SHELDRICK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

SMITH, P. P. K. & HYDE, B. G. (1983). *Acta Cryst.* C**39**, 1498–1502.

WANG, N. (1977). *Neues Jahrb. Mineral. Monatsh.* H.**11**, 501–503.

Acta Cryst. (1990). C**46**, 531–534

Refinement of the Structure of Boulangerite, $Pb_5Sb_4S_{11}$

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Abstract. The structure of boulangerite, $Pb_5Sb_4S_{11}$, $M_r = 1875·7$, previously determined by Born & Hellner [*Am. Mineral.* (1960), **45**, 1266–1271] and by Petrova, Kuznetzov, Belokoneva, Simonov, Pobedimskaya & Belov [*Dokl. Akad. Nauk SSSR* (1978), **242**, 337–340] has been refined in the orthorhombic space group *Pnam*, $a = 23·490$ (5), $b = 21·245$ (5), $c = 4·020$ (1) Å, $V = 2006$ Å^3, $Z = 4$, $D_x = 6·21$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 462·8$ cm^{-1}, $F(000) = 3160$, room temperature, $R = 0·077$, $wR = 0·068$ for 2035 independent reflections. The crystal was prepared by annealing at 860 K in the presence of I_2 in vacuum-sealed ampoules. The basic arrangement of atoms previously proposed is confirmed but the cation distribution is determined more accurately by site-occupancy refinement and by bond-valence analysis.

Introduction. Although the structure of boulangerite has been the object of several studies the cation distribution has not been reliably determined. Berry (1940) and Palache & Berman (1942) determined the unit cell. Born & Hellner (1960) proposed a structure for natural boulangerite using *hk*0 and *hk*2 Weissenberg photographs. The structure was later confirmed by Petrova, Kuznetzov, Belokoneva, Simonov, Pobedimskaya & Belov (1978) on a synthetic crystal. Although the general features found in these studies were the same, we undertook an independent structure determination as part of a broader investigation into cation distributions in lead antimony sulfides in order to establish the correct cation distribution.

Experimental. Single crystals of $Pb_5Sb_4S_{11}$ were synthesized from elemental lead, antimony and sulfur of 'Specpure' grade, supplied by Johnson Matthey plc. Three samples were prepared by weighing the elements in proportions corresponding to 65, 66, 67 mol % of PbS. The samples were sealed in evacuated silica tubes, melted at 1150 K for 2 d and then annealed at 873 K for 2 d. Considerable ingot separation occurred in all the ampoules. The separate portions of the ingots were then ground and pressed into seven 1 g pellets which were separately annealed for 3 d in evacuated silica tubes in a two-zone horizontal furnace after the addition of approximately 1 mg of I_2 to each. At the end of the 20 cm ampoules where the pellets were placed the temperature was 860 K. The other end was kept at 880 K. Acicular crystals of $Pb_5Sb_4S_{11}$ and $Pb_2Sb_2S_5$ grew in various parts of the ampoules, most often near the cooler end. The structure of $Pb_2Sb_2S_5$ is reported by Skowron & Brown (1990*b*). Good quality crystals of $Pb_5Sb_4S_{11}$ were found in the sample prepared from 66 mol% PbS. A needle-shaped crystal, 0·15 × 0·3 × 0·6mm, was mounted with the needle axis along the goniometer axis for the X-ray study.

The unit-cell parameters were refined from 15 well centered reflections in the range $19 < 2\theta < 26°$ measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Intensities of 3700 reflections were measured in the range $2\theta < 50°$ and $0 \leq h \leq 27$, $0 \leq k \leq 25$, $-4 \leq l \leq 4$ with a $\theta/2\theta$ scan. Two standard reflections, $\bar{9}61$ and $10,\bar{4},0$, measured every 50 reflections, varied by 1·4%. The systematic absences, 0*kl*: $k + l = 2n + 1$; *h*0*l*: $h = 2n + 1$, found using precession photographs indicate space groups *Pnam* or $Pna2_1$. The former was chosen and led to a satisfactory refinement. The absorption correction was based on ψ scans of 20 reflections (maximum correction 1·67 for the intensity of the 15,0,4 reflection). The intensities were corrected for Lorentz and polarization effects. Equivalent reflections were averaged ($R_{int} = 0·037$ before the absorption correction, $R_{int} = 0·035$ after) to give 2035 unique reflections.

