The Crystal Structure of $(Pb_{1-x}, Bi_x)Bi_2Cu_2Cu_{2-x}S_5I_2$ $(x=0.88)$

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The crystal structure of $(Pb_{1-x}, Bi_x)Bi_2Cu_2Cu_{2-x}S_5I_2$ $(x=0.88)$ has been determined from three-dimensional intensity data. Four formula units of the compound are contained in the orthorhombic cell: $a=13.236$ (5), $b=23.630$ (16), $c=4.010$ (5) Å of the space group *Bbmm*. The structure was derived from Patterson, Fourier and difference syntheses, and was refined by a least-squares method. The final R for 725 independent reflexions is 7·4%. (Pb, Bi) and Bi have three nearest sulphur atoms and form trigonal pyramids. One of the two independent copper atoms is trigonally coordinated with three sulphur atoms. Two sulphur and two iodine atoms are arranged tetrahedrally around the second copper atom. The occupancy of this copper atom is 56%. The material has a layer structure, the layers being parallel to (010) and connected by weak Bi–I bonds.

Introduction

The compound $PbBi_2Cu_4S_5I_2$ has been synthesized by transport reactions. As only a few structures of bismuth sulphiodides have been studied so far, the present investigation was undertaken to compare the coordination of iodine atoms around bismuth atoms in this material with iodine atoms in other bismuth sulphiodides.

Experimental

The material was synthesized by chemical transport reaction from a mixture of appropriate proportion of PbS, Bi_2S_3 and Cu_2S. The mixed suphides and 0·1 N HI solution were sealed in a silica glass tube and were kept at a temperature of 430°C with a gradient of about 15°C for 12 days. The crystals obtained were needles of the length 0·1–0·7 mm, and of radius 0·005–00·5 mm.

Semi-quantitative electron microprobe analysis of the crystals revealed that the content of Pb, Bi and Cu varies for different crystals (Fig. 1) and that the chemical formula of these substances is expressed by $Pb_{1-x}Bi_{2+x}Cu_{4-x}S_5I_2$ $(0 \le x \le 1)$.

Table 1. *Crystal data*

$(Pb_{1-x}, Bi_x)Bi_2Cu_2Cu_{2-x}S_5I_2$
($x=0.88$: determined from the structure)
Orthorhombic, space group *Bbmm*
$a=13.236 \pm 0.005$, $b=23.630 \pm 0.016$, $c=4.010 \pm 0.005$ Å
($\lambda=1.5418$ Å)
$Z=4$
$D_{calc}=6.570$ g cm^{-3}
$\mu=1322$ cm^{-1} for Cu $K\alpha$ radiation
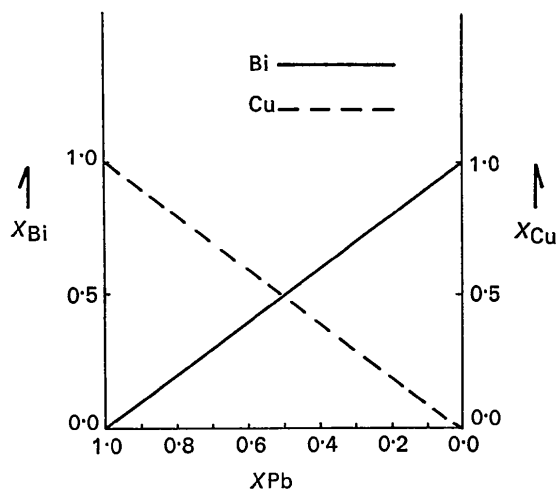
Fig. 1. Variations of the parameter x of Pb, Bi and Cu for different crystals.

Table 2. *Fractional coordinates, temperature factors in the expression*
$$exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$$ *and occupancies*

Estimated standard deviations are in parentheses.

	Site	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	m
(Pb,Bi)	8(*f*)	0·1058 (2)	0·2407 (2)	½	0·00184 (9)	0·00105 (15)	0·0143 (9)	0·00002 (6)	0	0	½
Bi	8(*f*)	0·0546 (1)	0·0874 (1)	0	0·00324 (6)	0·00051 (2)	0·0169 (5)	0·00027 (3)	0	0	1
Cu(1)	8(*f*)	0·3671 (4)	0·1861 (2)	0	0·00336 (28)	0·00171 (11)	0·0167 (23)	0·00072 (15)	0	0	1
Cu(2)	8(*f*)	0·3159 (6)	0·1098 (4)	½	0·00189 (44)	0·00110 (16)	0·0685 (69)	0·00022 (22)	0	0	0·560 (13)
S(1)	4(*c*)	0·2393 (6)	¼	0	0·00057 (40)	0·00170 (21)	0·0036 (39)	0	0	0	1
S(2)	8(*f*)	0·1593 (5)	0·1324 (3)	½	0·00216 (34)	0·00081 (11)	0·0126 (29)	0·00003 (16)	0	0	1
S(3)	8(*f*)	0·4487 (4)	0·1781 (3)	½	0·00134 (32)	0·00068 (11)	0·0148 (29)	0·00007 (15)	0	0	1
I	8(*f*)	0·3629 (1)	0·0406 (1)	0	0·00264 (11)	0·00073 (3)	0·0130 (9)	0·00010 (5)	0	0	1

