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$Pb_{5.0(1)}In_{8.4(1)}Bi_{1.6(1)}S_{20}$, a new quaternary lead indium bismuth sulfide

I. Reis,[a]‡ V. Krämer,[a] A. Seiler,[a] D. Topa[b] and E. Keller[a]*

[a]Kristallographie, Institut für Geowissenschaften, Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Strasse 5, D-79104 Freiburg, Germany, and [b]Fachbereich Materialforschung und Physik, Universität Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria
Correspondence e-mail: egbert.keller@krist.uni-freiburg.de

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The title phase, first detected in the early 1980s but hitherto unpublished, has been resynthesized and structurally characterized. Unambiguous determination of the chemical composition was not possible by structure analysis alone, but required additional analytical methods. The complex structure shows a close similarity to the structures of two related compounds, one known by the formula $Pb_{1.6}In_8Bi_4S_{19}$ and the other being the ternary compound $Pb_6In_{10}S_{21}$. This is despite the fact that the three phases correspond to very different Pb:Bi ratios. A geometric mechanism is described by which the three structures can be transformed into each other, provided that the heavy atoms Pb and Bi are treated as equivalent.

Comment

In the first half of the 1980s, six different quaternary lead indium bismuth sulfides were synthesized (Reis, 1984), of which only three have hitherto been fully characterized with respect to their structures (Krämer, 1983, 1986; Krämer & Reis, 1986); the other three were structurally characterized only by the determination of lattice constants and space groups (Reis, 1984). No other structures of quaternary lead indium bismuth sulfides have been published since then. The title phase is thus the fourth of the six phases to be structurally characterized. Determining the chemical identity of the obtained compositional variant of this phase was not possible by structure analysis alone, but required additional analytical methods (see *Experimental*).

Like most of the structurally known phases in the quaternary Pb–In–Bi–S system and its three ternary sulfidic subsystems, $Pb_{5.0(1)}In_{8.4(1)}Bi_{1.6(1)}S_{20}$ adopts a structure where one of the unit vectors (*b*) has a magnitude of only about 4 Å, while the other two are much longer. Fig. 1 shows a projection of the structure parallel to this short vector. Bond-length ranges for the different metal atoms (Table 1) agree with those from the known binary and ternary subsystem compounds and the other structurally known quaternary sulfides. The asymmetric unit of our structure model contains five positions with a mixed In_xBi_{1-x} occupancy (atom labels denoted with the suffix *F*; see *Experimental*). Such mixing of In and Bi at one position has previously been observed for $Pb_4In_2Bi_4S_{13}$ (Krämer, 1986) and $Pb_4In_3Bi_7S_{18}$ (Krämer & Reis, 1986). It is not really evident in the bond-length ranges and mean bond lengths (Table 1), except perhaps for site In9*F*, for which the largest Bi content (28%) is found. All Pb atoms show an eightfold coordination, with a coordination polyhedron that can be described as a trigonal prism with two rectangular faces capped. Such coordination has been observed, for example, for Pb in $PbIn_2S_4$ (Arriortua *et al.*, 1983) and for Bi in $Bi_3In_5S_{12}$ (Krämer, 1980). If the Bi1—S6 distance of 3.650 (2) Å is interpreted as a Bi—S bond, then atom Bi1 in the title compound is also coordinated this way. Otherwise, its coordination polyhedron can be described as a monocapped trigonal prism or a 'tri/tetragonal antiprism'. The In atoms (and the Bi atoms replacing them statistically) are coordinated octahedrally with various degrees of distortion.