The initial atomic positions, found by direct methods using *SHELXS*86 (Sheldrick, 1986), were refined using *SHELX*76 (Sheldrick, 1976) by full-matrix least squares (on *F*) with anisotropic atomic

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displacement parameters for all the 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 1·97, g was fixed at 0·0006 and $\sigma(F_o)$ was the uncertainty derived from the counting statistics. The Pb occupation numbers of sites 13, 14 and 15 quickly refined to values close to 1·0 and were kept fixed at this value in the subsequent stages of the refinement. The refinement converged to $wR = 0{\cdot}066$, $R = 0{\cdot}075$ and $S = 1{\cdot}51$.

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 4 of Table 1, result in a formula of $Pb_{4.65}Sb_{4.35}S_{11}$ which is different from the expected electrically neutral formula $Pb_5Sb_4S_{11}$. 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 $r_0 = 2{\cdot}529$ Å for Sb—S bonds. The valence analysis is presented in Table 2 and both the X-ray and valence occupation numbers are compared in Table 1.

Because the occupation numbers determined from the bond valences correspond to an electrically neutral crystal we consider these values to be more reliable. We used them as fixed parameters in *SHELX76* and refined all positional and atomic displacement parameters to obtain $wR = 0{\cdot}068$, $R = 0{\cdot}077$ and $S = 1{\cdot}56$. Maximum final shift/e.s.d. 0·053, mean 0·014, maximum density in the final difference Fourier map 3·5 e Å^{-3}, minimum −3·9 e Å^{-3}. This refinement was used to generate the final atomic coordinates listed in Table 3. The interatomic distances are given in Table 4.*

Table 1. *Percentage of* Sb *on cation sites in boulangerite*

	Born & Hellner (1960)	Petrova *et al.* (1978)	X-ray	Bond valence
M(1)	100	50	76	70
M(2)	50	55	50	36
M(3)	50	40	41	38
M(10)	100	100	100	100
M(11)	100	100	100	100
M(12)	50	55	68	56
M(13)	0	0	0	0
M(14)	0	0	0	0
M(15)	0	0	0	0
Formula	$Pb_{4.5}Sb_{4.5}S_{11}$	$Pb_5Sb_4S_{11}$	$Pb_{4.65}Sb_{4.35}S_{11}$	$Pb_5Sb_4S_{11}$

Discussion. Our results confirm the structures reported by Born & Hellner (1960) and by Petrova *et al.* (1978). The structure (Figs. 1 and 2) consists of two types of ribbon made of back-to-back square-pyramidal $(Pb,Sb)S_5$ groups. The ribbons extend indefinitely in the **c** direction, are one pyramid thick but have different widths. In the narrow ribbon the width equals three times the basal distance of the $(Pb,Sb)S_5$ pyramid while in the wider ribbon it is six times this distance. The ribbons can be derived from the building unit, Sb_4S_6, in stibnite (Bayliss & Nowacki, 1972) by splitting it in the middle and inserting two PbS_5 pyramids to form the narrower and eight to form the wider ribbon.

The stoichiometry can be determined by the total number of PbS units that have to be incorporated into the ribbons as:

$$\underbrace{[Sb_2S_3 + (PbS)_2 + Sb_2S_3]}_{\text{narrow ribbon}} + \underbrace{[Sb_2S_3 + (PbS)_8 + Sb_2S_3]}_{\text{wide ribbon}}$$

$$= 2Pb_5Sb_4S_{11}.$$

* Lists of 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 52412 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond valences in boulangerite weighted according to X-ray occupation number*

