Zeitschrift für Kristallographie 209, 475–478

Refinement of the crystal structure of hutchinsonite, $TlPbAs_5S_9$

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Received March 3, 1993; accepted April 30, 1993

Hutchinsonite / Crystal structure / Sulfosalts

Abstract. Hutchinsonite, $TlPbAs_5S_9$, $M_r = 1074.72$, orthorhombic, *Pbca*, $a = 10.786(3)$ Å, $b = 35.389(8)$ Å, $c = 8.141(3)$ Å, $Z = 8$, $D_x = 4.59$ g/cm^3, $\mu(MoK_\alpha) = 330.60$ cm^{-1}, $F(000) = 3776$, locality: Quiruvilca, Peru. The anisotropic refinement converged to give the value of $R = 0.045$ ($wR = 0.046$) for 2992 reflections used. The Pb and Tl atoms occupy distinct sites M1 and M2, respectively. The former has seven S neighbours while the latter ten, giving average M – S distances 3.056(3) Å and 3.451(4) Å, respectively. The ordered arrangement of Pb and Tl has been fully supported by the Hamilton test and bond-valence calculations. The average values of As – S, S – S distances and S – As – S angles of the AsS_3 trigonal pyramids are 2.278(1) Å, 3409(1) Å and 96.93(2)°, respectively.

Introduction

The structure of hutchinsonite was worked out by Takéuchi, Ghose and Nowacki (1965) based on film diffraction data, showing that it consists of two kinds of slabs A and B. The latter has a PbS-like structure while the former is composed of twofold spiral chains with the composition As_4S_8. These chains are joined together by AsS_3 pyramids in the border of the slab to form a composite As – S sheet. The slabs A and B are alternately juxtaposed to build up the bulk of the structure. The structure thus provides a basic chemical formula, $(Tl, Pb)_2As_5S_9$ for this mineral species.

The present paper reports results of our refinement carried out to elucidate more details of the structure. Its brief account has appeared (Matsushita, Takéuchi, 1990). Although Wulf (1990) mentioned that the structure was studied with synchrotron radiation, no detailed report has been published.

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Experimental and refinement

The crystals used for the present study which came from Quiruvilca, Peru. The chemical composition of Quiruvilca hutchinsonites has been reported to be $Tl_{1.050}Pb_{1.156}As_{4.632}Sb_{0.183}S_9$ (White, Nelen, 1985). Another chemical analysis of hutchinsonite from the same locality was carried out by Sasaki (1983) and Sasaki and Miyake (1984), showing that the Pb and Tl ration is closely unit and As to S is 5/10 rather than 5/9.

A crystal specimen with dimensions $0.18 \times 0.16 \times 0.10$ mm^3 was selected and used for the structural study. The cell dimensions were obtained by the least-squares

Table 1. Experimental conditions for the refinement of hutchinsonite.

Crystal data	
Unit cell dimension (Å)	$a = 10.786(3)$, $b = 35.389(8)$, $c = 8.141(3)$
Z	8
Space group	*Pbca*
Intensity data collection	
Scan technique	ω
Scan width (°)	$1 + 0.3 \tan\theta$
Scan speed (°/min)	10
Max. number of repetition	10
Max. $(\sin\theta)/\lambda$ (Å^{-1})	0.8091
Max. $h, k, l, 2\theta$ (°)	18, 58, 14, 70.2
No. of measured reflections	6873
Intensity monitorius	
Reference reflections	270, 172, 2$\bar{7}$0
Interval	Every 150 reflections
Intensity variation (%)	±0.2
Intensity data reduction	
Lp correction	Yes
Absorption correction method	Ψ-scans (004, 043, 024)
Absorption coefficient (cm^{-1})	$\mu = 330.60$
Min./Max./Ave. transmission	0.5288/1.000/0.7975
Structure refinement	
No. of used reflections	2992 [$I_{obs} > 3.00\,\sigma(I_{obs})$]
Final R/wR-values	0.045/0.046
Final scale factor	0.183(1)
Max. final shift/e.s.d.	0.005
Goodness of fit	1.06
Max./Min. density in the final D-Fourier map (e/Å^3)	2.734/−2.609
Secondary extinction	$g = 7(4) \times 10^{-8}$

procedure applied to the 2θ values of 20 reflections ($28 < 2\theta < 56°$) measured on a RIGAKU AFC-5S diffractometer, using pyrolitic-graphite monochromatized MoK_α radiation, $\lambda = 0.71069$ Å. Details are summarized in Table 1.