Fig. 1 illustrates a two-dimensional pattern composed of M_2S_2 quadrangles and M_3S_3 hexagons (M = Pb, Bi or In), which are the cross-sections of one-dimensionally infinite columnar aggregates (like rods and ribbons) oriented parallel to *b*. Fig. 2 shows another representation of the structure, in which quadrangles containing two Bi atoms (*e.g.* the quadrangle at 0, *y*, 0) are shaded by grey dots (blue in the electronic version of the paper), those with two Pb atoms shaded dark grey, those containing a Bi and a Pb atom medium grey (blue–grey in the electronic version) and those containing two In (or In_xBi_{1-x}) atoms light grey (pink in the electronic version). These last form different motifs: finite chains set up by three corner-sharing quadrangles (**A** in Fig. 2), slightly distorted rectangles built from four edge-sharing quadrangles (**B**) and infinite chains (**C**) composed of five-membered **A**-like chains (**C₁**), which are concatenated *via* single rectangles (**C₂**) by edge-sharing.

In ternary subsystem compounds, motifs of type **A** are found in $Bi_3In_5S_{12}$ (Krämer, 1980), while those of types **B** and **C** are found in $Pb_6In_{10}S_{21}$ (Krämer & Berroth, 1980). The motif formed by the heavy atoms (Pb and Bi) in Fig. 2 can also be found in the latter phase (except for the Bi_2S_2 rhomb), and also in the structure of another quaternary compound, $Pb_{1.6}In_8Bi_4S_{19}$ (Krämer, 1983). Fig. 3 shows a representation of this latter structure, which also contains motifs **A** and **B**. The published formula (derived solely from structure-analytical considerations) corresponds to a net positive charge of 1.2. Preliminary re-investigation of this phase by electron-microprobe analysis (Topa & Keller, 2011) shows that the formula is rather $Pb_2In_8Bi_{3.33}S_{19}$, with no net charge, meaning that the assignments of Pb and Bi to the corresponding heavy-atom positions should probably be modified. In Fig. 3, all heavy-atom positions are shown as Pb/Bi mixtures. All quadrangles containing two of these hybrids are shown with grey shading

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‡ Present address: Fraunhofer Institut für Solare Energiesysteme ISE, Heidenhofstrasse 2, D-79110 Freiburg, Germany.

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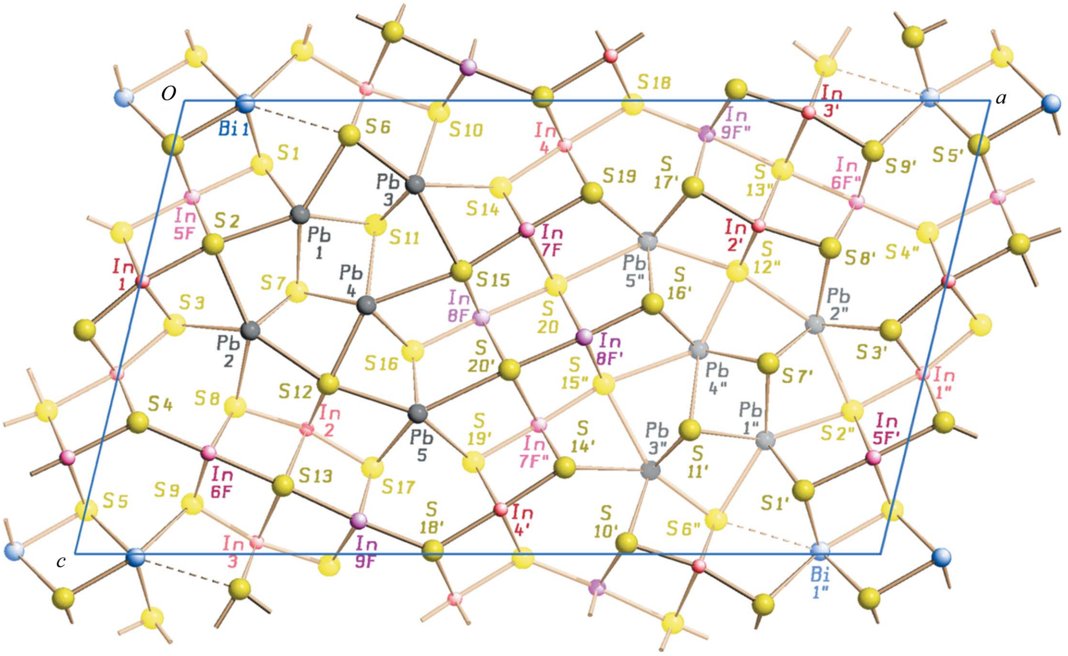

