

Crystal and electronic structure of the ternary monoclinic selenide $\text{Tl}_{2.59}\text{Sb}_{8.41}\text{Se}_{14}$ (TlSb_3Se_5)

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Received May 4, 2016; accepted June 29, 2016; available on-line November 7, 2016

The ternary selenide $\text{Tl}_{2.59}\text{Sb}_{8.41}\text{Se}_{14}$ crystallizes with a monoclinic structure in space group $P2_1/m$ where the atoms are located on $2e$ sites (site symmetry m). The structure of the title compound is closely related to the strongly disordered structure of $\text{K}_{2.5}\text{Sb}_{8.5}\text{Se}_{14}$. The coordination polyhedra of the thallium atoms are trigonal prisms with additional selenium atoms centering lateral faces. All the antimony atoms are coordinated by slightly deformed Se_6 octahedra. Three types of polyhedron: octahedron, trigonal bipyramid and tetrahedron, are observed for the selenium atoms. The crystal chemical analysis and electronic structure calculations by the TB-LMTO-ASA method show that the antimony and selenium atoms form a polyanionic network the negative charge of which is compensated by the thallium cations.

Selenide / Crystal structure / Electronic structure

Introduction

The ternary selenides Tl_9SbSe_6 , TlSbSe_2 , and TlSb_3Se_5 were detected during an investigation of the $(\text{Tl}_2\text{Se})_{3x}-(\text{Sb}_2\text{Se}_3)_{1-x}$ system by DTA and XRD [1]. Among these compounds, only Tl_9SbSe_6 melts congruently (at 629 K), the others melting incongruently (at 723 and 743 K, respectively). The TlSbSe_2 selenide undergoes a polymorphic transition at 658 K. According to this work TlSb_3Se_5 forms by peritectic reaction at 743 K due to the interaction of the melt with Sb_2Se_3 . A similar description of the above-mentioned phases was later presented by Gotko *et al.* [2].

According to Babanly *et al.* [3], the formation of four intermediate ternary compounds, Tl_9SbSe_6 , TlSbSe_2 , Tl_5SbSe_4 , and TlSb_3Se_5 , was observed in the $\text{Tl}_2\text{Se}-\text{Sb}_2\text{Se}_3$ section. The Tl_9SbSe_6 and TlSbSe_2 phases melt congruently at 740 and 750 K, respectively, and Tl_5SbSe_4 and TlSb_3Se_5 are formed by peritectic reactions at 625 and 740 K, respectively. For the ternary selenide TlSbSe_2 the polymorphic transition temperature was estimated to 665 K.

Some other results are given in [4,5]. Four ternary compounds, Tl_9SbSe_6 , Tl_3SbSe_3 (new phase), TlSbSe_2 ,

and TlSb_3Se_5 , were found in the $\text{Tl}_2\text{Se}-\text{Sb}_2\text{Se}_3$ system. Only two of them, Tl_9SbSe_6 (at 725 K) and TlSbSe_2 (at 730 K), melt congruently. The rest of the ternary phases, Tl_3SbSe_3 and TlSb_3Se_5 , melt incongruently at 625 K and 725 K, respectively. For the intermediate phases Tl_3SbSe_3 and TlSbSe_2 polymorphic transformation were observed at 575 and 665 K, respectively.

According to the most recent literature data [6], four individual intermediate compounds, Tl_9SbSe_6 , $\text{Tl}_{26}\text{Sb}_4\text{Se}_{19}$ (new phase), TlSbSe_2 , and TlSb_3Se_5 , exist in the $\text{Tl}_2\text{Se}-\text{Sb}_2\text{Se}_3$ section. Congruent melting was observed for Tl_9SbSe_6 (at 730 K) and TlSbSe_2 (at 727.6 K). $\text{Tl}_{26}\text{Sb}_4\text{Se}_{19}$ (at 650.1 K) and TlSb_3Se_5 (at 722.4 K) form by peritectic reactions. The $\text{Tl}_{26}\text{Sb}_4\text{Se}_{19}$ and TlSbSe_2 phases undergo polymorphic transformations at 570 and 669.7 K, respectively.

Although the TlSb_3Se_5 compound has been known for nearly twenty years, its crystal structure was first investigated in 2008 ($\text{Tl}_{2.35}\text{Sb}_{8.65}\text{Se}_{14}$) [7]. In this paper we present the results of a redetermination of the crystal structure and results of electronic structure calculations.

Experimental section

Alloys of the $\text{Tl}_2\text{Se}-\text{Sb}_2\text{Se}_3$ section were prepared by the direct temperature method in evacuated quartz ampoules, using appropriate amounts of binary thallium(I) and antimony(III) selenides. The composition of the ternary alloys corresponded to the individual TlSbSe_2 and TlSb_3Se_5 phases. The maximum temperature for synthesis was 950 K. To achieve equilibrium and a homogeneous state, the alloys were annealed at 700 K for 290 h, and then quenched. The reaction products were examined by X-ray diffraction (XRD), differential thermal analysis (DTA), scanning electron microscopy (SEM), wavelength-dispersive spectrometry (WDS), and electron probe microanalysis (EPMA). For the X-ray powder diffraction (XRD) analysis the samples were ground in an agate mortar. X-ray powder diffraction of the samples was carried out using a STOE STADI P powder diffractometer (Cu-radiation, step scanning). Rietveld refinements of the data were performed using the FULLPROF program [8]. A TESCAN electron microscope equipped with WDS/EDXS detectors was used for the analysis of the phase content of the synthesized alloys. For the structure investigation a prismatic single crystal, of metallic gray appearance, was isolated from the TlSb_3Se_5 alloy by mechanical fragmentation. Single-crystal diffraction data were collected at room temperature using a four-circle diffractometer (Xcalibur Oxford Diffraction) with a CCD detector (graphite-monochromatized $\text{Mo K}\alpha$ -radiation, $\lambda = 0.071073$ nm). Scans were made in the ω -mode; empirical absorption corrections were made by CrysAlis RED [9]. The crystal structure of the ternary compound investigated in the present work was successfully solved by direct methods and refined using SHELX-97 package programs [10]. The composition refined from the single-crystal X-ray diffraction data was $\text{Tl}_{10.3}\text{Sb}_{33.7}\text{Se}_{56.00}$. The composition $\text{Tl}_{11.2}\text{Sb}_{34.6}\text{Se}_{54.2}$ obtained by EPMA agrees well with the XRD data, the difference being less than 2 at.%