The initial atomic parameters were provided by Takéuchi et al. (1965). The structural refinement was executed using TEXRAY program system (TEXSAN, 1985) with a weighting scheme of $1/\sigma^2 |F_{obs}|$. During anisotropic refinement, a Hamilton test (Hamilton, 1965) was made to decide the mode of distribution of Pb and Tl over the possible sites M1 and M2, which correspond to the original notations $(Pb, Tl)_I$ and $(Tl, Pb)_{II}$ (Takéuchi et al., 1965), respectively. The result revealed with high level of significance, $R_{146,2992,0.005}$ that, Pb is allocated to M1 and Tl to M2. The occupancy refinement of the cation sites, including As, was carried out without constraint (Table 2). Neutral atomic form factors and values for dispersion corrections for all atoms were provided by International Tables for X-ray Crystallography Vol. IV (1974). Further details of the refinement and final values of R are to be refered to Table 1. The resulting atomic parameters are listed in Table 3 [1].

Table 2. Occupancies in the cation sites of hutchinsonite.

Site	X-ray refinement	Bond-valence calculation (Brown, Altermatt, 1985)
M1	0.976(6) Pb	1.000 Pb
M2	0.981(6) Tl	1.000 Tl
As1	1.002(8) As	1.000 As
As2	1.010(8) As	0.9449 As + 0.0551 Sb
As3	1.065(9) As	0.8368 As + 0.1632 Sb
As4	0.994(8) As	1.000 As
As5	1.003(8) As	1.000 As

formula $Tl_{0.981}Pb_{0.976}As_{5.074}S_9$ $Tl_{1.000}Pb_{1.000}As_{4.7817}Sb_{0.2183}S_9$

Parameters using for calculated bond-valence are
$B = 0.37$, $V_{Pb} = 2$, $V_{Tl} = 1$, $V_{As} = 3$, $V_{Sb} = 3$,
$r_0(Pb-S) = 2.5357$, $r_0(Tl-S) = 2.5165$,
$r_0(As-S) = 2.272$, $r_0(Sb-S) = 2.474$.

Table 3. Fractional atomic coordinates, equivalent isotropic temperature factors B_{eq} (Å^2) for hutchinsonite. (Estimated standard deviations in parentheses.)

Atom	X	Y	Z	B_{eq}
M1 (Pb)	0.36090(5)	0.24688(1)	0.10582(7)	1.04(2)
M2 (Tl)	0.33847(6)	0.12202(2)	0.63384(8)	1.82(2)
As1	0.1110(1)	0.19488(4)	0.7045(2)	0.74(5)
As2	0.1021(1)	0.18479(3)	0.1262(2)	0.66(4)
As3	0.4347(1)	0.11605(4)	0.1331(2)	0.75(5)
As4	0.1367(1)	0.04815(4)	0.2161(2)	0.96(5)
As5	0.3823(1)	0.02875(3)	0.9544(2)	0.79(5)
S1	0.3975(3)	0.1893(1)	0.3648(4)	0.9(1)
S2	0.4119(3)	0.1906(1)	0.8637(4)	1.0(1)
S3	0.1150(3)	0.25409(9)	0.3696(4)	0.8(1)
S4	0.1303(3)	0.1374(1)	0.3237(4)	1.0(1)
S5	0.1156(3)	0.14665(9)	0.8960(4)	1.0(1)
S6	0.3876(4)	0.0150(1)	0.6853(5)	1.5(1)
S7	0.1949(4)	0.0570(1)	0.9529(5)	1.8(2)
S8	0.4372(3)	0.0670(1)	0.3267(4)	1.1(1)
S9	0.0076(3)	0.0796(1)	0.5851(5)	1.2(1)

Results and discussion

The structure thus refined is essentially the same as reported by Takéuchi et al. (1965). The present results provide, however, more details of the structure. Selected atomic distances and angles are listed in Table 4 and Table 5.