Figure 1

The structure of $Pb_{5.0(1)}In_{8.4(1)}Bi_{1.6(1)}S_{20}$, viewed along the *b* axis. Atoms and bonds in the layer more distant to the viewer have been drawn paler. Some long Bi—S bonds [3.650 (2) Å] are represented by dashed lines. Primed and double primed atoms are generated by the symmetry codes $(-x + 1, y + \frac{1}{2}, -z + 1)$ and $(-x + 1, y - \frac{1}{2}, -z + 1)$, respectively.

(blue–grey in the electronic version), with the exception of some rhombs (*e.g.* the rhombs at $\frac{1}{4}, y, 0$ and $\frac{3}{4}, y, 0$), which are shaded by grey dots (blue in the electronic version) for ease of comparison with Fig. 2. It is clear that the heavy-atom motif of Fig. 2 also occurs in Fig. 3, albeit in a concatenated one-dimensionally infinite way (two-dimensionally infinite when considered in three dimensions).

In Figs. 2 and 3, we have defined a stripe running parallel to *c* by drawing its left and right borders [saw-tooth-like dashed black lines along $x = -0.47$ and $x = 0.47$ (Fig. 2), and $x = -\frac{1}{4}$ and $x = \frac{3}{4}$ (Fig. 3)]. The two lines are identical by lattice translation in Fig. 3 but not in Fig. 2. Nevertheless, the stripes in the two figures are almost identical if the differences in the assignment of Pb and Bi to the different heavy-atom sites and the In/Bi mixing in the title phase are neglected. Let us consider now, for both structures, the identical stripe which is obtained from the original one by a shift $\mathbf{t} = a$ (with different *a* vectors in the two cases). In $Pb_{1.6}In_8Bi_4S_{19}$ (Fig. 3), the original and the copied stripe match perfectly. In the title compound, however, some gaps remain between the original and the copied stripe, the latter here visualized by its left-hand dashed border line around $x = 0.53$, drawn in grey (green in the electronic version). These gaps contain two S atoms (2 × S20) and two In atoms (2 × In4) per unit cell. If the copied stripe is shifted further by $\mathbf{t}' = -0.050a + 0.387c$ (arrow in Fig. 2), all gaps between the two stripes disappear, *i.e.* the 'superfluous'

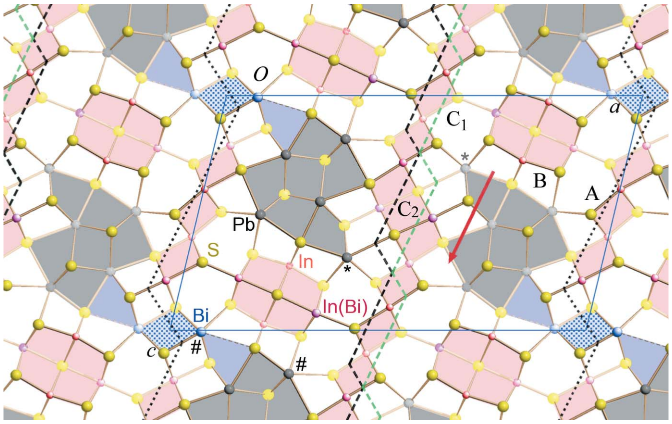

Figure 2

The structure of $Pb_{5.0(1)}In_{8.4(1)}Bi_{1.6(1)}S_{20}$. Two representatives of atom Pb1 are indicated by asterisks (*). One representative of atoms Bi1 and Pb3 is indicated by a hash symbol (#). For the meaning of these symbols, the arrow, the dashed lines and the shading scheme, see *Comment* and Table 1.

