Phase equilibria in the Tl_2S–HgS–SnS_2 system at 520 K and crystal structure of Tl_2HgSnS_4

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The phase equilibria in the quasi-ternary system Tl_2S–HgS–SnS_2 at 520 K were investigated by X-ray diffraction. The isothermal section of the system at 520 K was constructed. One quaternary compound, Tl_2HgSnS_4, was found at this temperature. Tl_2HgSnS_4 crystallizes in a tetragonal structure, non-centrosymmetric space group $I\text{-}42m$, unit cell parameters $a = 7.8571(6)$ Å, $c = 6.6989(7)$ Å, $V = 413.5(1)$ Å^3.

Introduction

Quaternary compounds that form in the quasi-ternary systems A^I_2X–$B^{II}X$–$D^{IV}X_2$ (where A^I = Cu, Ag; B^{II} = Zn, Cd, Hg; D^{IV} = Si, Ge, Sn; X = S, Se, Te) are known for seven different ratios of the components [1]. Most common are the compounds of equimolar composition of all three components, described by the formula $A^I_2B^{II}D^{IV}X_4$ (2-1-1-4), of which there are over 40 representatives. Most of them crystallize in tetragonal structures (space group (SG) $I\text{-}4$ (kesterite) or $I\text{-}42m$ (stannite)), which are derivatives of the sphalerite structure, or orthorhombic structures, space group $Pmn2_1$ or $Cmc2_1$, which are superstructures of wurtzite [1-6]. Additionally, 2-1-1-4 compounds form in the case of A^I = Li ($Li_2CdGe(Sn)S_4$ [7], $Li_2CdGe(Sn)Se_4$ [8], SG $Pmn2_1$). Only two such compounds are known for B^{II} = Pb, Cu_2PbSiS_4 (SG $P3_221$) [9] and Ag_2PbGeS_4 (SG $Ama2$) [10], whereas almost all possible variants are formed with B^{II} = Mn, Fe, Co, Ni (SG $I\text{-}42m$ and $Pmn2_1$) [11-13]. The non-centrosymmetricity of the structures makes the compounds promising materials for non-linear optics. The non-linear optical parameters have been most thoroughly studied for lithium-containing compounds, which exhibit a high laser damage threshold (*e.g.* 0.7 GW·cm^{-2} for $Li_2CdGeSe_4$ [8]). Compounds of this type are also of interest in photovoltaics, as the absorbing layer for thin-film solar cells [14,15]. The efficiency using kesterites $Cu_2ZnSnS_xSe_{4-x}$ reaches 12.6% [15]. Recent papers [16,17] report that some representatives of this composition have quite

promising thermoelectric parameters. For instance, the thermoelectric quality coefficient (*ZT*) of $Cu_2CdSnSe_4$ is 0.71 at 685 K [13], and that of $Cu_2HgSnSe_2Te_2$ (the $Cu_2HgSnSe_4$–$Cu_2HgSnTe_4$ system) is 0.6 at 575 K [17].

The systems where A^I = Tl are also promising for the search for new quaternary phases. We have previously studied the systems Tl_2S–PbS–SiS_2 [18], Tl_2S–PbS–GeS_2 [19], $Tl_2S(Se)$–$PbS(Se)$–$SnS(Se)_2$ [20], Tl_2Se–$HgSe$–$Si(Sn)Se_2$ [21], and Tl_2Se–$HgSe$–$GeSe_2$ [22]. The systems with B^{II} = Pb feature the compounds $Tl_2PbSi(Ge)S_4$, which crystallize with monoclinic structures (SG $P2_1/a$) [18,19,23], and $Tl_{0.5}Pb_{1.75}GeS_4$, which crystallizes in the cubic space group $I\text{-}43d$ [19]. For another group of $Tl_2PbSi(Ge)_3S_8$ compounds, the crystal structure is not yet known. Two series of compounds were found in the mercury- and selenium-containing systems, 2-1-1-4 ($Tl_2HgSi(Ge,Sn)Se_4$), which crystallize in the tetragonal space group $I\text{-}42m$ [21,22], and 2-1-2-6 ($Tl_2HgSi(Ge)_2Se_6$), the structure of which was not determined. Additionally, a series of tellurium-containing phases $Tl_2B^{II}D^{IV}Te_4$ (B^{II} = Cd, Hg, Mn; D^{IV} = Ge, Sn) that crystallize in space group $I\text{-}42m$ are known [24].

