and obtained a lower agreement index. The resulting interatomic distances are sufficiently accurate to allow the occupation numbers to be reliably determined using the bond-valence method.

In their isotropic determination, Born & Hellner (1960) split the Sb(11) atom in the *xy* plane. We used an unsplit atom but find that the atomic displacement parameter U_{11} is enhanced (0·062 Å^2). There seems to be no reason to believe that this atom is statically disordered.

We are indebted to R. Faggiani for help in the data collection and the Natural Sciences and Engineering Research Council of Canada for an operating grant.

References

BAYLISS, P. & NOWACKI, W. (1972). *Z. Kristallogr.* **135**, 308–315.
BERRY, L. G. (1940). *Univ. Toronto Stud. Geol. Ser.* **44**, 5–19.
BORN, L. & HELLNER, E. (1960). *Am. Mineral.* **45**, 1266–1271.
International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers.)
PALACHE, C. H. & BERMAN, M. (1942). *Am. Mineral.* **27**, 552–556.
PETROVA, I. V., KUZNETZOV, E. L., BELOKONEVA, A. M., SIMONOV, E. A., POBEDIMSKAYA, E. A. & BELOV, N. V. (1978). *Dokl. Akad. Nauk SSSR*, **242**, 337–340.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.
SKOWRON, A. & BROWN, I. D. (1990*a*). *Acta Cryst.* **C46**, 527–531.
SKOWRON, A. & BROWN, I. D. (1990*b*). *Acta Cryst.* **C46**, 534–536.

Acta Cryst. (1990). **C46**, 534–536

Structure of $Pb_2Sb_2S_5$

BY A. SKOWRON AND I. D. BROWN

Institute for Materials Research, McMaster University, 1280 *Main St. West, Hamilton, Ontario, Canada L8S 4M1*

(*Received* 13 *April* 1989; *accepted* 11 *July* 1989)

Abstract. $M_r = 818{\cdot}2$, orthorhombic, *Pbnm*, $a = 11{\cdot}355\,(4)$, $b = 19{\cdot}783\,(8)$, $c = 4{\cdot}042\,(1)$ Å, $V = 908$ Å^3, $Z = 4$, $D_x = 5{\cdot}95$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 421{\cdot}3$ cm^{-1}, $F(000) = 1384$, room temperature, $R = 0{\cdot}071$, $wR = 0{\cdot}063$ for 931 independent reflections. The crystal was prepared by annealing at 860 K in the presence of I_2 in vacuum-sealed ampoules. The structure proposed by Smith & Hyde [*Acta Cryst.* (1983), **C39**, 1498–1502] is confirmed. The distribution of Sb/Pb over the atomic positions was determined by site-occupancy refinement and, independently, by bond-valence analysis.

Introduction. $Pb_2Sb_2S_5$ was first synthetized by Wang (1973). He reported the cell $a = 19{\cdot}80$, $b = 11{\cdot}40$, $c = 4{\cdot}04$ Å and proposed the space group D_{2h}^{16}. Smith & Hyde (1983) obtained the lattice parameters $a = 19{\cdot}808$, $b = 4{\cdot}042$, $c = 11{\cdot}353$ Å for $Pb_2Sb_2S_5$ using powder X-ray diffraction and they proposed a structure derived from that of the Cu-containing meneghinite, $CuPb_{13}Sb_7S_{24}$ (Euler & Hellner, 1960) in space group *Pnma*.

Experimental. Single crystals of $Pb_2Sb_2S_5$ were found in the same preparation as synthetic boulangerite (Skowron & Brown, 1990*b*). A needle-shaped crystal of $Pb_2Sb_2S_5$, 0·2 × 0·3 × 0·6 mm, which was found in the sample that initially contained 67 mol% of PbS, was mounted with the needle axis along the X-ray goniometer axis.