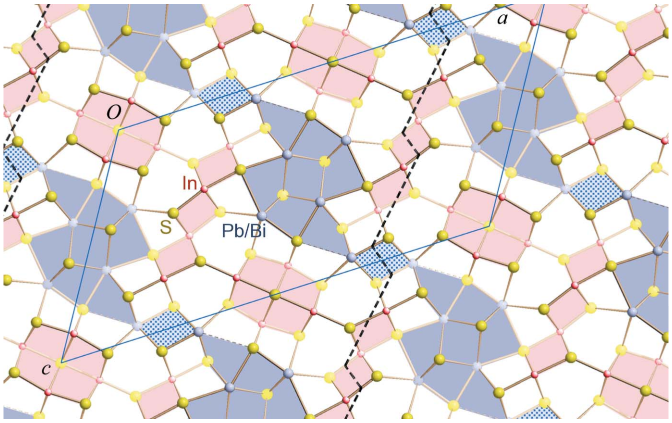

Figure 3

The structure of $Pb_{1.6}In_8Bi_4S_{19}$ (Krämer, 1983). For the meaning of the dashed lines and the shading scheme, see *Comment*.

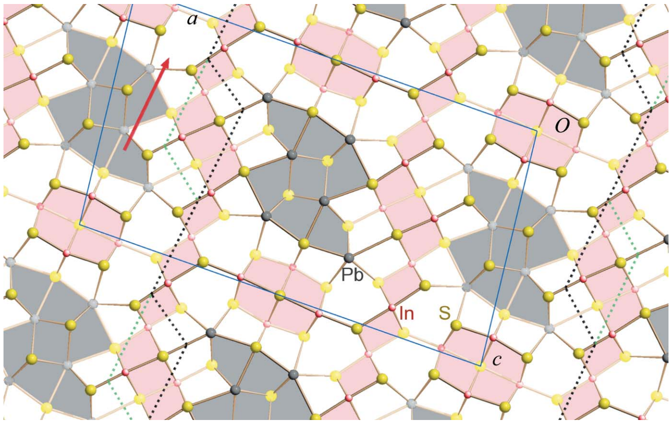

Figure 4
The structure of $Pb_6In_{10}S_{21}$ (Krämer & Berroth, 1980). For the meaning of the arrow, the dashed lines and the shading scheme, see *Comment*.

atoms are 'eliminated'. The complex of the two 'united' stripes would then have to undergo another shift of $\mathbf{t}'$ to match with the next stripe on the left-hand side (with its right-hand dashed border line along $x = -0.53$), and so on. Additional small 'annealing' shifts for some atoms, the largest one affecting Pb5 (about 0.45 Å approximately parallel to a), generate the complete structure pattern of $Pb_{1.6}In_8Bi_4S_{19}$, which contains two fewer In-atom and two fewer S-atom positions per unit cell. In Fig. 2, two copies of Pb5 which will belong to one common quadrangle after the application of $\mathbf{t}'$ are indicated by asterisks (*). Finally, it should be mentioned that, while in $Pb_{1.6}In_8Bi_4S_{19}$ apparently one heavy-atom position is occupied by only $\frac{4}{5}$ of a Pb atom (Krämer, 1983) or $\frac{2}{3}$ of a Bi atom (Topa & Keller, 2011) (with no In), a corresponding partial occupancy is not observed in the title compound.

A very similar structural relationship (but inverted) exists between the title phase and the already mentioned ternary phase $Pb_6In_{10}S_{21}$ (Fig. 4). The more central stripe in Fig. 2, defined by the two lattice-translationally related dotted black lines around $x = -0.03$ and $x = 0.97$, is just a section of the $Pb_6In_{10}S_{21}$ structure, provided again that Pb and Bi are not distinguished from each other and In/Bi mixing in the title phase is neglected. In the $Pb_6In_{10}S_{21}$ structure (Fig. 4), the two border lines (around $x = 0.26$ and $x = 1.20$) of the section are not related by lattice translation. Thus, again, gaps exist between the stripe and its copy obtained by a shift of $\mathbf{t} = a$. The right-hand border line of the copied stripe is visualized in Fig. 4 by the grey dotted line (green in the electronic version) around $x = 0.20$. To transform the ternary structure into the quaternary one, each stripe in Fig. 4 must be shifted by the grey vector (red in the electronic version) relative to its vicinal one on the right-hand side. This shift vector is the counter vector to $\mathbf{t}'$ (arrow in Fig. 2), both vectors being mean vectors between an In atom in the $\mathbf{C_1}$ motif (Fig. 2) and its second-nearest In neighbour in the same motif. Again, the disappearance of the gaps eliminates two In atoms and two S atoms per unit cell, this time all gathered into one gap, instead of two gaps as in Fig. 2.