	M(1)	*M*(2)	*M*(3)	*M*(10)	*M*(11)	*M*(12)	*M*(13)	*M*(14)	*M*(15)	Σs
%Sb	76	50	41	100	100	68	0	0	0	
S(1)	0·79		0·57 × 2					0·15		−2·08
S(2)		0·71 + 0·39 × 2	0·24 × 2							−1·97
S(3)	0·21 × 2	0·41 × 2	0·73							−1·97
S(4)	0·67 × 2								0·18 × 2	−1·70
S(10)				1·30			0·18 × 2		0·32 × 2	−2·30
S(11)					1·18			0·33 × 2	0·26 × 2	−2·36
S(12)						0·81	0·36 × 2	0·31 × 2		−2·15
S(13)						0·72 × 2	0·20 + 0·13 × 2			−1·90
S(14)					0·46 × 2	0·15 × 2		0·57		−1·79
S(15)				0·24 × 2	0·36 × 2				0·40	−1·60
S(16)				0·70 × 2			0·32	0·12		−1·84
Σs	2·55	2·31	2·35	3·18	2·82	2·55	1·86	2·12	1·92	
V	2·76	2·50	2·41	3·00	3·00	2·68	2·00	2·00	2·00	

Table 3. *Atomic coordinates and equivalent isotropic atomic displacement parameters for boulangerite*

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

	x	y	z	U_{eq}(Å^2)
M(1)	0·2675 (1)	0·5505 (1)	0·75	0·035 (1)
M(2)	0·4325 (1)	0·4580 (1)	0·75	0·037 (1)
M(3)	0·5975 (1)	0·3688 (1)	0·75	0·031 (1)
M(10)	0·4625 (1)	0·2889 (1)	0·75	0·031 (1)
M(11)	0·2953 (1)	0·3820 (1)	0·75	0·043 (2)
M(12)	0·1290 (1)	0·4855 (1)	0·75	0·032 (1)
M(13)	0·0021 (1)	0·6179 (1)	0·75	0·032 (1)
M(14)	0·1602 (1)	0·3062 (1)	0·25	0·021 (1)
M(15)	0·3229 (1)	0·2080 (1)	0·25	0·022 (1)
S(1)	0·6743 (3)	0·3454 (4)	0·25	0·022 (4)
S(2)	0·5166 (4)	0·4304 (4)	0·25	0·022 (4)
S(3)	0·3620 (3)	0·5147 (4)	0·25	0·021 (4)
S(4)	0·2057 (4)	0·5962 (4)	0·25	0·033 (5)
S(10)	0·4137 (3)	0·1876 (3)	0·75	0·017 (4)
S(11)	0·2486 (3)	0·2780 (3)	0·75	0·015 (6)
S(12)	0·0878 (3)	0·3717 (3)	0·75	0·015 (4)
S(13)	0·0593 (4)	0·5126 (4)	0·25	0·033 (5)
S(14)	0·2180 (4)	0·4187 (4)	0·25	0·024 (5)
S(15)	0·3725 (4)	0·3319 (4)	0·25	0·030 (5)
S(16)	0·5293 (4)	0·2531 (4)	0·25	0·023 (4)

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

Narrow ribbon			Wide ribbon		
M(1)—S(1)		2·602 (8)	M(10)—S(10)		2·432 (7)
	S(4) × 2	2·662 (6)		S(16) × 2	2·661 (5)
	S(3) × 2	3·090 (6)		S(15) × 2	3·058 (2)
M(2)—S(2)		2·659 (8)	M(11)—S(11)		2·468 (8)
	S(3) × 2	2·869 (6)		S(14) × 2	2·817 (6)
	S(2) × 2	2·880 (6)		S(15) × 2	2·907 (7)
M(3)—S(3)		2·651 (8)	M(12)—S(12)		2·609 (7)
	S(1) × 2	2·744 (5)		S(13) × 2	2·656 (6)
	S(2) × 2	3·059 (6)		S(14) × 2	3·230 (6)
			M(13)—S(13)		3·130 (9)
				S(12) × 2	2·920 (5)
				S(16)	2·965 (8)
				S(10) × 2	3·186 (6)
				S(13) × 2	3·293 (7)
			M(14)—S(14)		2·749 (8)
				S(11) × 2	2·954 (5)
				S(12) × 2	2·979 (5)
				S(1)	3·236 (7)
				S(16)	3·322 (8)
			M(15)—S(15)		2·877 (9)
				S(10) × 2	2·964 (5)
				S(11) × 2	3·046 (5)
				S(4) × 2	3·182 (7)

In the crystal, however, the Pb atoms are not found only in the middle of the ribbons. The ribbons stack face-to-face with a narrow ribbon between each wide one. The cation sites where parallel ribbons face each other mostly contain five-coordinated antimony. The cation sites on the faces that connect to the edges of other ribbons have higher coordination numbers and are occupied by lead. All the cation positions in the narrow ribbon have mixed occupancy, while there is only one such site in the wide ribbon.