The unit-cell parameters were refined from 15 well centered reflections in the range $20 < 2\theta < 47°$ measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Intensities of 1750 reflections were measured in the range $2\theta < 50°$ and $0 \le h \le 13$, $0 \le k \le 23$, $-4 \le l \le 4$ with a $\theta/2\theta$ scan. Two standard reflections, 310 and $\bar{2}31$, measured every 50 reflections, varied by 1·7%. The systematic absences, $0kl$: $k = 2n + 1$; $h0l$: $h + l = 2n + 1$, found on precession photographs indicate the space groups *Pbnm* or $Pbn2_1$. The former was chosen and led to a satisfactory refinement. The absorption correction was based on ψ scans of 20 reflections (maximum correction 1·65 for the intensity of the 082 reflection). The intensities were corrected for Lorentz and polarization effects. Equivalent reflections were averaged ($R_{int} = 0{\cdot}037$ before the absorption correction, $R_{int} = 0{\cdot}031$ after) to give 931 unique reflections.

The initial atomic positions, found by direct methods using *SHELXS86* (Sheldrick, 1986), were refined using *SHELX76* (Sheldrick, 1976) by full-matrix least squares (on *F*) with anisotropic atomic

0108-2701/90/040534-03$03.00

Table 1. *Percentage of* Sb *on cation sites in* $Pb_2Sb_2S_5$

	Smith & Hyde (1983)	X-ray	Bond valence
$M(1)$	100	100	100
$M(2)$	100	90	82
$M(3)$	0	32	10
$M(4)$	0	34	8
Formula	$Pb_2Sb_2S_5$	$Pb_{1\cdot44}Sb_{2\cdot56}S_5$	$Pb_2Sb_2S_5$

Table 2. *Bond valences in* $Pb_2Sb_2S_5$ *weighted according to X-ray occupation numbers; V is the valence sum expected using these occupancies*

	$M(1)$	$M(2)$	$M(3)$	$M(4)$	$\sum s$
%Pb	—	10	68	66	
S(1)	1·12	—	0·12	0·42 × 2	−2·08
S(2)	—	1·07	0·33 × 2	0·25 × 2	−2·23
S(3)	—	0·34 × 2	0·49 + 0·32 × 2	—	−1·81
S(4)	0·19 × 2	0·53 × 2	—	0·44	−1·88
S(5)	0·76 × 2	—	0·17	0·14 × 2	−1·97
$\sum s$	3·02	2·81	2·08	2·06	
V	3·00	2·90	2·32	2·34	

Table 3. *Atomic coordinates and equivalent isotropic displacement parameters for* $Pb_2Sb_2S_5$

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}(Å^2)
$M(1)$	0·3757 (2)	0·3715 (1)	0·25	0·0182
$M(2)$	0·7022 (2)	0·4758 (1)	0·25	0·0326
$M(3)$	0·9983 (1)	0·4008 (1)	0·75	0·0288
$M(4)$	0·6678 (1)	0·2914 (1)	0·75	0·0407
S(1)	0·4950 (6)	0·2670 (4)	0·25	0·0189
S(2)	0·8183 (7)	0·3685 (4)	0·25	0·0187
S(3)	0·8690 (6)	0·5212 (4)	0·75	0·0210
S(4)	0·5659 (7)	0·4221 (4)	0·75	0·0250
S(5)	0·2495 (7)	0·3288 (4)	0·75	0·0304

Table 4. *Interatomic distances* (Å) *less than* 3·4 Å *in* $Pb_2Sb_2S_5$

$M(1)$ − S(1)	3·475 (7)		$M(3)$ − S(3)	2·795 (7)
S(5) × 2	2·621 (5)		S(2) × 2	2·947 (5)
S(4) × 2	3·124 (5)		S(3) × 2	2·952 (5)
			S(5)	3·183 (8)
$M(2)$ S(2)	2·497 (7)			
S(4) × 2	2·757 (5)		$M(4)$ − S(4)	2·836 (7)
S(3) × 2	2·915 (5)		S(1) × 2	2·858 (5)
			S(2) × 2	3·052 (5)
			S(5) × 2	3·253 (6)

displacement parameters for all atoms and with mixed occupancies for the metal sites. Complex scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Intensities were weighted by $w = k/[\sigma^2(F_o) + gF_o^2]$, where k refined to 1·35, g was fixed at 0·0006 and $\sigma(F_o)$ was the uncertainty derived from the counting statistics. The Sb occupation number of site 1 quickly refined to a value close to 1·0 and was kept fixed at this value in the subsequent stages of the refinement. The refinement converged to $wR = 0{\cdot}058$, $R = 0{\cdot}067$, goodness-of-fit $S = 1{\cdot}40$.