The X-ray photographs of the crystals showed that the needles were always accompanied by small fragments of the same material, and that the c axis of the fragments was almost parallel to that of the hosts ($\doteqdot 3°$). The crystal used for the determination of the lattice parameters and the intensities was a needle 0·4 mm long and 0·012 mm diameter. Some extra reflexions from a fragment were observed in oscillation photographs ($\|c$) of this crystal. Since these reflexions were very weak, their effect on the structure determination was not taken into account. The cell dimensions were measured on a single-crystal diffractometer. The observed diffraction symmetry, $mmmBb$--, permits $Bbmm$ (No. 63), $Bbm2$ (No. 40) and $Bb2_1m$ (No. 36) as possible space groups. The correct space group determined from the structure is $Bbmm$. The crystal data of the material are given in Table 1.

The intensities were measured from $hk0$ to $hk4$ on an automated Weissenberg diffractometer (STAD I–2 system from Stoe) using nickel-filtered copper radiation and were corrected for Lorentz and polarization effects. Absorption corrections for cylindrical shape were also applied. 74 of the 725 independent reflexions had $I < 2\sigma(I)$ and were designated unobservable reflexions.

Determination and refinement of the structure

The reflexions from the layers with $l = 2n$ show approximately the same intensity distributions. The intensity distributions of the odd layers are similar to each other but not to that of the even layers. This characteristic of the intensity distribution suggested that almost all atoms should be on the levels with $z = 0$ and $\frac{1}{2}$, and that $Bbm2$ could be omitted from the possible space groups. $Bb2_1m$ was also excluded by the interpretation of the Patterson projection, $P(uv)$, along the c axis. At first, $PbBi_2Cu_4S_5I_2$ was assumed to be the chemical formula of the specimen. The coordinates of Pb, Bi and I were determined from the Patterson diagrams, $P(uv)$ and $P_1(uv)$ (generalized projection). Those of the other atoms were determined by successive Fourier and difference syntheses. The structure was refined by a least-squares method. The conventional R index was 8·4% at this stage. During the process of refinement, two anomalies were noted: the temperature factor of Cu(2) (6·81 Å^2); further, the β_{22} component of the anisotropic temperature factor of Pb was extremely high ($\sqrt{u^2} = 0·24$ Å). The occupancy of Cu(2) was then varied and the position for Pb [$4(c)mm$] was divided into two positions [$8(f)m$]. Further refinement by a least-squares method reduced $R = \sum \|F_{obs}\| - \|F_{calc}\|/\sum \|F_{obs}\|$ for all 725 reflexions to 7·4% and $R' = \{\sum w(\|F_{obs}\| - \|F_{calc}\|)^2\}^{1/2}/\{\sum w\|F_{obs}\|^2\}^{1/2}$ to 6·5%. The anomaly, formerly found in the difference map, disappeared thereafter. The occupancy of Cu(2), determined by the least-squares refinement, is 56% and the parameter x of the chemical formula, calculated from this value, is 0·88. At the final stage of the refinement, an atom form factor for bismuth was therefore used instead of that for lead.

A local version* of the full-matrix least-squares program $ORFLS$ (Busing, Martin & Levy, 1962) was used for structure-factor calculations and refinement. Neutral-atom form factors from $International\ Tables\ for$

Table 3. *Observed and calculated structure factors*

* A version to calculate the effect of anomalous dispersion.

X-ray Crystallography (1968) were used. Corrections for anomalous dispersion were employed for all atoms using the values published by Cromer (1965). Individual weights, $1/\sigma^2(F_o)$, based on counting statistics were used during the course of the refinements. Five reflexions were excluded from the least-squares calculations because they seemed to be affected strongly by the parallel-grown crystal fragment.

The atomic positions, anisotropic temperature factors and the occupancies are listed in Table 2. The observed and the computed structure factors are presented in Table 3.

Discussion of the structure

The interatomic distances and angles computed by the program *ORFFE* (Busing, Martin & Levy, 1964) are given in Table 4. The structure is illustrated in Fig. 2.