To confirm the allocations of Pb to M1 and Tl to M2, an attempt was made of evaluating bond valences for cations, including As atoms, using the procedure given by Brown and Altermatt (1985). As shown in Table 2, the results are well in accord with the above assignment of atomic locations. The relationship between hutchinsonite $TlPbAs_5S_9$ and bernardite $TlAs_5S_8$ (Pašava, Pertlik, Stumpfl, Zemann, 1989) may also support the above assignment of Pb. The chemical formula of the latter corresponds to that of hutchinsonite from which PbS is suppressed.

The Pb atom has seven S neighbours, giving an average of the Pb–S distances 3.056(3) Å which is to be

[1] Additional materials of this paper can be ordered referring to the no. CSD 58501, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

Table 4. M–S and As–S distances (Å) under 4.0 Å in hutchinsonite. (Estimated standard deviations in parentheses. Upper indices refer to symmetry codes.)

	S1	S2	S3	S4	S5	S6	S7	S8	S9	MEAN	As1	As2
M1 (Pb)	2.959(3)^a	2.856(4)^b	2.760(3)^c								3.487(2)^j	3.556(1)^a
	3.018(4)^j	3.100(4)^j	3.276(3)^j							3.056(3)	3.729(2)^d	
			3.422(3)^a									
M2 (Tl)	3.297(4)^a	3.165(4)^a		3.422(3)^a	3.123(3)^g	3.847(4)^a	3.800(4)^a	3.343(4)^a	3.289(4)^g			3.605(2)^a
										3.451(4)		
					3.331(3)^a				3.892(4)^a			
As1		2.224(4)^h	2.252(3)^i		2.313(4)^a					2.262(4)		
As2	2.215(4)^f			2.343(4)^a	2.314(4)^b					2.290(4)		
As3				2.268(4)^e				2.345(4)^a	2.332(4)^e	2.315(4)		
As4						2.264(4)^c	2.255(4)^b	2.280(4)^f		2.266(4)		
As5						2.245(4)^a	2.255(4)^a		2.273(4)^h	2.258(4)		

Symmetry codes:
^{a} x, y, z ^{b} $x, y, z-1$ ^{c} $\bar{x}+1/2, y, z-1/2$ ^{d} $x+1/2, \bar{y}+1/2, \bar{z}+1$ ^{e} $x+1/2, y, \bar{z}+1/2$
^{f} $x-1/2, y, \bar{z}+1/2$ ^{g} $x+1/2, y, \bar{z}+3/2$ ^{h} $x-1/2, y, \bar{z}+3/2$ ^{i} $x, \bar{y}+1/2, z+1/2$ ^{j} $x, \bar{y}+1/2, z-1/2$