Finally, in comparing Figs. 2, 3 and 4, we can state that the geometry of the atomic arrangement in the title compound between $x \simeq -0.45$ and $x \simeq 0.45$ has grown 'monoculturally' in the structure of $Pb_{1.6}In_8Bi_4S_{19}$, while the arrangement between $x \simeq 0.03$ and $x \simeq 0.93$ has grown monoculturally in the structure of $Pb_6In_{10}S_{21}$. Thus, the title structure can be viewed as a genuine hybrid of the other two. We also can formulate the following structural transition scheme, in which each step involves the loss of two In and two S atoms per unit cell by the above-described shearing mechanisms. The aforementioned In/Bi mixing in the title compound is responsible for the fact that the second formula in the scheme contains $In_{8.4}$ instead of the expected In_9 (all In atoms eliminated in the two steps are nevertheless 'pure' In atoms):

$$(Pb_6In_{10}S_{21})_2 \rightarrow (Pb_{5.0}In_{8.4}Bi_{1.6}S_{20})_2 \rightarrow (Pb_{1.6}In_8Bi_4S_{19})_2\ [(Pb_2In_8Bi_{3.33}S_{19})_2].$$

Replacing Pb and Bi by a common atom type M, the scheme becomes:

$$(M_6In_{10}S_{21})_2 \rightarrow (M_{6.6}In_{8.4}S_{20})_2 \rightarrow (M_{5.6}In_8S_{19})_2\ [(M_{5.33}In_8S_{19})_2].$$

Looking at all of these formulae, the strong similarity between the three structures suggests that the structural pattern in this type of compound is determined mainly by the M:S and In:S ratios, while the Pb:Bi ratio seems to be of much less importance.

Experimental

The binary sulfides PbS, In_2S_3 and Bi_2S_3 were synthesized from nearly stoichiometric amounts of the elements [5 *N* Pb (Strem Chemicals Inc.); 5 *N* In (Johnson Matthey GmbH); 5 *N* Bi (Chempur Feinchemikalien); 5 *N* S (Johnson Matthey GmbH)] in evacuated quartz ampoules. Before adding S (*ca* 1% more than calculated), the metals (except In) were purified by reaction with hydrogen at 770 K. The reaction mixtures were heated to 670 K (870 K for In_2S_3) for 4–5 d. The end of the ampoule holding the reaction mixture was then heated to 570 K for 1 d and the other end to 540 K, to remove excess S by sublimation. Powder diffractograms of the reaction products showed only the peak patterns of the corresponding pure sulfides.

A mixture of PbS (860 mg, 3.6 mmol), In_2S_3 (593 mg, 1.8 mmol), Bi_2S_3 (308 mg, 0.6 mmol) and I_2 (40 mg, as a transport agent) was placed in a quartz ampoule of length ~20 cm and internal diameter 1.3 cm. The ampoule was sealed under vacuum and placed in a two-zone tube furnace. The end containing the reaction mixture (zone *A*) was heated to 940 K and the other end (zone *C*) to 870 K. After eight weeks, a carpet of comparatively large black needle-like crystals of the title compound had grown on a bulk which had formed in zone *A*. In the centre of the ampoule (zone *B*), more of these crystals had been deposited. At the cool end of the ampoule (zone *C*), a conglomerate of crystals of a different phase had grown. Structural investigation and electron-microprobe analysis showed them to be $Pb_4In_{3.7}Bi_{2.3}S_{13}$, a compositional variant of $Pb_4In_2Bi_4S_{13}$ (Krämer, 1986).