Born & Hellner (1960) used $\frac{1}{2}(f_{Pb} + f_{Sb})$ scattering factors for the mixed-occupancy sites* while Petrova *et al.* (1978) refined the occupancies for four mixed-occupancy sites obtaining the occupation numbers shown in column 3 of Table 1. The previous results are in general agreement with ours but we have refined anisotropic atomic displacement parameters

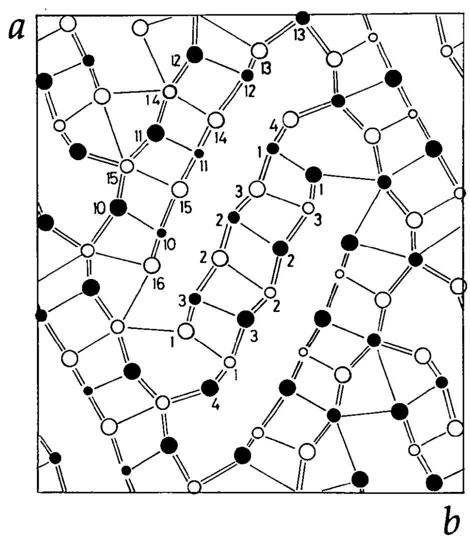

Fig. 1. The unit cell of boulangerite projected down [001]. In order of decreasing size, the circles denote S, Pb, mixed sites and Sb. Atoms at $z = 0·25$ and $z = 0·75$ are indicated by open and full circles respectively.

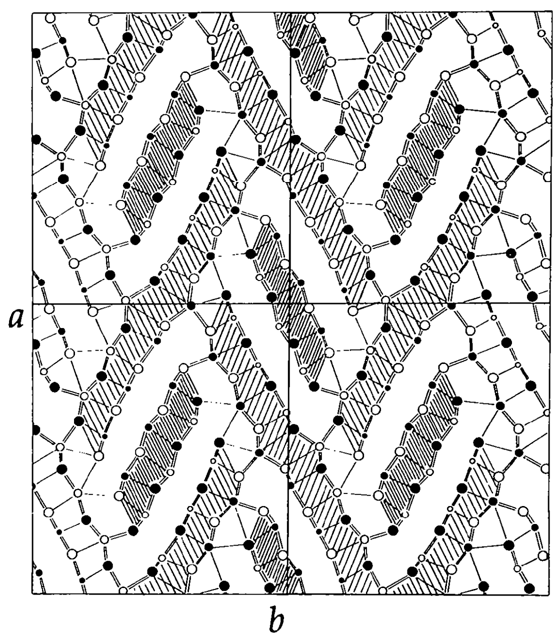

Fig. 2. Four unit cells of the crystal structure of boulangerite projected down [001] with the wide and narrow ribbons indicated by coarse and fine ruling. Conventions for indicating the atoms are the same as in Fig. 1.

* The formula resulting from the Born & Hellner (1960) assignment does not correspond to an electrically neutral crystal.

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.

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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.

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Structure of $Pb_2Sb_2S_5$

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Abstract. M_r = 818·2, orthorhombic, $Pbnm$, a = 11·355 (4), b = 19·783 (8), c = 4·042 (1) Å, V = 908 Å^3, Z = 4, D_x = 5·95 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 421·3 cm^{-1}, $F(000)$ = 1384, room temperature, R = 0·071, wR = 0·063 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 = 19·80, b = 11·40, c = 4·04 Å and proposed the space group D_{2h}^{16}. Smith & Hyde (1983) obtained the lattice parameters a = 19·808, b = 4·042, c = 11·353 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 $0 \leq h \leq 13$, $0 \leq k \leq 23$, $-4 \leq l \leq 4$ 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} = 0·037 before the absorption correction, R_{int} = 0·031 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

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