Results and discussion

A detailed investigation of the crystal structure was carried out on an alloy of the composition $\text{Tl}_{11}\text{Sb}_{33}\text{Se}_{56}$. According to the phase analysis by X-ray powder diffraction, scanning electron microscopy and electron probe microanalysis, the prepared alloy consisted of two phases: TlSbSe_2 and TlSb_3Se_5 (Fig. 1a,b). The DTA curve of the sample (Fig. 2) exhibits two endothermic peaks at 705 K and 739 K. The first peak is likely to correspond to the peritectic reaction $\text{TlSb}_3\text{Se}_5 \leftrightarrow \text{L} + \text{Sb}_2\text{Se}_3$. The second peak, at 739 K, corresponds to primary crystallization of the Sb_2Se_3 phase. The crystal structure of the TlSbSe_2 phase is monoclinic with space group $P2_1$ and

the unit cell parameters refined by X-ray powder diffraction were: $a = 9.1356(8)$ Å, $b = 4.0924(4)$ Å, $c = 12.617(1)$ Å, $\beta = 110.503(7)^\circ$. The crystal structure of TlSb_3Se_5 was investigated by single-crystal X-ray diffraction. The obtained single crystal data (Table 1) showed that the title compound crystallizes with a monoclinic structure (space group $P2_1/m$) in which all the atoms are located on sites in Wyckoff position $2e$. The refined positional and thermal displacement parameters are given Table 2 and Table 3. The structure of the title compound is closely related to the structure of $\text{K}_{2.5}\text{Sb}_{8.5}\text{Se}_{14}$ [11], in which several sites are positionally disordered with the following ratios: Sb5/K1 (16/84); Sb7/K3 (48/52); Se2/Se2' (62/38); Se4/Se4' (70/30); Se6/Se6' (48/52). The potassium and antimony atoms form statistical mixtures, while part of the selenium atoms occupy pairs of split positions. Compared to the structure of $\text{K}_{2.5}\text{Sb}_{8.5}\text{Se}_{14}$, the structure of the title compound is more ordered, because the selenium atoms do not form split positions. Sb4/Tl4 and Sb5/Tl5 form statistical mixtures with the occupation ratio 86/14. The pairs Tl2/Sb2 (67/33) and Tl3/Sb3 (64/36) also form split positions. It should be noted that this disordered model provides better refinements than the structure model proposed by Xu Jianxiao *et al.*, which has only two split Tl/Sb positions [7]. The content of one unit cell and the coordination polyhedra of the atoms are shown in Fig. 3. The coordination polyhedra around the thallium atoms are trigonal prisms with two or three additional selenium atoms that center lateral faces. All of the antimony atoms are enclosed in deformed Se_6 octahedra. The arrangement of the polyhedra described above is shown in Fig. 4. The selenium atoms have three kinds of coordination polyhedron: octahedron (Se12, Se14, Se19 and Se21), trigonal bipyramid (Se17 and Se18), and tetrahedron (the rest of the Se atoms). The arrangement of these polyhedra in the unit cell is shown in Fig. 5. The interatomic distances are given in Table 4.

As in the case of other selenides of thallium and antimony, for TlSb_3Se_5 the following formal charges should be assigned: 1+ for the thallium atoms, 3+ for the antimony atoms and 2- for the selenium atoms. Hence, the charge-balanced formula can be written as $[(\text{Tl}^+)(\text{Sb}^{3+})_3][(\text{Se}^{2-})_5]$. The crystal chemical analysis shows that the selenium and bismuth atoms form a negatively charged polyanionic network, the charge of which is compensated by the thallium cations (Fig. 6). This assumption is confirmed by the results of calculations of the electronic structure. The data of electronic structure calculations using the TB-LMTO-ASA approach [12] show high values of the electron localization function (ELF) around the selenium and antimony atoms and much lower ELF values around the thallium atoms (Fig. 7a). Isosurfaces of the electron localization function for the title compound are shown in Fig. 7b. Strong chemical bonding exists within the network of Sb–Se interactions with

