2.35
Pb–Pb [a]	4.289	Ti–Ti	3.396		
Pb–Pb	4.253	Ti–Tic	3.390		
Pb–Pbc[b]	4.110				

[a] Refers to opposite sides.
[b] Refers to same side.
[c] O = octahedral site.

of the |PbS| double layers. In this way, each Pb atom is also coordinated by two or three S atoms of the $|TiS_2|$ slabs, depending on the actual position along the misfit direction. Indeed, with respect to the incommensurability, and in order to minimize atomic repulsions, Pb atoms should readjust their positions; an equilibrium position for Pb would correspond to three equal Pb–S distances with respect to S atoms of the $|TiS_2|$ lattice (S in a honeycomb arrangement).

Within the $|TiS_2|$ subsystem, each Ti atom is coordinated by six S atoms in a trigonal antiprismatic arrangement. The $|TiS_2|$ slab is slightly distorted compared with 1T–TiS_2. The Ti–S distances are summarized in Table 7. The average distance (2.44 Å) is close to that observed in 1T–TiS_2 (2.428 Å) [10]. Two $|TiS_2|$ slabs are stacked along the *c* axis, between |PbS| units.

5. Conclusion

This is the first structural study made on a misfit compound with a 1:2 ($|MS|:|TS_2|$) ratio where both subsystems are of monoclinic symmetry (T of $|TS_2|$ is octahedrally coordinated). The study was carried out using the composite approach and without considering the mutual modulation of the two sublattices. Diffuse scattering due to stacking disorder also contributes to the total diffracted intensity. This explains the rather high *R* factor values. Nevertheless, the results appear to be very reliable in comparison to what has been found for the parent structures.

The 1:2 ratio has also been found in $(PbS)_{1.14}(NbS_2)_2$ [11] for which two successive (NbS_2) slabs, separated by a |PbS| layer, are stacked in such a way that they represent two-thirds of the 3R-NbS_2 structure (and not the two-slab arrangement of 2H-NbS_2, as could have been expected). This 1:2 ratio was previously mentioned by Guemas *et al.* [12] and Gotoh *et al.* [13].

In the van der Waals gap between adjacent $|TiS_2|$ slabs, the vacant interlayer sites are of octahedral symmetry. Their sizes, $(O.\text{-}S)_{av} \approx 2.35$ Å, are as large as those within the $|TiS_2|$ slab itself (see Table 7). This should allow intercalation, the study of which is already in progress for $(PbS)_{1.14}(NbS_2)_2$ with lithium as an intercalating species [14].

Such a study can provide direct proof for a charge transfer (if it exists) from $|MS|$ to $|TS_2|$. Indeed, the number of intercalated Li atoms and then of transferred $e^-(Li \rightarrow Li^+ + e^-)$ is related to the number of empty electronic states, mainly the "d" type conduction band, to be filled. Transport measurements (resistivity and Hall effect *vs.* temperature) will also be carried out in the near future.

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