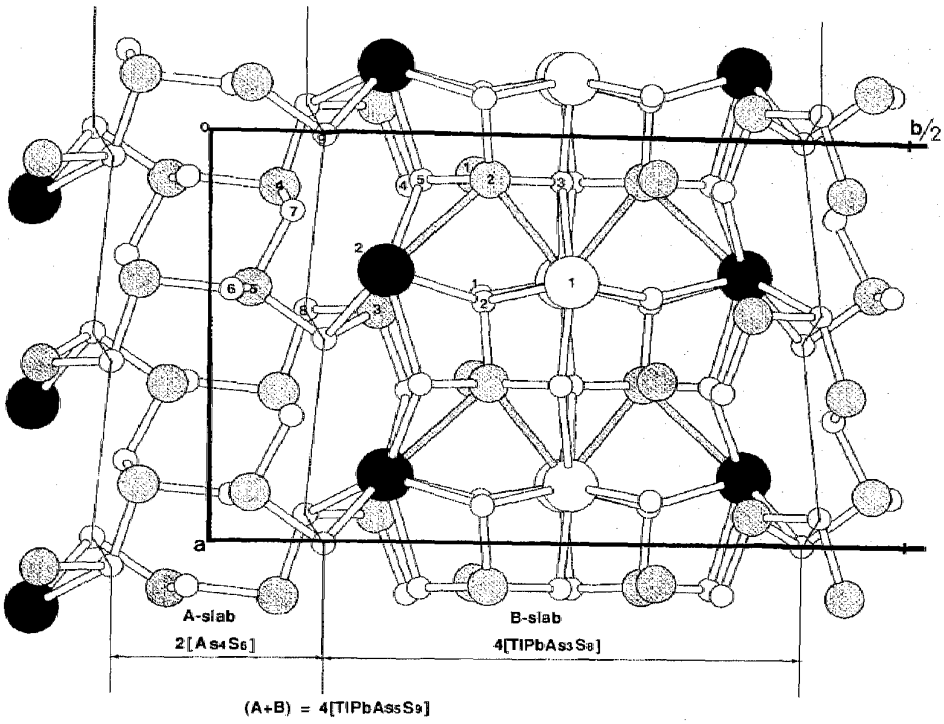

Fig. 1. The crystal structure of hutchinsonite projected down *c*, showing A and B slabs. Large solid circles, large open circles, shaded circles, and small open circles represent Tl, Pb, As and S atoms, respectively. Independent As and S atoms (Table 3) are indicated by corresponding figures. Bong-lengths Tl–S, Pb–S < 3.5 Å and As–S < 2.4 Å are drawm by open sticks and extra metal-As distances smaller than 3.61 Å are drawn by dotted sticks.

Table 5. Bond angles (°) and S–S edge lengths (Å) of As–S pyramids in hutchinsonite. (Estimated standard deviations in parentheses. Upper indices refer to symmetry codes in Table 4.)

As1-pyramid			
$S3^{i}-S5^{a}$	3.519(5)	S3–As1–S5	100.8(1)
$S3^{i}-S2^{k}$	3.498(5)	S3–As1–S2	102.9(1)
$S5^{a}-S2^{k}$	3.423(5)	S5–As1–S2	98.0(1)
mean	3.480(5)	mean	100.6(1)
As2-pyramid			
$S4^{a}-S5^{b}$	3.501(5)	S4–As2–S5	97.7(1)
$S4^{a}-S1^{e}$	3.469(5)	S4–As2–S5	99.2(1)
$S5^{b}-S1^{f}$	3.406(5)	S5–As2–S1	97.6(1)
mean	3.459(5)	mean	98.0(1)
As3-pyramid			
$S8^{a}-S9^{e}$	3.466(5)	S8–As3–S9	95.7(1)
$S8^{a}-S4^{e}$	3.470(5)	S8–As3–S4	97.6(1)
$S4^{e}-S9^{e}$	3.235(5)	S4–As3–S9	89.4(1)
mean	3.390(5)	mean	94.2(1)
As4-pyramid			
$S7^{b}-S6^{e}$	3.296(5)	S7–As4–S6	93.7(1)
$S7^{b}-S8^{f}$	3.327(5)	S7–As4–S8	94.4(1)
$S6^{e}-S8^{f}$	3.464(5)	S6–As4–S8	99.4(1)
mean	3.362(5)	mean	95.8(1)
As5-pyramid			
$S6^{a}-S7^{a}$	3.358(6)	S6–As5–S7	96.5(2)
$S6^{a}-S9^{h}$	3.224(5)	S6–As5–S9	91.1(2)
$S7^{a}-S9^{h}$	3.480(6)	S7–As5–S9	100.4(1)
mean	3.354(6)	mean	96.0(2)

compared with 3.05(1) Å in the original structure (Takéuchi et al., 1965).

Regarding Tl, we note that it has seven near S atoms at the distances ranging from 3.123 Å to 3.343 Å (Table 4). The coordination polyhedra formed by those S atoms about Tl is very irregular, giving rise to an open space towards the A slab (Fig. 1). In the space, there are three further neighbours of S atoms at longer distances (Table 4). The Tl atom then has ten S neighbours, the average bond length is 3.451(4) Å. From the ionic radii of Tl for six-, eight- and twelve-fold coordinations (Shannon, 1976), we find, by interpolation, the ionic radius 1.65 Å for ten-fold coordinated Tl. Then using the ionic radius 1.84 Å for S^{-2} (Shannon, 1976), the Tl–S distance for ten-fold coordinated Tl is calculated to be 3.49 Å. This value compares rather well with the above value 3.451 Å when we take into account of the large size and very irregular coordination of the Tl atom.