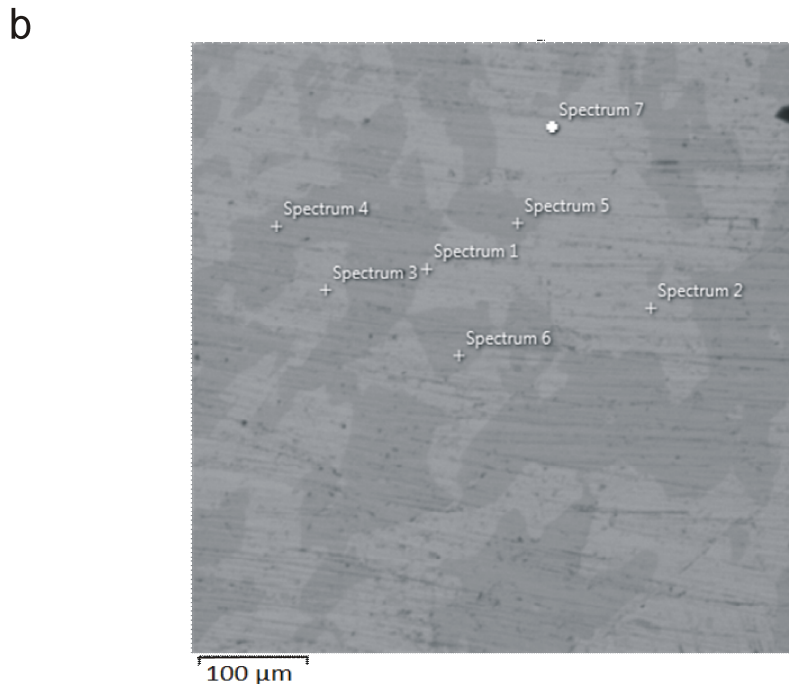
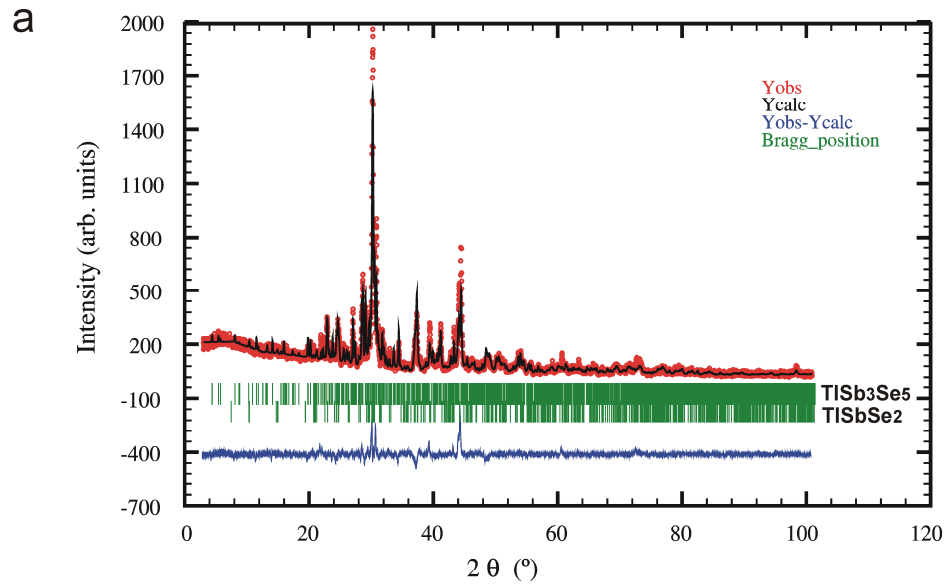


Fig. 1 X-ray powder diffraction pattern (a), scanning electron microscopy and electron probe microanalysis data (b): gray phase – TlSb_3Se_5 , dark gray phase – TlSbSb_2 .

interatomic distances ranging from $d = 2.602 \text{ \AA}$ to $d = 2.761 \text{ \AA}$, where the integrated crystal orbital Hamilton population (iCOHP) takes values between $-\text{iCOHP} = 3.004 \text{ eV}$ and $-\text{iCOHP} = 1.457 \text{ eV}$ (Fig. 8). The interaction between Tl and Se atoms for the range of interatomic distances from $d = 3.114 \text{ \AA}$ to $d = 3.283 \text{ \AA}$ is much weaker and iCOHP varies from $-\text{iCOHP} = 0.347 \text{ eV}$ to $-\text{iCOHP} = 0.294 \text{ eV}$. These data confirm our assumption that the selenium and antimony atoms form a complex polyanion.

Acknowledgements

Financial support from the Ministry of Education and Science of Ukraine is gratefully acknowledged.

We are grateful to Dr. P. Demchenko for helping us with the X-ray powder diffraction measurements.

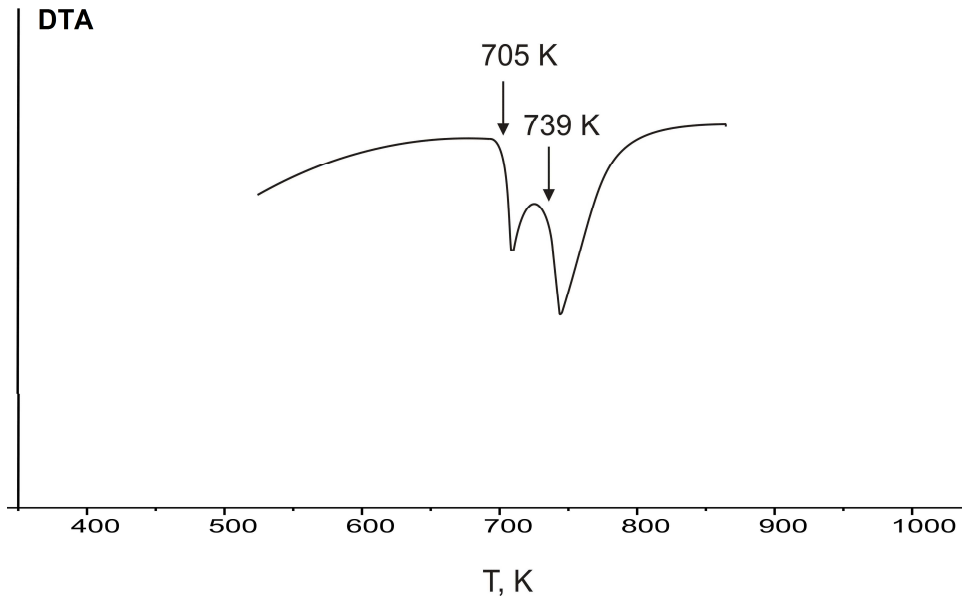


Fig. 2 DTA curve of the TlSb_3Se_5 sample.

Table 1 Structure data and data collection.

