

Pb₅In₃Bi₅S₁₇ [Pb_{4.94(3)}In_{3.05(3)}Bi_{4.99(3)}S₁₇] and its structural relationship with Pb₄In₃Bi₇S₁₈

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The title phase (pentalead triindium pentabismuth heptadecasulfide) has been synthesized and structurally characterized. Its structure contains mixed Bi/In, In/Bi and Pb/In positions; all atoms lie on crystallographic mirror planes. The structural relationship between Pb₅In₃Bi₅S₁₇ and a phase known by the formula Pb₄In₃Bi₇S₁₈ is discussed. A comparatively large and complex structural ‘seed’ is defined which is common to both phases. The structural changes within this seed when moving from one phase to the other are described by graphical means.

Comment

In the first half of the 1980s, six different quaternary lead indium bismuth sulfides were synthesized (Reis, 1984), of which four have since been fully characterized with respect to their structures (Krämer, 1983, 1986; Krämer & Reis, 1986; Reis *et al.*, 2012); the other two have been structurally characterized only by the determination of lattice constants and space groups (Reis, 1984). In the course of an attempt to re-synthesize one of these two phases, a new quaternary phase was obtained, and this is described here. The new compound can chemically be described as Pb_{4.94(3)}In_{3.05(3)}Bi_{4.99(3)}S₁₇. For sake of readability it is addressed as Pb₅In₃Bi₅S₁₇ in the following.

Like most of the related structurally known sulfides in this quaternary system and the corresponding sulfidic ternary subsystems, Pb₅In₃Bi₅S₁₇ adopts a structure with one of the unit vectors (*b*) being close to 4.0 Å. All atoms are distributed on the two layers $y = \frac{1}{4}$ and $y = \frac{3}{4}$. Fig. 1 shows a projection of the structure onto (010). The bond-length ranges for the different metal atoms (Table 2) are comparable with those known from the binary and ternary subsystem compounds and the other structurally known quaternary sulfides.

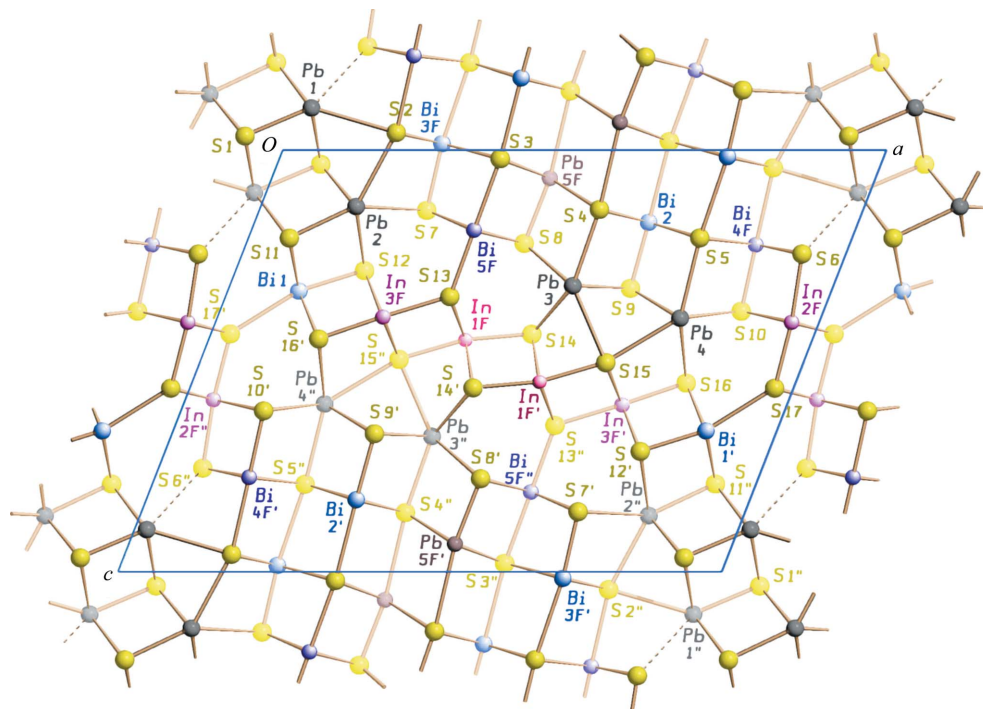
Atoms Pb2, Pb3 and Pb4 show an eightfold coordination, like the Pb atoms in Pb₅In_{8.4}Bi_{1.6}S₂₀ (Reis *et al.*, 2012). If a distance of 3.748 (3) Å is interpreted as a Pb–S bond, then