Here we present the results of a study of the isothermal section of the Tl_2S–HgS–SnS_2 system at 520 K and the crystal structure of the new quaternary compound Tl_2HgSnS_4. The quasi-binary systems that form the Tl_2S–HgS–SnS_2 system have been studied earlier [24-26]. The crystal structures of the ternary compounds formed in these systems are summarized in Table 1 [27-30].

Experimental

A series of alloys of 2 g mass were prepared for the investigation of the isothermal section of the quasi-ternary system at 520 K. They were synthesized from high-purity elements, Tl (99.99 wt.%), Sn (99.99 wt.%), and S (99.999 wt.%), and HgS (prepared from the elements, mercury 99.999 wt.%). Appropriate amounts of the starting materials were placed in quartz ampoules, which were evacuated to a residual pressure of 10^{-2} Pa and soldered. The samples were heated in a shaft-type furnace to 720 K at a rate of 30 K/h and kept throughout the day for maximum binding of elemental sulfur. At the second stage the samples were heated at a rate of 10-20 K/h to 1170 K. The melts were kept at this temperature for 6 h and then cooled to 520 K at 20 K/h. The alloys were annealed at this temperature for 250 h. The synthesis ended in quenching the alloys in air. The resulting samples were compact black ingots, which were then used for X-ray studies. X-ray powder diffraction (XRD) spectra were recorded on a DRON 4-13 diffractometer (CuK_α radiation). Structure refinements

were performed using the full-profile Rietveld method as included in the CSD software package [31].

Results and discussion

The isothermal section of the Tl_2S–HgS–SnS_2 system at 520 K was investigated by XRD on 40 alloys and is presented in Fig. 1. Only one quaternary compound was found in the system at this temperature; it is formed at the equimolar ratio of the components and is described by the formula Tl_2HgSnS_4. This quaternary phase, formed in the Tl_2SnS_3–HgS section, has a narrow homogeneity region. No solid solubility was found for the system components or the ternary compounds. Tl_2HgSnS_4 has two-phase equilibria with the ternary sulfides of thallium and tin, as well as with the binary components HgS and SnS_2. It is cut off from the third component (Tl_2S) by the two-phase equilibria Tl_4SnS_4–HgS and Tl_4SnS_4–$Tl_2Hg_3S_4$. These two-phase equilibria separate the concentration triangle of the quasi-ternary system into seven three-phase regions.

Table 1 Melting point and type, and crystallographic parameters of the ternary compounds in the systems Tl_2S–HgS and Tl_2S–SnS_2.

| Compound	T_m (K)	Space group	Lattice parameters (Å)				Ref.
			a	b	c	β	
$Tl_2Hg_3S_4$	648 (i)	$C2/c$	11.493	6.6953	12.937	114.98°	[27]
$Tl_2Sn_2S_5$	733 (i)	$C2/c$	11.115	7.723	11.492	108.60°	[28]
Tl_2SnS_3	698 (k)	$C2/m$	23.03	3.834	7.379	94.07°	[29]
Tl_4SnS_4	738 (k)	$P2_1/c$	8.395	8.280	15.398	103.69°	[30]

k – congruent type of formation; i – incongruent type of formation.

Table 2 Crystallographic data for Tl_2HgSnS_4.

Compound	Tl_2HgSnS_4
Space group	$I\text{-}42m$
a (Å)	7.8571(6)
c (Å)	6.6989(7)
Cell volume (Å^3)	413.5(1)
Calculated density (g/cm^3)	6.876(2)
Pearson code	$tI16$
Wyckoff sequence	$icba$
Radiation and wavelength (Å)	CuK_α and 1.54185
Diffractometer	Powder DRON 4-13
Mode of refinement	Full profile
Number of atom sites	4
Number of free parameters	15
2θ (°) and $\sin\theta/\lambda$ max (1/Å)	100.02 and 0.497
R(intensity) and R(profile)	0.0602 and 0.1252
Texture axis and parameter	[110] and 0.425(9)

Table 3 Atomic coordinates and isotropic displacement parameters for Tl_2HgSnS_4.