<i>Crystal data</i>	
$\text{Tl}_{2.59}\text{Sb}_{8.41}\text{Se}_{14}$	$F(000) = 2229$
$M_r = 5316.41$	$D_x = 6.312 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 17.1847(5) \text{ \AA}$	Cell parameters from 2874 reflections
$b = 4.07227(17) \text{ \AA}$	$\theta = 2.0\text{--}25.2^\circ$
$c = 21.1856(7) \text{ \AA}$	$\mu = 41.02 \text{ mm}^{-1}$
$\beta = 109.381(4)^\circ$	$T = 293 \text{ K}$
$V = 1398.57(9) \text{ \AA}^3$	Prism, metallic grey
$Z = 1$	$0.14 \times 0.06 \times 0.04 \text{ mm}$
<i>Data collection</i>	
Oxford Diffraction Xcalibur3 CCD diffractometer	2874 independent reflections
Radiation source: fine-focus sealed tube	2545 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.025$
ω scans	$\theta_{\text{max}} = 25.2^\circ$, $\theta_{\text{min}} = 2.0^\circ$
Absorption correction: analytical [9]	$h = -20 \rightarrow 20$
$T_{\text{min}} = 0.067$, $T_{\text{max}} = 0.192$	$k = -4 \rightarrow 4$
5748 measured reflections	$l = -25 \rightarrow 25$
<i>Refinement</i>	
Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 1.63 \text{ e \AA}^{-3}$
2874 reflections	$\Delta\rho_{\text{min}} = -1.99 \text{ e \AA}^{-3}$
163 parameters	Extinction correction [10]:
0 restraints	$k[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.00086(5)

Table 2 Fractional positional coordinates and equivalent isotropic displacement parameters (\AA^2).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Occ. (<1)
Tl1	0.92490(3)	¼	0.85792(3)	0.02391(16)	
Tl2	0.16139(4)	¼	0.78867(6)	0.0172(3)	0.666(3)
Sb2	0.15552(17)	¼	0.8175(2)	0.0172(3)	0.334(3)
Tl3	0.64374(7)	¼	0.69453(5)	0.0201(3)	0.637(3)
Sb3	0.6831(2)	¼	0.71075(16)	0.0201(3)	0.363(3)
Sb4	0.37100(4)	¼	0.11827(4)	0.01317(18)	0.86
Tl4	0.37100(4)	¼	0.11827(4)	0.01317(18)	0.14
Sb5	0.61126(4)	¼	0.07252(4)	0.01260(18)	0.86
Tl5	0.61126(4)	¼	0.07252(4)	0.01260(18)	0.14
Sb6	0.42310(4)	¼	0.77521(4)	0.01105(19)	
Sb7	0.15778(5)	¼	0.35737(4)	0.0144(2)	
Sb8	0.83525(4)	¼	0.01892(4)	0.01014(19)	
Sb9	0.02687(4)	¼	0.58937(4)	0.01257(19)	
Sb10	0.40633(5)	¼	0.50879(5)	0.0155(2)	
Sb11	0.77531(5)	¼	0.43449(5)	0.0184(2)	
Se12	0.71113(9)	¼	0.56659(9)	0.0300(4)	
Se13	0.46776(6)	¼	0.24332(6)	0.0114(3)	
Se14	0.28665(7)	¼	0.94550(6)	0.0139(3)	
Se15	0.68340(6)	¼	0.20166(6)	0.0115(3)	
Se16	0.48405(7)	¼	0.41796(6)	0.0130(3)	
Se17	0.72279(7)	¼	0.86086(6)	0.0144(3)	
Se18	0.95589(8)	¼	0.69860(7)	0.0195(3)	
Se19	0.50815(6)	¼	0.91103(6)	0.0119(3)	
Se20	0.08290(6)	¼	0.01128(6)	0.0119(3)	
Se21	0.09482(6)	¼	0.48387(6)	0.0121(3)	
Se22	0.86110(7)	¼	0.34541(6)	0.0173(3)	
Se23	0.32993(9)	¼	0.62818(8)	0.0276(3)	
Se24	0.92748(7)	¼	0.14729(6)	0.0161(3)	
Se25	0.20855(7)	¼	0.25316(7)	0.0162(3)	

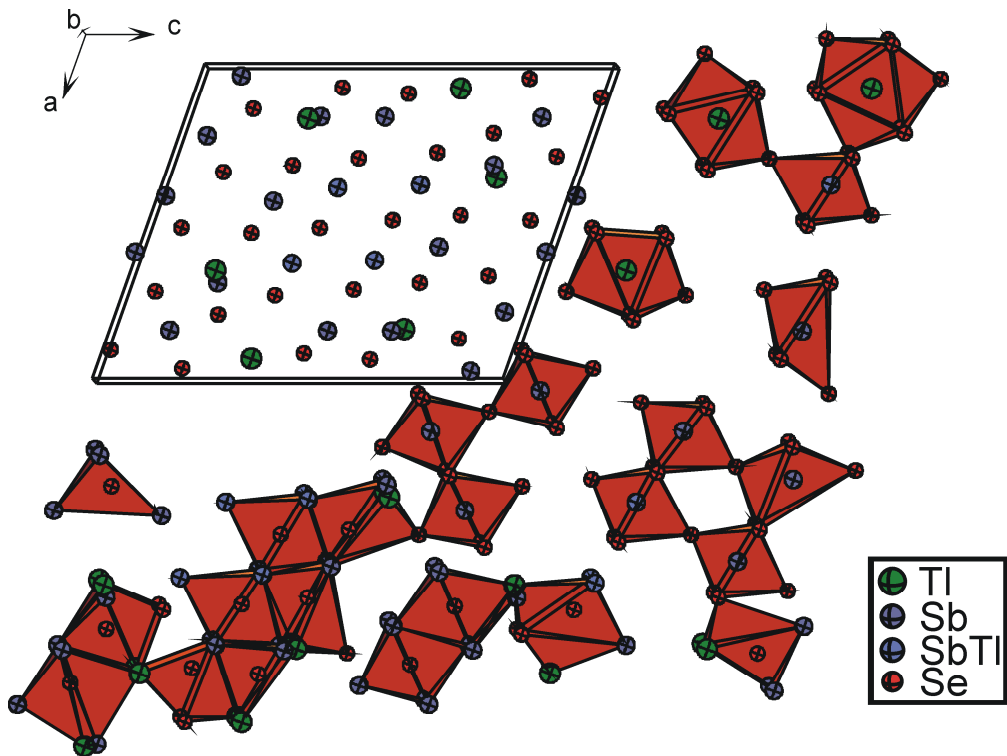


Fig. 3 Projection of the unit cell content and coordination polyhedra of the atoms.