Pb1 would also be coordinated in this way; otherwise its coordination polyhedron is a distorted octahedron, which is rather unusual for Pb in compounds of this kind (Reis *et al.*, 2012). The assignment of Pb to this metal position should anyway be correct, as indicated by bond-valence-sum calculations (Table 2). Pb is also coordinated octahedrally in, for example, PbS (*e.g.* Ramsdell, 1925). Atoms Pb5*F* (see below), Bi and In are also coordinated octahedrally, with different degrees of distortion.

As can be seen from the ‘*x*’ column of Table 2, all In positions have a certain amount of Bi mixed in, while three of the five Bi positions are mixed with a fraction of In, this fraction being very small in one case (Bi3*F*). ‘Mixed atoms’ of the former kind have also been observed in the structures of Pb₅In_{8.4}Bi_{1.6}S₂₀ (Reis *et al.*, 2012), Pb₄In₂Bi₄S₁₃ (Krämer, 1986) and Pb₄In₃Bi₇S₁₈ (Krämer & Reis, 1986). As both elements, *viz.* Bi and In, carry a valence of +3, the occurrence of such mixed atoms seems chemically reasonable, even though there is an ‘isotopic’ size (radius) difference (Keller & Krämer, 2006) of 0.21 Å between the two elements. As, at most, 21% of an atom of the respective other kind is mixed in (Table 2), the bond lengths should be affected by at most 0.04 Å. The mean Bi–S and, to a lesser degree, mean In–S bond lengths (Table 2) show roughly the expected behaviour.

Surprisingly, one Pb atom (Pb5*F*, valence +2) is also apparently mixed with In. The assignment of Pb (instead of Bi) to the corresponding position is strongly suggested by bond-valence-sum calculations (Table 2). Pb/In mixing at an octahedrally coordinated position has also been observed in Pb₃In_{6.67}S₁₃ (Ginderow, 1978), but with In being the dominant partner. Another hint that our assignment is correct will be given in more detail below.

The two-dimensional projection of the overall structure of Pb₅In₃Bi₅S₁₇ can be seen as a pattern composed of *M*₂S₂ quadrangles and *M*₃S₃ hexagons (*M* = metal; see also Reis *et al.*, 2012) which are, when seen in three dimensions, the cross sections of one-dimensionally infinite columnar aggregates (like rods and ribbons) oriented parallel to *b*. In Fig. 2, quadrangles containing two Bi (or Bi_{*x*}/In_{1–*x*}) atoms are shaded dotted grey (blue in the electronic version of the journal), those with two Pb (or Pb_{*x*}/In_{1–*x*}) atoms are shaded dark grey and those containing two In_{*x*}/Bi_{1–*x*} atoms light grey (pink in the electronic version). The latter form two different motifs: isolated quadrangles flanked by two S₂Bi(In) units, and chains set up by three corner-sharing quadrangles, each chain flanked by two S₂Bi units. Isolated quadrangles of this kind have also been found in Bi_{1.47}In_{11.3}S₃₈ (Yin *et al.*, 2010), while the chain motif is known from Bi₃In₅S₁₂ (Krämer, 1980), Pb_{1.6}In₈Bi₄S₁₉ (Krämer, 1983) and Pb₅In_{8.4}Bi_{1.6}S₂₀ (Reis *et al.*, 2012). Bi and Bi(In) form only one kind of motif composed of three edge-sharing quadrangles. This motif is found (as part of an 11-quadrangles complex) also in Pb₄In₃Bi₇S₁₈ (Krämer & Reis, 1986; see below). Pb and Pb(In) generate novel five-membered chains, of which the central three-membered parts occur in Pb₃In_{6.67}S₁₃ (Ginderow, 1978), and a different kind of five-membered complex, its shape reminiscent of a bow. Similarly shaped Pb complexes have been found (as central