The program did not permit a constraint to be put on the total number of Pb or Sb atoms in the unit cell and the refined occupation numbers, shown in column 3 of Table 1, result in the formula $Pb_{1\cdot44}Sb_{2\cdot56}S_5$ which is appreciably different from the expected electrically neutral formula $Pb_2Sb_2S_5$. In order to clarify this discrepancy we determined an independent set of occupation numbers using the bond-valence method described by Skowron & Brown (1990*a*). In this we use the refined atomic parameters to calculate bond lengths (r) from which bond valences (s) were calculated using the equation

$$s = \exp[(r_0 - r)/0{\cdot}37], \qquad (1)$$

where $r_0 = 2{\cdot}541$ Å for Pb—S and $r_0 = 2{\cdot}518$ Å for Sb—S bonds. The valence analysis is presented in

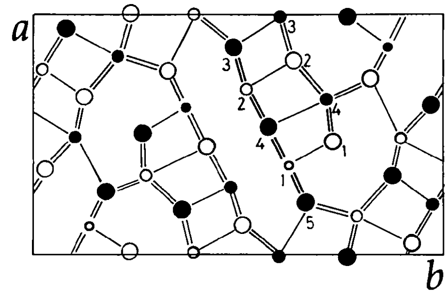

Fig. 1. The unit cell of $Pb_2Sb_2S_5$ projected down [001]. In order of decreasing size, the circles denote S, Pb, mixed sites and Sb. Atoms at $z = 0{\cdot}25$ and $z = 0{\cdot}75$ are indicated by open and full circles respectively.

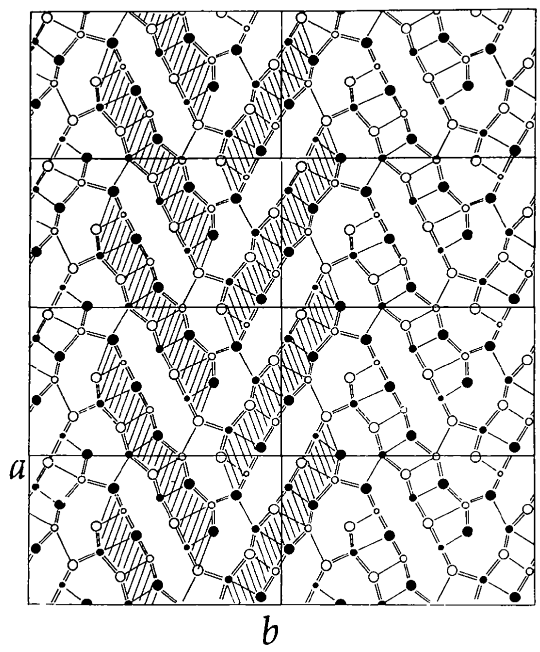

Fig. 2. Eight unit cells of the crystal structure of $Pb_2Sb_2S_5$ projected down [001] with one set of ribbons shaded. Conventions for indicating the atoms are the same as in Fig. 1.

Table 2 and both the X-ray and valence occupation numbers are compared in Table 1.