Table 3 Atomic displacement parameters (\AA^2).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl1	0.0183(2)	0.0284(3)	0.0243(3)	0	0.0060(2)	0
Tl2	0.0150(3)	0.0213(4)	0.0151(6)	0	0.0047(3)	0
Sb2	0.0150(3)	0.0213(4)	0.0151(6)	0	0.0047(3)	0
Tl3	0.0153(6)	0.0259(4)	0.0164(5)	0	0.0016(4)	0
Sb3	0.0153(6)	0.0259(4)	0.0164(5)	0	0.0016(4)	0
Sb4	0.0092(3)	0.0179(4)	0.0104(4)	0	0.0004(3)	0
Tl4	0.0092(3)	0.0179(4)	0.0104(4)	0	0.0004(3)	0
Sb5	0.0084(3)	0.0176(4)	0.0103(4)	0	0.0012(3)	0
Tl5	0.0084(3)	0.0176(4)	0.0103(4)	0	0.0012(3)	0
Sb6	0.0075(3)	0.0155(4)	0.0083(4)	0	0.0000(3)	0
Sb7	0.0113(3)	0.0191(5)	0.0140(4)	0	0.0060(3)	0
Sb8	0.0074(3)	0.0098(4)	0.0154(4)	0	0.0068(3)	0
Sb9	0.0089(3)	0.0174(4)	0.0104(4)	0	0.0020(3)	0
Sb10	0.0127(4)	0.0179(5)	0.0174(4)	0	0.0069(3)	0
Sb11	0.0140(4)	0.0202(5)	0.0189(5)	0	0.0027(3)	0
Se12	0.0237(6)	0.0280(8)	0.0368(9)	0	0.0078(6)	0
Se13	0.0083(5)	0.0160(6)	0.0106(6)	0	0.0040(4)	0
Se14	0.0094(5)	0.0171(6)	0.0174(6)	0	0.0072(4)	0
Se15	0.0064(5)	0.0190(7)	0.0066(6)	0	-0.0013(4)	0
Se16	0.0090(5)	0.0185(7)	0.0089(6)	0	-0.0005(4)	0
Se17	0.0080(5)	0.0185(7)	0.0147(6)	0	0.0012(4)	0
Se18	0.0187(6)	0.0242(8)	0.0137(6)	0	0.0027(5)	0
Se19	0.0082(5)	0.0164(7)	0.0082(6)	0	-0.0013(4)	0
Se20	0.0076(5)	0.0127(6)	0.0166(6)	0	0.0057(4)	0
Se21	0.0076(5)	0.0143(6)	0.0150(6)	0	0.0045(4)	0
Se22	0.0147(5)	0.0253(7)	0.0097(6)	0	0.0010(4)	0
Se23	0.0231(6)	0.0355(9)	0.0227(8)	0	0.0057(5)	0
Se24	0.0156(5)	0.0198(7)	0.0129(6)	0	0.0048(5)	0
Se25	0.0140(5)	0.0195(7)	0.0162(6)	0	0.0065(5)	0

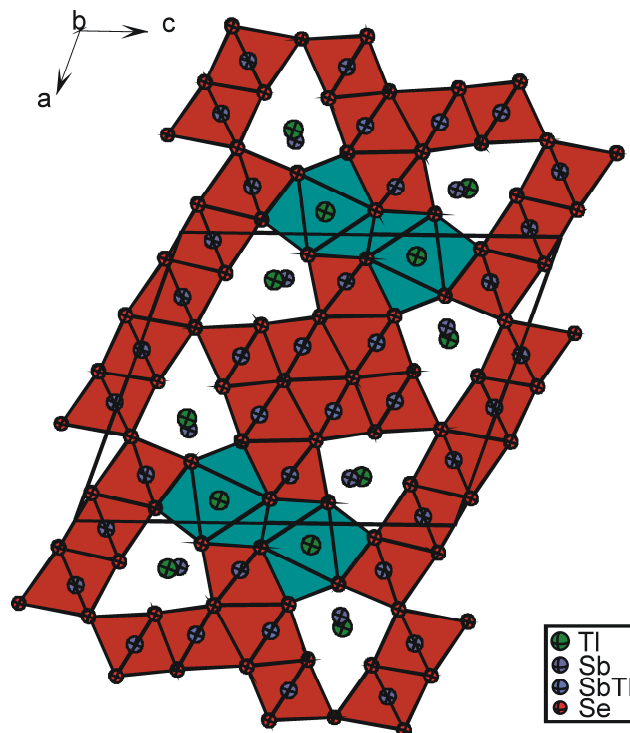


Fig. 4 Arrangement of $[(\text{Sb},\text{Tl})\text{Se}_6]$ octahedra and $[\text{TlSe}_6]$ tricapped trigonal prisms in the structure of $\text{Tl}_{2.59}\text{Sb}_{8.41}\text{Se}_{14}$.

Table 4 Geometric parameters (Å, °).