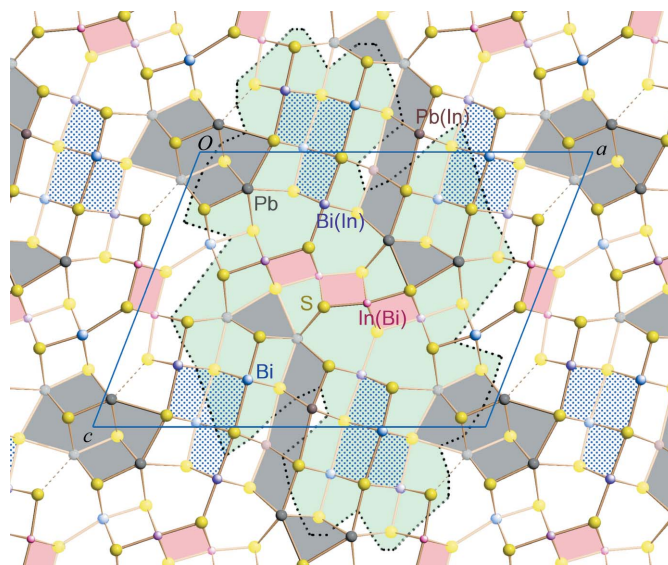

Figure 1

The structure of $\text{Pb}_5\text{In}_3\text{Bi}_5\text{S}_{17}$, viewed along the b axis. Atoms and bonds in the layer further from the viewer are drawn paler. Some very long Pb—S bonds [3.748 (3) 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.

parts of slightly larger complexes) in $\text{Pb}_6\text{In}_{10}\text{S}_{21}$ (Krämer & Berroth, 1980) and $\text{Pb}_5\text{In}_{8.4}\text{Bi}_{1.6}\text{S}_{20}$ (Reis *et al.*, 2012). However, the distribution of the atoms between the two atomic layers perpendicular to b is different in these structures, such that the symmetry of a unique three-dimensional section (two atomic layers) is close to $mm2$, while it is $\bar{1}$ in $\text{Pb}_5\text{In}_3\text{Bi}_5\text{S}_{17}$. A similar Bi bow complex, however of symmetry 1, is found (again as part of a larger complex) in the structure of $\text{Bi}_{14.7}\text{In}_{11.3}\text{S}_{38}$ (Yin *et al.*, 2010).