Atom	Wyck.	x/a	y/b	z/c	B(iso/eq)
Tl	4*c*	½	0	½	1.63(3)
Hg	2*b*	0	0	½	2.96(8)
Sn	2*a*	0	0	0	2.30(10)
S	8*i*	0.1660(5)	*x*	0.251(2)	1.26(15)
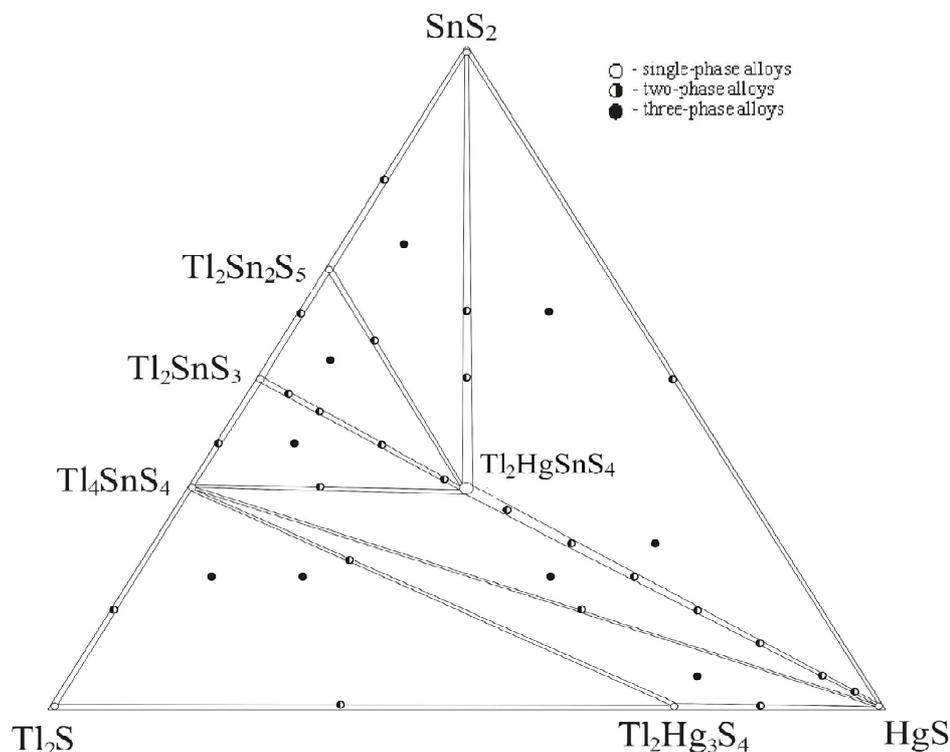
Fig. 1 Isothermal section of the Tl₂S–HgS–SnS₂ system at 520 K.

It was found by powder diffraction that Tl_2HgSnS_4 crystallizes with tetragonal symmetry, non-centrosymmetric space group *I*-42*m*, unit cell parameters $a = 7.8571(6)$ Å, $c = 6.6989(7)$ Å. The quaternary compound found here is isostructural with the previously obtained Se- and Te-containing compounds of the same composition [21-23]. The crystallographic parameters of the compound are presented in Table 2, the atomic coordinates and isotropic displacement parameters are listed in Table 3. The starting model was the structure of the $Tl_2HgGeSe_4$ compound [23], and the atomic coordinates, isotropic displacement parameters and the texture parameter were refined by the Rietveld method (Fig. 2, Tables 2 and 3). The closest coordination surroundings of the Hg and Sn atoms are tetrahedra of sulfur atoms (Fig. 3). The Tl atoms have tetragonal-antiprismatic surrounding of sulfur atoms, whereas the S atoms are surrounded by trigonal prisms of Tl, Hg and Sn atoms.

The structure of Tl_2HgSnS_4 may be presented as a packing of SnS_4^{4-} ($\delta_{Sn-S} = 2.491$ Å) tetrahedra with Tl^+ and Hg^{2+} cations in the closest surrounding (Fig. 4, top-left). The Tl atoms are surrounded by six SnS_4^{4-} tetrahedra, the centers of which form an octahedron (Fig. 5), while the Hg atoms are located between two SnS_4^{4-} tetrahedra.