As a check we used the occupation numbers determined from the bond valences as fixed parameters in *SHELX76* and refined all positional and anisotropic atomic displacement parameters obtaining $wR = 0{\cdot}063$, $R = 0{\cdot}071$ and $S = 1{\cdot}56$. Maximum final shift/e.s.d. 0·07, mean 0·02, maximum density in the final difference Fourier map 3·4 e $Å^{-3}$, minimum $-3{\cdot}3$ e $Å^{-3}$. because these occupation numbers correspond to an electrically neutral crystal we consider them as more reliable although, as expected, the agreement indices are slightly larger. This refinement was used to generate the final atomic coordinates listed in Table 3. Interatomic distances are given in Table 4.*

Discussion. The structure of $Pb_2Sb_2S_5$ proposed by Smith & Hyde (1983) has been confirmed. It consists of ribbons composed of square-pyramidal $(Pb,Sb)S_5$ groups. The ribbons extend indefinitely in the **c** direction, are one pyramid thick and have a width that equals four times the basal distance of the $(Pb,Sb)S_5$ pyramid (Figs. 1 and 2). The ribbons occurring in $Pb_2Sb_2S_5$ can be formed from the unit ribbon, Sb_4S_6, in stibnite (Bayliss & Nowacki, 1972) by splitting it and introducing four PbS_5 pyramids in the middle or, as in the alternative description of Smith & Hyde (1983), by introducing layers of the thallium iodide type structure (*B*33) into the stibnite structure. The stoichiometry is determined by the total number of PbS units that have been incorporated as:

$$Sb_2S_3 + (PbS)_4 + Sb_2S_3 = 2Pb_2Sb_2S_5.$$

However, the lead is not found in the middle of the ribbons. The ribbons are arranged facing each other but translated parallel to their width so that only half of each ribbon overlaps with the next. The cation sites in these parts of the ribbon are five-coordinated and are occupied mostly by antimony. The other cation sites, in places where the ribbons join with the edges of the glide-related ribbons, are seven-coordinated and are occupied mostly by lead. The cation distribution proposed by Smith & Hyde (1983) for the structure is simpler but similar to ours.

We are indebted to R. Faggiani for help in the data collection and to the Natural Sciences and Engineering Research Council of Canada for an operating grant.

* Observed and calculated structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52413 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bayliss, P. & Nowacki, W. (1972). *Z. Kristallogr.* **135**, 308–315.
Euler, R. & Hellner, E. (1960). *Z. Kristallogr.* **113**, 345–372.
International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.
Skowron, A. & Brown, I. D. (1990*a*). *Acta Cryst.* **C46**, 527–531.
Skowron, A. & Brown, I. D. (1990*b*). *Acta Cryst.* **C46**, 531–534.
Smith, P. P. K. & Hyde, B. G. (1983). *Acta Cryst.* C**39**, 1498–1502.
Wang, N. (1973). *Neues Jahrb. Mineral. Monatsh.* pp. 79–81.

Acta Cryst. (1990). **C46**, 536–538

Structure of $Na_{0{\cdot}56}V_2O_5$

By Yasushi Kanke, Katsuo Kato, Eiji Takayama-Muromachi and Mitsumasa Isobe

National Institute for Research in Inorganic Materials, 1-1 *Namiki, Tsukuba, Ibaraki* 305, *Japan*

(*Received* 10 *June* 1989; *accepted* 14 *July* 1989)

Abstract. $M_r = 194{\cdot}75$, monoclinic, $C2/m$, $a = 11{\cdot}663\,(9)$, $b = 3{\cdot}6532\,(7)$, $c = 8{\cdot}92\,(1)$ Å, $\beta = 90{\cdot}91\,(4)°$, $V = 379{\cdot}9\,(7)$ $Å^3$, $Z = 4$, $D_x = 3{\cdot}405$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 4{\cdot}774$ mm^{-1}, $F(000) = 368{\cdot}64$, room temperature, final $R = 0{\cdot}056$ for 1234 unique observed reflections. Distorted octahedra of VO_6 are linked together to form V_2O_5 layers parallel to (001). Na ions are situated between the layers and surrounded by seven O atoms. The structure is closely related to that of δ-$Ag_{1-x}V_2O_5$.

Introduction. In the course of a phase equilibrium study on the NaV_2O_5–V_2O_3–V_2O_5 system (Kanke,

0108-2701/90/040536-03$03.00