The $\text{Pb}_5\text{In}_3\text{Bi}_5\text{S}_{17}$ structure is related to the structure of $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ (Krämer & Reis, 1986); Fig. 3 shows a representation of this latter structure. The published formula [derived mainly by structure-analytical/geometric considerations (Krämer, 2011)] corresponds to a net positive charge of 1.5. In the quaternary phase system Pb—In—Bi—S and its ternary subsystems, a comparatively small number of other structures have been published with such stoichiometrically unusual chemical formulae. Besides $\text{Bi}_{41.88}\text{Pb}_{9.32}\text{S}_{76}$ (Takeuchi *et al.*, 1979; formula as specified in the ICSD, 2012), these are $\text{Pb}_4\text{In}_9\text{S}_{17}$ (Ginderow, 1978; Arriortua *et al.*, 1983), $\text{Bi}_3\text{In}_4\text{S}_{10}/\text{Bi}_{14.7}\text{In}_{11.3}\text{S}_{38}$ (Yin *et al.*, 2010) and $\text{Pb}_{1.6}\text{In}_8\text{Bi}_4\text{S}_{19}$ (Krämer, 1983; but see also Reis *et al.*, 2012). The corresponding formulae imply unusual oxidation states for the elements involved, for instance, in $\text{Bi}_3\text{In}_4\text{S}_{10}/\text{Bi}_{14.7}\text{In}_{11.3}\text{S}_{38}$ (Yin *et al.*, 2010), where the Bi—Bi bonds indicate the occurrence of lower-valent Bi atoms. Such compounds, known also from other sulfidic phase systems, have been classified as complex sulfides (Nowacki, 1969). However, by far the majority of structures in all these phase systems have been published under stoichiometrically normal formulae. Furthermore, the five quaternary Pb—In—Bi—S phases we have investigated so far

(Reis *et al.*, 2012; Topa & Keller, 2011), including the title compound, are also stoichiometrically normal, as confirmed by analytical electron-microprobe results. If we therefore postulate that $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ (Krämer & Reis, 1986) should also be described by such a formula, this could be achieved by substituting two Bi atoms with (structure-analytically not distinguishable) Pb atoms to yield the formula $\text{Pb}_6\text{In}_3\text{Bi}_5\text{S}_{18}$. If, additionally, the three In atoms with site-occupancy factors greater than unity (Krämer & Reis, 1986) were interpreted as


Figure 2

The structure of $\text{Pb}_5\text{In}_3\text{Bi}_5\text{S}_{17}$. For the meaning of the dotted outline and the shading scheme, see the *Comment*.

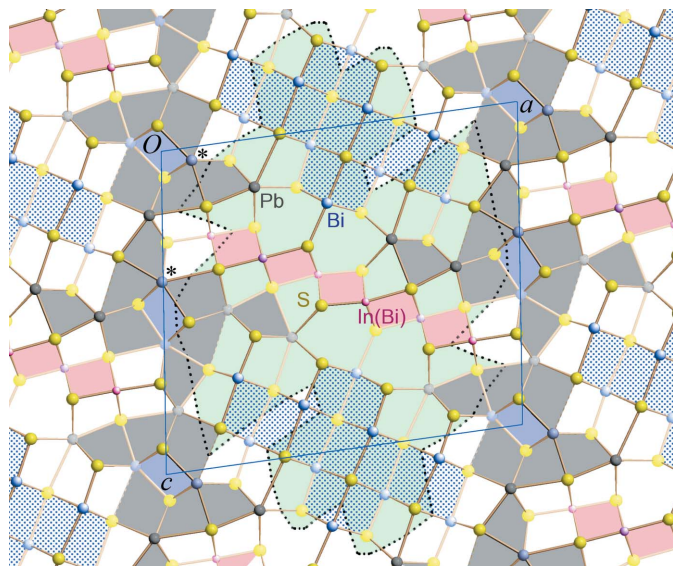


Figure 3

The structure of $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ (Krämer & Reis, 1986). For the meaning of the asterisks (*), the dotted outline and the shading scheme, and for a possible alternative to the chemical formula, see the *Comment*.

$\text{In}_x/\text{Bi}_{1-x}$ pairs, the approximate result would be the electrically neutral formula $\text{Pb}_6\text{In}_{2.5}\text{Bi}_{5.5}\text{S}_{18}$.

In Fig. 3, we have introduced Pb in place of Bi for the two 'Bi' atoms with coordination numbers greater than 6 (see also Reis *et al.*, 2012). The corresponding atoms are indicated by asterisks (*), and the quadrangles (rectangles) formed by them are shaded medium grey (blue–grey in the electronic version). Note that, if we accept these replacements, the one-dimensionally infinite Pb motif (two-dimensionally infinite if seen in three dimensions) in Fig. 3 would contain a third form (also of symmetry $\bar{1}$) of a Pb bow complex (see above) in two different alternating orientations.