The formula of this material is expressed as $(Pb_{1-x}, Bi_x)Bi_2Cu_2Cu_{2-x}S_5I_2$ and that of the crystal used for the structure determination corresponds to $x=0\cdot88$.

Since (Pb, Bi) is slightly shifted from a mirror plane, it is statistically distributed between two positions with a separation of $0\cdot44$ Å. Six sulphur atoms around (Pb, Bi) form a trigonal prism and two more bonds to sulphur atoms are arranged in the directions perpendic-

ular to the prism faces. This type of coordination is very common for lead atoms in many substances. However, the ratio of the occupancies, $m_{Bi}:m_{Pb}$, is $0\cdot88:0\cdot12$ in the crystal studied and the space around (Pb, Bi) is probably too large for short Bi–S distances. This misfit of size should cause the statistical distribution of the (Pb, Bi). The distances between (Pb, Bi) and the three nearest sulphur atoms, being around $2\cdot67$ Å, coincide well with those values in Bi sulphosalts (Kupčik, 1972). The coordination of these three sulphur atoms to (Pb, Bi) is trigonal pyramidal.

Bi has three nearest S atoms at distances of $2\cdot56$ and $2\cdot66$ Å ($\times 2$), and forms with them a flat trigonal pyramid. One copper atom, Cu(2), and four iodine atoms also surround the bismuth atom at distances of $3\cdot20$, $3\cdot42$ ($\times 2$) and $3\cdot79$ Å ($\times 2$). An idealized drawing of the coordinations around Bi is illustrated in Fig. 3 together with those of bismuth atoms in $Bi(Bi_2S_3)_9I_3$ (Miehe & Kupčik, 1971) and BiSI (Haase-Wessel, 1973).

There are two independent copper atoms in the structure. Cu(1) is in nearly trigonal planar coordination with S and the mean Cu–S distance is $2\cdot28$ Å. This atom is not, however, on the triangle formed by the three sulphur atoms. The displacement of Cu(1) from the plane is about $0\cdot4$ Å and the sum of the three S–Cu–S angles is $350\cdot7°$. Cu(2) is in a tetrahedron, formed by two sulphur and two iodine atoms, with an occupancy $0\cdot56$. The mean Cu–S distance is $2\cdot26$ Å. The Cu–I distance, $2\cdot66$ Å, coincides with the published Cu–I distance of fourfold coordination ($2\cdot62$ Å, *International Tables for X-ray Crystallography*, 1968). Table 5 lists some typical short Cu–Cu distances for comparison. The shortest distance between two copper atoms is $2\cdot78$ Å in this compound.

The structure of $(Pb_{1-x},Bi_x)Bi_2Cu_2Cu_{2-x}S_5I_2$ consists of sheets parallel to (010). These layers are connected to each other by weak Bi–I bonds ($3\cdot79$ Å).

Table 4. *Interatomic distances and angles*

Estimated standard deviations are in parentheses.

Superscript			
None	x	y	z
i	$-\frac{1}{2}+x$	y	$\frac{1}{2}-z$
ii	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
iii	x	y	$-z$
iv	$-\frac{1}{2}+x$	y	$-\frac{1}{2}-z$
v	x	$\frac{1}{2}-y$	z
vi	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$
vii	x	y	$1+z$

Table 4 (*cont.*)