The eighth neighbour of the Tl atom is in fact As1, not S, which is at a distance 3.605(2) Å. Similar Tl–As (Sb or other metal atoms) distances were observed in other Tl sulfosalts (Matsushita, Takéuchi, Sawada, 1991). Likewise, the Pb atom has two additional neighbours, As1 and As2, at distances 3.487(2) Å and 3.556(1) Å, respectively (Fig. 2). These situations are the consequence of distortion of the slab with the PbS-like structure to an SnS type (Hofmann, 1935; Del Bucchia, Jumas, Maurin, 1981), owing to the strong stereochemical effect of the lone electron pairs of the As atoms. Such a mode of distortion of the hutchinsonite slab has been pointed out by Makovicky (1985). The shift of the "half-octahedral sheet" with respect to its adjacents is slightly over 0.40 of an average value of the pseudooctahedral edge lengths.

The atomic distances for the AsS_3 pyramids (Table 5) in the refined structure give average values: As–S = 2.248(1) Å, S–As–S angle = 96.93(2)°, and S–S edge = 3.409(1) Å. They agree well with the corresponding values of orpiment, As_2S_3 (Mullen, Nowacki, 1972). The pyramids formed by sulfur atoms about As4 and As5 built up a two-fold helical chain with a chemical composition As_4S_8. As pointed out by Takéuchi et al. (1965), these chains are joined together with the AsS_3 pyramids by sharing sulfur atoms, forming a sheet parallel to (010) which has a composition $As_{12}S_{20}$. One of the sulfur atoms of the AsS_3 pyramid, however, is shared with one sulfur of the As_2S_5 group (Takéuchi et al., 1965) in the B slab. Thus, the sheet is in fact a branched sheet having a chemical composition $As_{20}S_{36}$ (or As_5S_9).

As observed in Table 2, the bond-valence calculations show that the minor content Sb is preferably located in the As3 site which joins together the A and B slabs. This

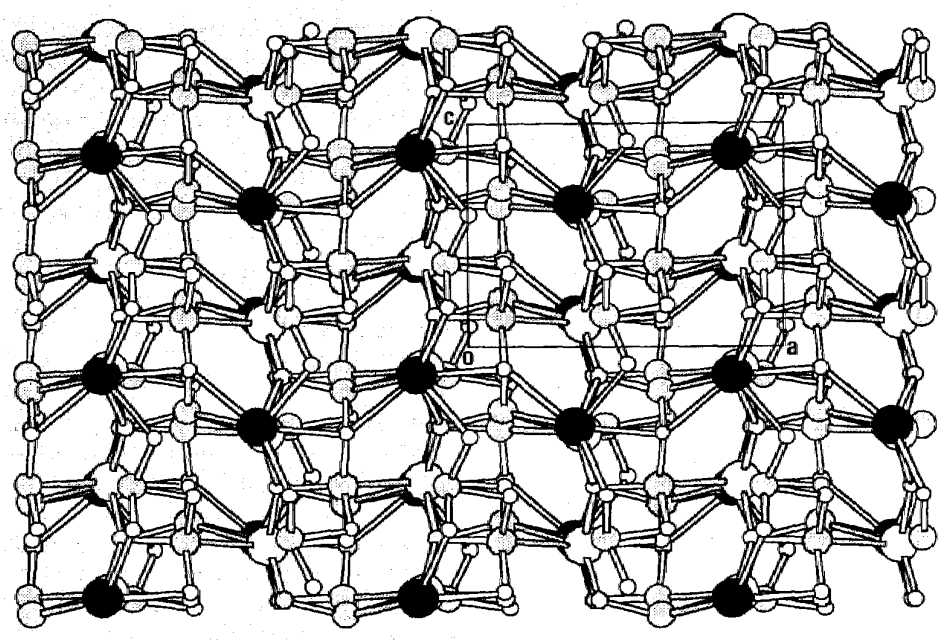

Fig. 2. The conformation of the B slab viewed down *b*, showing alternate displacements of the (Tl, Pb, As)−S layers. Atoms are represented as in Fig. 1. Bond lengths Tl−S < 3.4 Å, Pb−S < 3.1 Å and As−S < 2.4 Å are drawn by open sticks and extra metal-As distances are drawn by dotted sticks.

result is in conformity with the relatively high occupancy 1.065(8) obtained when refinement was made by locating only the As atom at the site (Table 2).

Acknowledgements. We wish to thank Prof. Terumi Miyake for putting Quiruvilca hutchinsonites at our disposal. Our thanks are due to Dr. Haruo Sawasa for assistance in experiment.

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