Whether or not the Bi/Pb replacements of Fig. 3 are correct, the following discussion is valid. In both Figs. 2 and 3, a large central section has been emphasized by very light grey (light green in the electronic version) and a dotted outline. While the patterns of the shaded quadrangles are rather different in the two figures, the two structures are in fact practically identical with respect to the observed types of atoms and their connectivity within these two central sections (possible contamination of Bi by In being neglected). In a layer of thickness b , each section contains 62 atoms, which is 103% (97% in Fig. 3) of the respective numbers of atoms per unit cell. If only lattice-translationally non-equivalent atoms are counted, the above figures become 42 atoms/70% (48 atoms/75% in Fig. 3). Thus, there is a comparatively large and complex common 'seed' which is developed by the formation of appropriate interfaces and the application of two different translation lattices into the two different structures, such that the two unit cells of similar size (1477 versus 1582 Å³) are not (much) larger than the seed itself. In Fig. 4, the two structures are superimposed such that the unit-cell centres coincide. The geometric changes within the central sections in the transition $\text{Pb}_5\text{In}_3\text{Bi}_5\text{S}_{17} \rightarrow \text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ become visible and give an idea of how flexible such a part of a sulfidic framework can be when

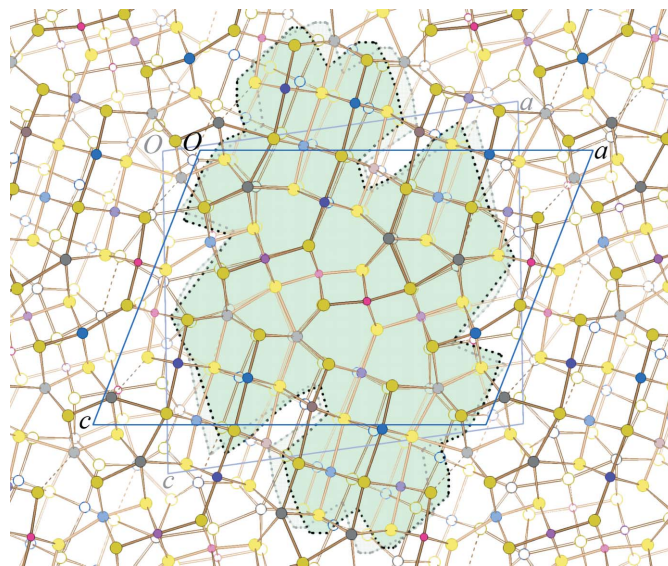


Figure 4

A superposition of the structures of $\text{Pb}_5\text{In}_3\text{Bi}_5\text{S}_{17}$ and $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$. Atoms and bonds are drawn as solid for the former and hollow for the latter. Outlines of the central sections (see the *Comment*) are drawn dotted black (dotted grey).

exposed to a change in the external crystal field. The difference between the two structures originates, of course, in the difference in chemical composition. The close relationship between the structures, on the other hand, is anticipated by the similarity of the stoichiometric coefficients in the two chemical formulae $\text{Pb}_5\text{In}_3\text{Bi}_5\text{S}_{17}$ and $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ ($\text{Pb}_6\text{In}_{2.5}\text{Bi}_{5.5}\text{S}_{18}$).