| Distances (Å)		Angles (°)	
(Pb, Bi)–S(2)	2·655 (9)	S(2)–(Pb, Bi)—S(1)	84·5 (2)
(Pb, Bi)–S(1)	2·682 (6)	S(1)–(Pb, Bi)—S(1^{vii})	96·8 (3)
(Pb, Bi)–S(2^v)	3·083 (9)	S(2)–(Pb, Bi)—S(3^i)	74·5 (2)
(Pb, Bi)–S(3^i)	3·244 (6)	S(3^i)–(Pb, Bi)^{iii}–S(3^{iv})	76·4 (2)
(Pb, Bi)–Cu(1^i)	3·412 (6)	S(1)–(Pb, Bi)—S(3^i)	89·9 (2)
(Pb, Bi)–S(3^{vi})	3·468 (6)		
Bi–S(3^i)	2·563 (6)	S(3^i)–Bi–S(2)	87·1 (2)
Bi–S(2)	2·659 (5)	S(2)–Bi–S(2^{iii})	97·9 (2)
Bi–Cu(2^i)	3·204 (8)	S(3^i)–Bi–I^i	82·2 (1)
Bi–I^i	3·417 (3)	I^i——Bi–I^{iv}	71·9 (1)
Bi–I^{ii}	3·789 (3)	S(2)–Bi–I^i	94·2 (1)
Cu(1)–S(1)	2·267 (8)	S(1)–Cu(1)–S(3)	114·0 (2)
Cu(1)–S(3)	2·285 (4)	S(3)–Cu(1)–S(3^{iii})	122·7 (3)
Cu(1)–Cu(2)	2·781 (8)		
Cu(1)–Cu(1^v)	3·020 (11)	S(2)–Cu(2)–S(3)	123·0 (5)
		S(2)–Cu(2)–I	112·3 (3)
Cu(2)–S(2)	2·140 (11)	S(3)–Cu(2)–I	104·1 (2)
Cu(2)–S(3)	2·387 (11)	I——Cu(2)–I^{vii}	97·8 (3)
Cu(2)–I	2·661 (7)		
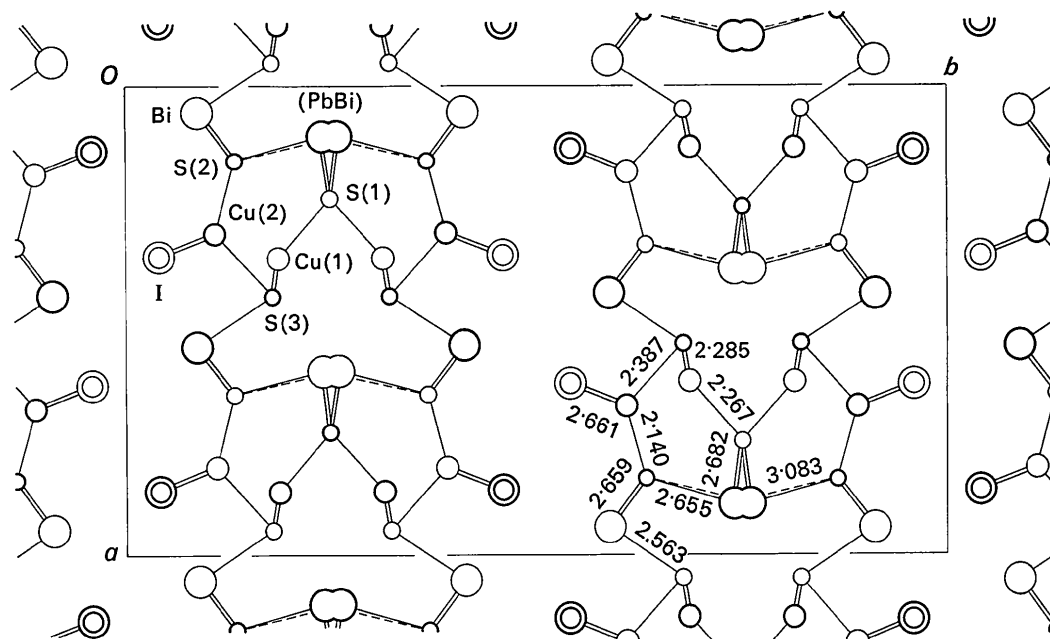
Fig. 2. Projection of the structure along the c axis. Thin circles indicate the atoms at $z=0$ and thick circles the atoms at $z=\frac{1}{2}$
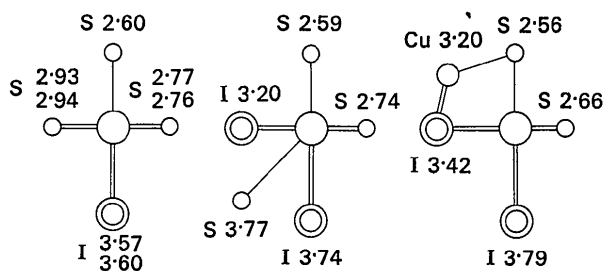

Fig. 3. Comparison of the coordinations around Bi in (a) $Bi(Bi_2S_3)_9I_3$, (b) BiSI and (c) $(Pb_{1-x},Bi_x)Bi_2Cu_2Cu_{2-x}S_5I_2$. Distances from bismuth atoms to the corresponding atoms are indicated.

Table 5. *Typical short* Cu–Cu *distances in some compounds*

Cu (metal, at 20°C)	2·556 Å
$C_{12}H_{10}N_3Cu$	2·45
[diaminobenzene copper(I)][a]	
Cu_2S (chalcocite)	2·53*†
$CuBi_5S_8$[b]	2·56
$Bi_2Cu_3S_4Cl_1$[c]	2·79*
$Cu_2(O_2CCH_3)_4.2H_2O$	2·614
[dinuclear copper(II) acetate monohydrate][d]	

References: (a) Brown & Dunitz (1961). (b) Ohmasa & Nowacki (1973). (c) Lewis & Kupčík (1974). (d) Brown & Chidambaram (1973).

* The shortest distances are listed.
† This value was calculated from the data of Evans (1971).

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