Tl1—Se24 ⁱ	3.2833(10)	Sb10—Se16	2.8570(10)
Tl1—Se24 ⁱⁱ	3.2833(10)	Sb10—Se16 ^{vi}	2.8571(10)
Tl2—Se24 ⁱⁱⁱ	3.1136(13)	Sb10—Se12 ^{xi}	2.9379(12)
Tl2—Se24 ^{iv}	3.1136(13)	Sb10—Se12 ^x	2.9379(12)
Tl2—Se14	3.3056(16)	Sb11—Se22 ^{xii}	2.7533(16)
Tl2—Se15	3.3074(11)	Sb11—Se23 ^x	2.7542(11)
Tl2—Se15 ^v	3.3075(11)	Sb11—Se23 ^{vii}	2.7542(11)
Sb2—Se24 ⁱⁱⁱ	2.728(3)	Se12—Sb10 ^{xi}	2.9379(12)
Sb2—Se24 ^{iv}	2.728(3)	Se12—Sb10 ^x	2.9379(12)
Sb2—Se14	2.895(4)	Se12—Sb7 ^{vi}	3.0671(12)
Tl3—Se25	3.1662(12)	Se12—Tl3 ^{vi}	3.2820(19)
Tl3—Se25 ^v	3.1662(12)	Se13—Sb6 ^v	2.8821(9)
Tl3—Se12 ^v	3.2821(19)	Se14—Tl5 ^v	2.7954(9)
Sb3—Se25	2.703(3)	Se14—Sb5 ^v	2.7954(9)
Sb3—Se25 ^v	2.703(3)	Se15—Sb6 ^{iv}	2.8862(10)
Sb3—Se17	3.023(3)	Se15—Sb6 ⁱⁱⁱ	2.8862(10)
Sb4—Se13	2.6192(14)	Se15—Tl2 ^{vi}	3.3075(11)
Sb4—Se17	2.7225(9)	Se16—Sb10 ^x	2.6818(15)
Sb4—Se17 ^v	2.7226(9)	Se16—Sb10 ^v	2.8571(10)
Sb5—Se15	2.6020(14)	Se17—Tl4 ^{vi}	2.7226(9)
Sb5—Se14	2.7953(9)	Se17—Sb4 ^{vi}	2.7226(9)
Sb5—Se14 ^{vi}	2.7953(9)	Se18—Sb7 ^v	2.7983(10)
Sb5—Se19 ^{iv}	2.9921(10)	Se18—Sb9 ⁱⁱ	2.9523(16)
Sb5—Se19 ⁱⁱⁱ	2.9921(10)	Se19—Tl5 ^{iv}	2.9920(10)
Sb6—Se19	2.7613(14)	Se19—Sb5 ^{iv}	2.9920(10)
Sb6—Se13	2.8822(9)	Se19—Tl5 ⁱⁱⁱ	2.9920(10)
Sb6—Se13 ^{vi}	2.8822(9)	Se19—Sb5 ⁱⁱⁱ	2.9920(10)
Sb6—Se15 ^{iv}	2.8862(10)	Se19—Tl4 ^{vi}	3.1144(10)
Sb6—Se15 ⁱⁱⁱ	2.8862(10)	Se20—Sb8 ^{vi}	2.6704(9)
Sb6—Se23	2.9928(17)	Se21—Sb9 ^{vii}	2.8446(15)
Sb7—Se25	2.6189(15)	Se21—Sb9 ⁱⁱ	2.9619(10)
Sb7—Se18 ^{vi}	2.7983(10)	Se21—Sb9 ^{xiii}	2.9619(10)
Sb7—Se18	2.7983(10)	Se22—Sb11 ^{xiv}	2.7533(16)
Sb7—Se12 ^v	3.0671(12)	Se22—Sb9 ⁱⁱⁱ	2.8277(10)
Sb7—Se12	3.0671(12)	Se22—Sb9 ^{iv}	2.8277(9)
Sb8—Se24 ^{iv}	2.6547(15)	Se23—Sb11 ^x	2.7543(11)
Sb8—Se20	2.6704(9)	Se23—Sb11 ^{vii}	2.7543(11)
Sb8—Se20 ^v	2.6704(9)	Se24—Sb8 ^{iv}	2.6547(15)
Sb9—Se22 ⁱⁱⁱ	2.8277(9)	Se24—Sb2 ⁱⁱⁱ	2.728(3)
Sb9—Se22 ^{iv}	2.8277(9)	Se24—Sb2 ^{iv}	2.728(3)
Sb9—Se21 ^{vii}	2.8445(15)	Se24—Tl2 ⁱⁱⁱ	3.1135(13)
Sb9—Se18 ^{viii}	2.9523(16)	Se24—Tl2 ^{iv}	3.1135(12)
Sb9—Se21 ^{viii}	2.9619(10)	Se24—Tl1 ^{xv}	3.2833(10)
Sb9—Se21 ^{ix}	2.9619(10)	Se24—Tl1 ^{viii}	3.2833(10)
Sb10—Se16 ^x	2.6819(15)	Se25—Sb3 ^{vi}	2.703(3)
		Se25—Tl3 ^{vi}	3.1662(12)

Symmetry codes: (i) $x+1, y+1, z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$; (v) $x, y+1, z$; (vi) $x, y-1, z$; (vii) $-x+1, -y, -z$; (viii) $x-1, y, z$; (ix) $x-1, y+1, z$; (x) $-x+1, -y-1, -z$; (xi) $-x+1, -y-2, -z$; (xii) $x, y-1, z-1$; (xiii) $x+1, y-1, z$; (xiv) $x, y+1, z+1$; (xv) $x-1, y-1, z$.