Finally, comparing the two structures in more detail can give an additional hint that our assignment of a Pb(In) atom in Fig. 2 is correct. In Fig. 3 we have one Bi motif, emphasized by dotted grey (dotted blue in the electronic version), with a central linear ladder-like structure composed of seven edge-sharing (slightly distorted) rectangles. If the Pb(In) atoms were replaced by Bi(In) in Fig. 2, we would obtain a very similar Bi motif in this structure, also with a central ladder-like structure composed of seven edge-sharing quadrangles. However, the ladder would not be linear, because the central one of these quadrangles [at $(\frac{1}{2}, y, 0)$] differs substantially from a rectangle. In fact, the (two-dimensional) S—Pb(In)—S angle in Fig. 2 (112°) is about 20° larger than the corresponding S—Bi—S angles in Fig. 3 (90±5°). Taking into account that (almost) the complete environments (at least 11 of the 12 vicinal atoms) of the two corresponding quadrangles in Figs. 2 and 3 are identical, such a severe structural change would not be understandable if the Pb(In) positions in Fig. 2 were actually also occupied by Bi or Bi(In) as in Fig. 3.

Experimental

For the preparation of the reactants (PbS, In_2S_3 , and Bi_2S_3), see Reis *et al.* (2012). The title phase was obtained *via* two variants (*A* and *B*; see Table 1) of the following procedure.

A mixture of PbS, In_2S_3 , Bi_2S_3 and I_2 (the latter serving as a transport agent) was filled into a quartz ampoule of length L and

Table 1

Experimental conditions for synthesis variants *A* and *B*.

The masses of the binary sulfides and I₂ are given in mg [mmol]. *L* and *D* are given in mm.

Variant	<i>m</i> (PbS)	<i>m</i> (In ₂ S ₃)	<i>m</i> (Bi ₂ S ₃)	<i>m</i> (I ₂)	<i>L</i>	<i>D</i>
<i>A</i>	144 [0.6]	98 [0.3]	311 [0.6]	30 [0.1]	100	13
<i>B</i>	117 [0.49]	51 [0.16]	127 [0.25]	10 [0.04]	80	9

internal diameter *D* (Table 1). The ampoule was sealed under vacuum and placed in a slanting fashion in a two-zone half-shell furnace with vertical arrangement of the two halves. The lower half, containing the reaction mixture, was heated to 823 K and the upper half to 753 K.

Variant *A*: After two weeks, a bunch of long thin black needles (about 35 mg) of the title compound had grown at the cooler end of the ampoule. One of the crystal needles obtained was used for the X-ray structure analysis. Two other crystal needles were chemically analysed using a JEOL Superprobe JXA-8600 electron microprobe, controlled 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), Bi₂S₃ (Bi *L*α) and Sb₂S₃ (S *K*α). The raw data were corrected using the online *ZAF-4* procedure (Advanced MicroBeam, 2002). The averaged results for ten electron-probe analyses (five per crystal) are Pb 34.6 (1), In 12.1 (1), Bi 35.2 (2) and S 18.6 (1), total 100.4 (3) wt%. After reduction of all figures to sum to a total of 100%, this corresponds to the chemical formula Pb_{4.90(3)}In_{3.10(3)}Bi_{4.95(3)}S₁₇ with a net charge of 0.0 (3) (for an explanation of the formula syntax, see Reis *et al.*, 2012). In good agreement with these results, an atomic absorption spectroscopy (AAS) analysis of a 15 mg sample of the crystals yielded the following results: Pb 33.9, In 11.2 and Bi 34.3 wt%.

It should be noted that we were not able to synthesize the title phase a second time *via* variant *A*. However, we obtained it reproducibly by variant *B* (Table 1), for which the relative quantities of the binary sulfides had been calculated from the known composition of the compound.

Variant *B*: After one week, some needle crystals (about 15 mg) had grown in the cooler part of the ampoule. They showed an unknown powder diffractogram and were not investigated any further. In the hot part, a carpet of long thin black needles had grown on top of a bulk which had formed from the reaction mixture. Both the needles and the bulk showed the powder diffractogram of the title phase. Refined lattice parameters differed by less than 0.02 Å and 0.04° from those obtained from the crystals synthesized by variant *A*.