Two crystal needles grown in zone *A* were chemically analysed using a Jeol Superprobe JXA-8600 electron microprobe, controlled

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by the *Probe for Windows* system of programs (Advanced MicroBeam, 2002) and operated at 25 kV and 20 nA, with a beam diameter of 5 µm. Wavelength-dispersion data were collected using the following standards and emission lines: PbS (Pb L_α), InAs (In L_α), Bi_2S_3 (Bi L_α) and Sb_2S_3 (S K_α). The raw data were corrected using the online *ZAF-4* procedure (Advanced MicroBeam, 2002). Averaged results for ten electron-probe analyses (five per crystal) are Pb 35.0 (3), In 31.7 (1), Bi 12.2 (1) and S 21.3 (1), total 100.2 (3) wt%. In good agreement with these results, an atomic absorption spectroscopy (AAS) analysis of a 20 mg sample of crystals taken from zone *A* yielded the following results: Pb 34.5, In 31.2 and Bi 11.5 wt%.

Crystals of the title phase were also obtained and identified by powder diffractometry in a number of other similar experiments, where mixtures of the three binary sulfides in slightly different molar ratios (*e.g.* 5:4:1) were exposed to different temperature gradients (*e.g.* 860→810 K) (Reis, 1984; Seiler, 2009). Indexing of these powder patterns resulted in lattice parameters covering the ranges a = 27.05–27.17, b = 3.88–3.96 and c = 15.67–15.71 Å, and β = 103.59–103.65°, which suggests that most of these crystals have a higher Bi (and/or Pb) content and a lower In content than the crystals described here. These observations additionally justify the use of standard deviations in the stoichiometric coefficients of the chemical formula (see *Refinement*).

Crystal data

$Pb_5In_{8.38}Bi_{1.62}S_{20}$
$M_r = 2978.24$
Monoclinic, $P2_1/m$
$a = 27.065$ (4) Å
$b = 3.8825$ (3) Å
$c = 15.683$ (2) Å
$\beta = 103.59$ (1)°
$V = 1601.8$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 42.24$ mm^{-1}
$T = 293$ K
0.16 × 0.05 × 0.01 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: integration (*SHELXTL*; Sheldrick, 2008)
$T_{min} = 0.12$, $T_{max} = 0.55$
25700 measured reflections
5322 independent reflections
4539 reflections with $I > 2\sigma(I)$
$R_{int} = 0.094$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.088$
$S = 1.07$
5322 reflections
216 parameters
$\Delta\rho_{max} = 4.26$ e Å^{-3}
$\Delta\rho_{min} = -5.52$ e Å^{-3}

Table 1
Average, minimum and maximum M—S bond lengths (<3.5 Å) in $Pb_{5.0(1)}In_{8.4(1)}Bi_{1.6(1)}S_{20}$.

CN = coordination number, x refers to In_xBi_{1-x} and atoms flagged by a hash symbol (#) are possibly subject to Pb/Bi disorder.

M	CN	*x*	*M*—S (mean)	*M*—S (min)	*M*—S (max)
Pb1	8		3.11	2.8745 (15)	3.2368 (16)
Pb2	8		3.11	2.8200 (14)	3.2541 (16)
Pb3#	8		3.11	2.7169 (15)	3.4717 (17)
Pb4	8		3.12	2.9216 (16)	3.392 (2)
Pb5	8		3.09	2.8667 (15)	3.413 (2)
Bi1#	7		3.01	2.791 (2)	3.2686 (16)
In1	6		2.64	2.533 (2)	2.682 (2)
In2	6		2.64	2.521 (2)	2.8327 (14)
In3	6		2.65	2.523 (2)	2.8585 (15)
In4	6		2.64	2.570 (2)	2.6796 (15)
In5*F*	6	0.952 (4)	2.64	2.587 (2)	2.6959 (14)
In6*F*	6	0.947 (4)	2.65	2.592 (2)	2.728 (2)
In7*F*	6	0.932 (4)	2.66	2.519 (2)	2.8572 (17)
In8*F*	6	0.824 (4)	2.67	2.551 (2)	2.7749 (17)
In9*F*	6	0.723 (4)	2.69	2.6372 (15)	2.803 (2)