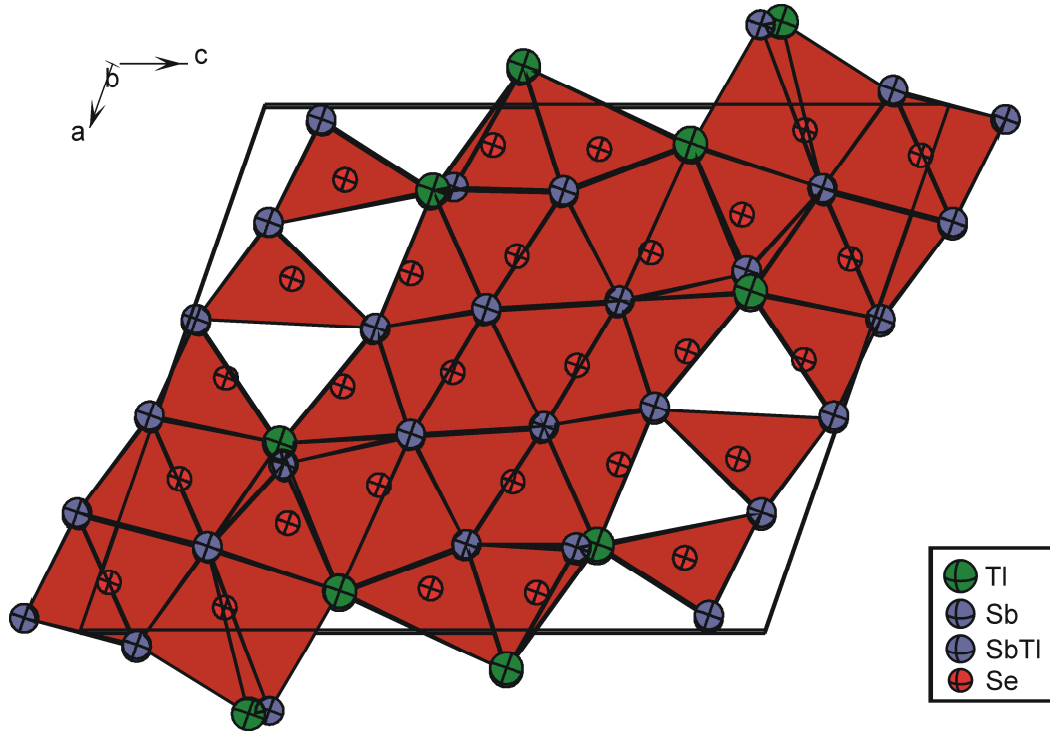


Fig. 5 Arrangement of Se-centered octahedra (Se12, Se14, Se19, and Se21), trigonal bipyramids (Se17 and Se18) and tetrahedra (remaining Se atoms) in the unit cell.

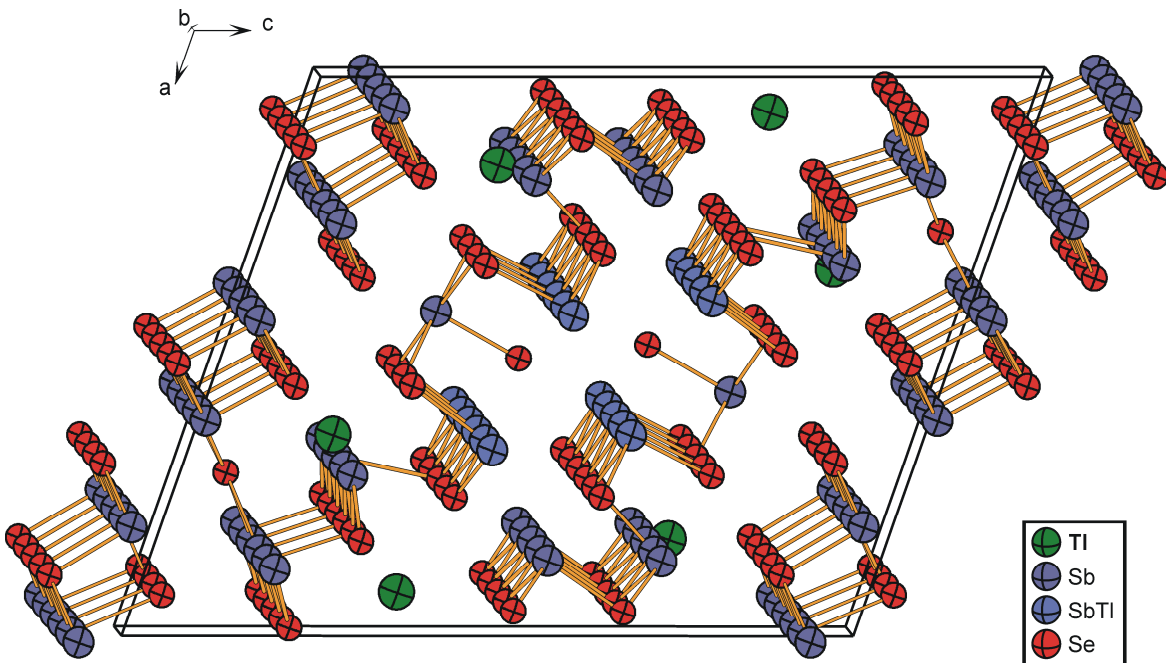


Fig. 6 Polyanionic 3D-network of selenium and antimony atoms.