Crystal data

Pb _{4.93} In _{3.05} Bi _{5.02} S ₁₇	<i>V</i> = 1476.8 (6) Å ³
<i>M_r</i> = 2966.21	<i>Z</i> = 2
Monoclinic, <i>P</i> 2 ₁ / <i>m</i>	Mo <i>K</i> α radiation
<i>a</i> = 23.030 (3) Å	<i>μ</i> = 61.33 mm ⁻¹
<i>b</i> = 3.985 (1) Å	<i>T</i> = 293 K
<i>c</i> = 17.275 (5) Å	0.16 × 0.03 × 0.02 mm
<i>β</i> = 111.33 (1)°	

Data collection

Bruker SMART CCD area-detector diffractometer	22185 measured reflections
Absorption correction: integration (<i>SHELXTL</i> ; Sheldrick, 2008)	4880 independent reflections
<i>T_{min}</i> = 0.127, <i>T_{max}</i> = 0.399	3979 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.111

Table 2

Average, minimum and maximum *M*–*S* bond lengths in Pb₅In₃Bi₅S₁₇.

CN = coordination number, *x* refers to Pb_{*x*}/In_{1–*x*}, Bi_{*x*}/In_{1–*x*} or In_{*x*}/Bi_{1–*x*} (*i.e.* the atoms with labels ending with '*F*'), and Δ(*BVS*) = deviation of the *softBV* (Adams, 2004) bond-valence sum from the formal valence (always calculated for pure Pb, In and Bi atoms).

<i>M</i>	CN	<i>x</i>	Δ(<i>BVS</i>)	<i>M</i> – <i>S</i> (mean)	<i>M</i> – <i>S</i> (min)	<i>M</i> – <i>S</i> (max)
Pb1	6		0.02†	2.99	2.755 (3)	3.366 (3)
Pb2	8		0.04	3.11	2.821 (3)	3.355 (2)
Pb3	8		–0.05	3.10	2.965 (2)	3.186 (2)
Pb4	8		–0.10	3.12	2.980 (2)	3.303 (3)
Pb5 <i>F</i>	6	0.935 (5)	0.09‡	2.96	2.674 (3)	3.422 (3)
In1 <i>F</i>	6	0.944 (5)	–0.10	2.65	2.534 (3)	2.715 (2)
In2 <i>F</i>	6	0.851 (5)	–0.22	2.67	2.591 (3)	2.799 (2)
In3 <i>F</i>	6	0.804 (4)	–0.23	2.67	2.594 (3)	2.756 (2)
Bi1	6		–0.13	2.84	2.629 (3)	3.081 (3)
Bi2	6		–0.14	2.84	2.613 (3)	3.183 (3)
Bi3 <i>F</i>	6	0.987 (5)	–0.22	2.89	2.612 (3)	3.273 (3)
Bi4 <i>F</i>	6	0.843 (5)	0.05	2.81	2.601 (3)	3.017 (3)
Bi5 <i>F</i>	6	0.788 (5)	–0.01	2.80	2.711 (3)	2.901 (3)

† –0.68, when Pb is replaced by Bi. ‡ –0.63, when Pb is replaced by Bi.

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.036	190 parameters
<i>wR</i> (<i>F</i> ²) = 0.083	Δρ _{max} = 2.89 e Å ⁻³
<i>S</i> = 0.97	Δρ _{min} = –3.52 e Å ⁻³
4880 reflections	