After solving the structure by direct methods, refinement showed that the electron density at five of the 15 non-S-atom positions was much too small for a heavy atom (Pb or Bi) but also much too large for an In atom, *i.e.* having site-occupancy factors (s.o.f.s) for In atoms refining to values significantly larger than 1. These positions were therefore modelled as In_xBi_{1-x} atom pairs, with the two atoms of each pair constrained to have the same coordinates and displacement parameters, and with x refining to values between 0.952 (4) and 0.723 (4). In Fig. 2, one of these positions is labelled as In(Bi). Free refinement of the s.o.f.s for all ten other non-S atoms (four In atoms and six heavy atoms) showed, by yielding values close to 1, that no significant heavy/light-metal atom mixing takes place. From the six heavy-atom positions, one with a coordination number (CN) of 7 [neglecting one long bond distance of 3.650 (2) Å] was assigned as a Bi atom, while the other five, with CN = 8, were assigned as Pb atoms. This was done because Pb has (with one exception where $\frac{1}{3}$ Pb is mixed with $\frac{2}{3}$ In; Ginderow, 1978) always been found with an eightfold coordination in ternary lead indium sulfides (Ginderow, 1978; Krämer & Berroth, 1980; Arriortua *et al.*, 1983), while Bi can have CN = 6 or 7 (the latter as in Bi_2S_3, *e.g.* Kupcik & Vesela-Novakova, 1970) as frequently as CN = 8 in ternary bismuth indium sulfides (Chapuis *et al.*, 1972; Krämer, 1980; Yin *et al.*, 2010; excluding lower-valent Bi atoms and 'bonds' with lengths > 3.5 Å). The described assignments, together with the refined x values of the five In_xBi_{1-x} atom pairs, led to the electrically neutral chemical formula $Pb_5In_{8.38}Bi_{1.62}S_{20}$ (with $Z = 2$). This is in good agreement with the formula obtained from the electron-microprobe results (see *Experimental*) under the assumption that there are exactly 20 S atoms, *i.e.* $Pb_{5.09(5)}In_{8.31(4)}Bi_{1.75(2)}S_{20}$ [with a net positive charge of 0.4 (3)]. Since the former formula is the electrically neutral one, it is used for the title compound, but with standard deviations of 0.1 for the stoichiometric coefficients of the non-S elements. For the final refinements, the reflections $\overline{1}01$ and 101 were removed from the data set as they had been identified as outliers by *checkCIF* (Spek, 2009).

Bond-valence sum (BVS) calculations performed using *softBV* (Adams, 2004) yielded an acceptable global instability index of 0.138 and values differing by less than 0.08 valence units (v.u.) from the ideal values for the non-S atoms with s.o.f.s of 1, except, however, for atoms Pb3 (0.28 v.u.) and Bi1 (−0.43 v.u.) [indicated by a hash symbol (#) in Fig. 2 and Table 1]. Interchanging these two atoms again led to unsatisfactory values (−0.41 and 0.23 v.u.). There is, therefore, a question of whether Pb/Bi mixing (as observed in ternary Pb–Bi sulfides; *e.g.* Berlepsch *et al.*, 2001) should be taken into account for the two positions. A check by structure refinement is not possible, because the two elements have almost the same number of electrons (82 *versus* 83). It should be noted that *softBV* also calculated large BVS deviations (−0.29 v.u.) for two S atoms, one of them coordinated to neither Bi1 nor Pb3. On judging all of the evidence, the original assignment of atom types according to the CN (see above) and s.o.f.s of 1 were retained for the two atoms in the structure model. However, some probability of Pb/Bi mixing at the two positions cannot be excluded.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SCHAKAL99* (Keller, 2004); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3029). Services for accessing these data are described at the back of the journal.

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