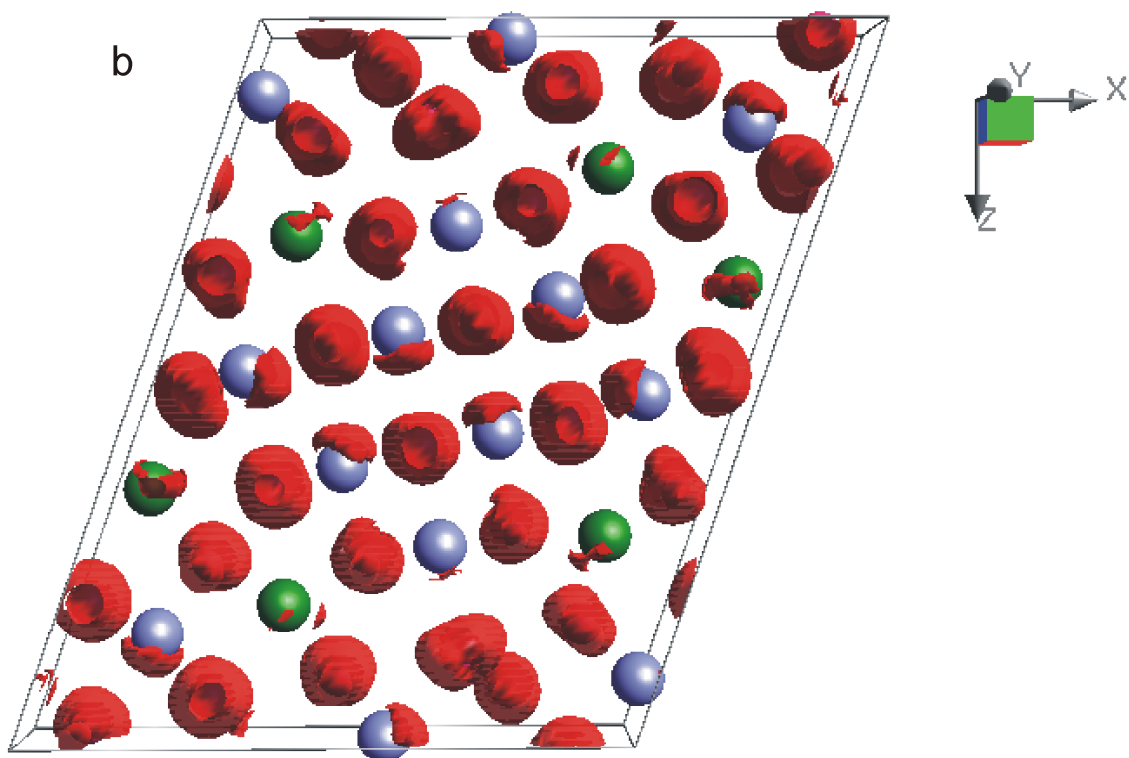
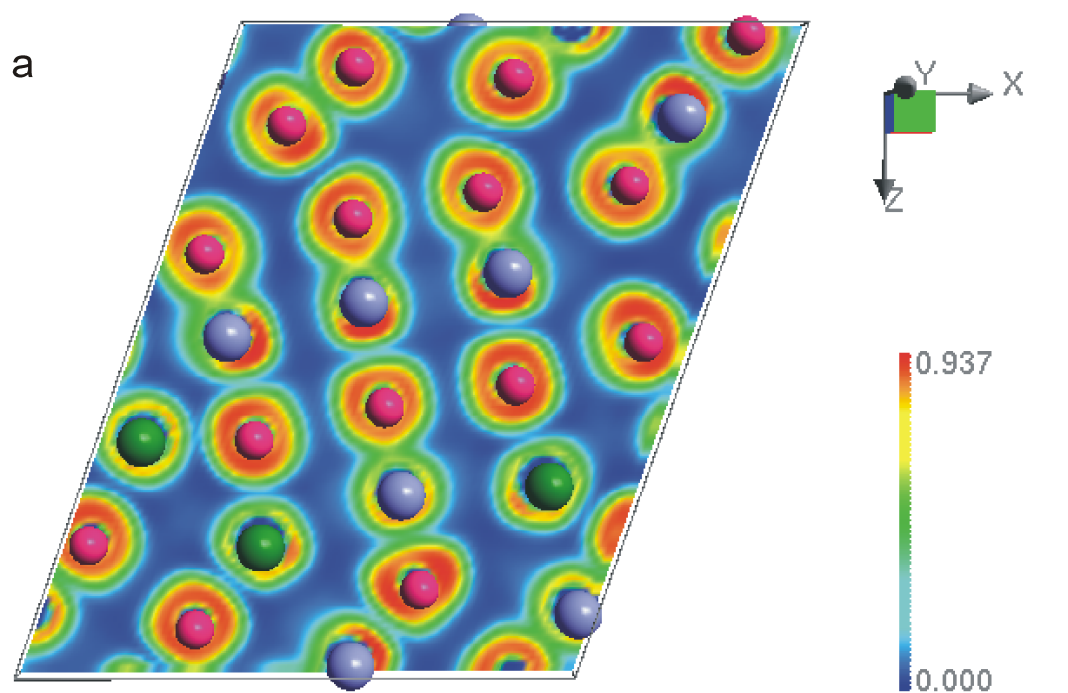


Fig. 7 Electron localization function (ELF) mapping (a) and isosurfaces of the electron localization function around the atoms (b) for the title compound.

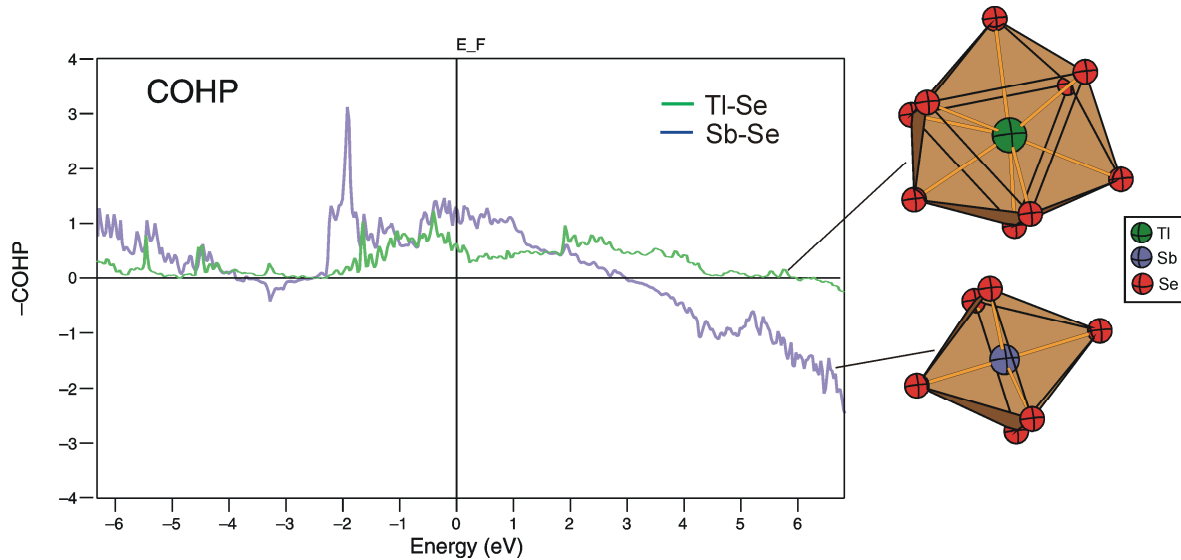


Fig. 8 $-i\text{COHP}$ curves from TB-LMTO-ASA calculations. It is shown polyhedra for which examined the interaction between atoms.

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