Single-crystal data were collected from one of the crystals obtained *via* synthesis variant *A* (above). The reported lattice parameters were refined from powder diffraction data. After solving the structure by direct methods, refinement showed that seven of the 13 metal positions had site-occupancy factors (s.o.f.) differing significantly from 1. Of these, four comparatively electron-rich positions were initially modelled with Bi_{*x*}/In_{1–*x*} atom pairs, with the two atoms of each pair constrained to have the same coordinates and displacement coefficients. In Fig. 2, one of these positions is labelled as Bi(In). To the remaining three positions, In_{*x*}/Bi_{1–*x*} atom pairs were correspondingly assigned. In Fig. 2, one of these positions is labelled as In(Bi). The other five metal positions were tentatively modelled as three Pb atoms [coordination number (CN) = 8] and two Bi atoms (CN = 6). However, the results of the bond-valence-sum calculations (Table 2) strongly suggested replacing one of the Bi atoms with a Pb atom (Pb1) and one of the Bi_{*x*}/In_{1–*x*} pairs with a Pb_{*x*}/In_{1–*x*} pair [Pb5*F* in Fig. 1 and Table 2; Pb(In) in Fig. 2].

In the final refinements, reflections 001 and $\bar{1}01$ were excluded, as they had been identified as outliers by *checkCIF* (Spek, 2009). Of the 24 unique minima < –2.5 e Å⁻³ in the final Δ*F* map, two have *S* atoms as closest neighbours: minima of –2.95 and –2.55 e Å⁻³ at distances of 1.64 and 0.89 Å from *S*5 or *S*1, respectively. As a reason for this, we assume deficiencies in the numerical absorption correction, as these minima disappeared when an empirical absorption correction was applied.

From all refined stoichiometric *x* values (see above), the chemical formula Pb_{4.93}In_{3.05}Bi_{5.02}S₁₇ results. It corresponds to a net positive charge of 0.07 and has therefore been slightly modified to Pb_{4.94(3)}In_{3.05(3)}Bi_{4.99(3)}S₁₇ (with a net charge of zero), such that all stoichiometric coefficients of the metal elements differ by about 0.04 from those in the electron-microprobe formula (from which the standard deviations were transferred).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; 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: BI3039). Services for accessing these data are described at the back of the journal.

References

- Adams, St. (2004). *softBV*. <http://kristall.uni-mki.gwdg.de/softbv>.
- Advanced MicroBeam (2002). *Probe for Windows*. Advanced MicroBeam, Vienna, Ohio, USA.
- Arriortua, M. I., Rius, J., Solans, X. & Amigo, J. M. (1983). *Neues Jahrb. Mineral. Monatsh.* pp. 343–350.
- Bruker (2001). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Ginderow, D. (1978). *Acta Cryst.* **B34**, 1804–1811.
- ICSD (2012). *Inorganic Crystal Structure Database*. Release 2012/1. FIZ Karlsruhe, D-76344 Eggenstein–Leopoldshafen, Germany.
- Keller, E. (2004). *SCHAKAL99*. University of Freiburg, Germany.
- Keller, E. & Krämer, V. (2006). *Acta Cryst.* **B62**, 411–416.
- Krämer, V. (1980). *Acta Cryst.* **B36**, 1922–1923.
- Krämer, V. (1983). *Acta Cryst.* **C39**, 1328–1329.
- Krämer, V. (1986). *Acta Cryst.* **C42**, 1089–1091.
- Krämer, V. (2011). Private communication.
- Krämer, V. & Berroth, K. (1980). *Mater. Res. Bull.* **15**, 299–308.
- Krämer, V. & Reis, I. (1986). *Acta Cryst.* **C42**, 249–251.
- Nowacki, W. (1969). *Schweiz. Miner. Petro. Mitt.* **49**, 109–156.
- Ramsdell, L. S. (1925). *Am. Mineral.* **10**, 281–304.
- Reis, I. (1984). Diploma thesis, University of Freiburg, Germany.
- Reis, I., Krämer, V., Seiler, A., Topa, D. & Keller, E. (2012). *Acta Cryst.* **C68**, i12–i16.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Takeuchi, Y., Ozawa, T. & Takagi, J. (1979). *Z. Kristallogr.* **150**, 75–84.
- Topa, D. & Keller, E. (2011). Unpublished results.
- Yin, W., Mei, D., Yao, J., Fu, P. & Wu, Y. (2010). *J. Solid State Chem.* **183**, 2544–2551.