A compound of analogous composition, Ag_2HgGeS_4 (*oP*16, 31) (Fig. 4) [32], was obtained in the closely related system Ag_2S–HgS–GeS_2. The second coordination surrounding (SCS) [33] of the GeS_4^{4-} anions has the shape of a rhombic dodecahedron, which indicates W-type (b.c.c.) packing of these anions. Regards the arrangement of the complex anions (Fig. 4), Tl_2HgSnS_4 is related to the ternary phase Tl_4SnS_4 [34], which has an analogous rhombododecahedral anion sub-lattice. This may indicate that Tl_2HgSnS_4 can be obtained by isovalent multiple substitution of one mercury atom for two thallium atoms in the structure of Tl_4SnS_4 ($Tl_4SnS_4 - 2Tl + Hg \rightarrow Tl_2HgSnS_4$). Further isovalent multiple replacement of thallium atoms by B^{II} element atoms may be seen in the structure of $BaHgSnS_4$ [35] (Fig. 4), which has the same anion sub-lattice and thus the same type of SCS.
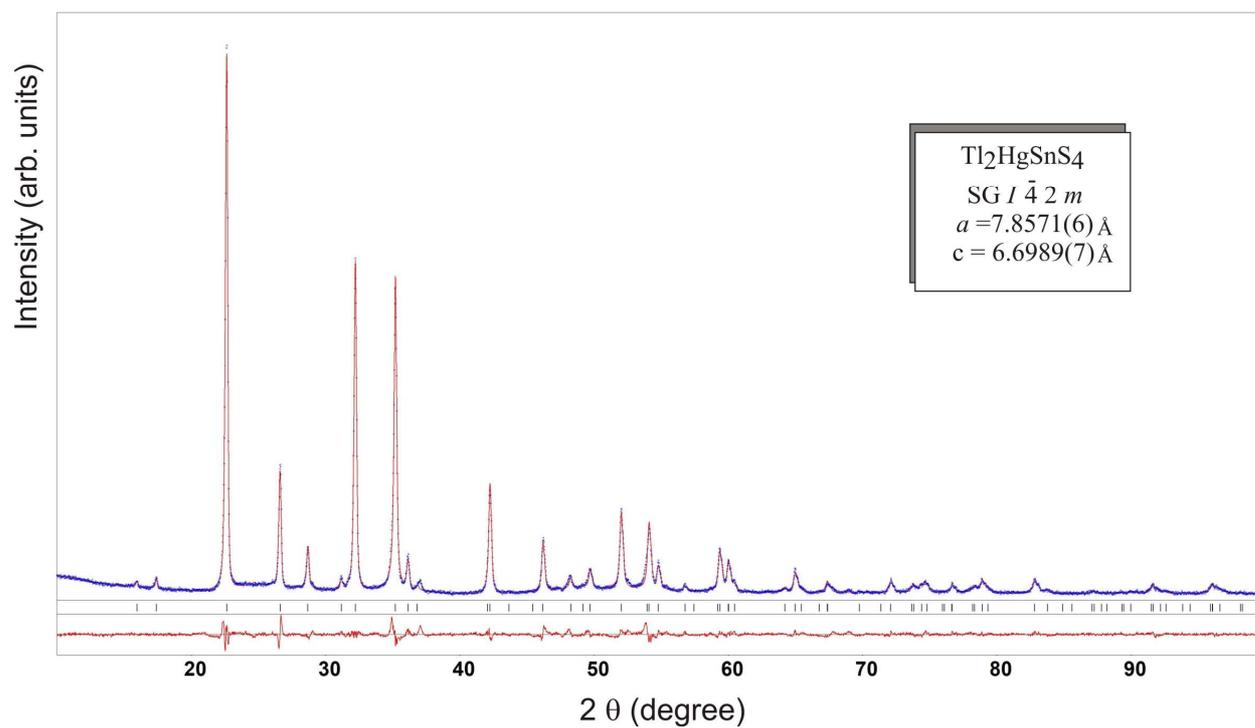
Tl$_2$HgSnS$_4$

SG $I\,\bar{4}\,2\,m$

$a =7.8571(6)$ Å

$c = 6.6989(7)$ Å

Fig. 2 Experimental (blue) and theoretical (red, top) diffraction patterns for Tl$_2$HgSnS$_4$ and their difference (red, bottom).
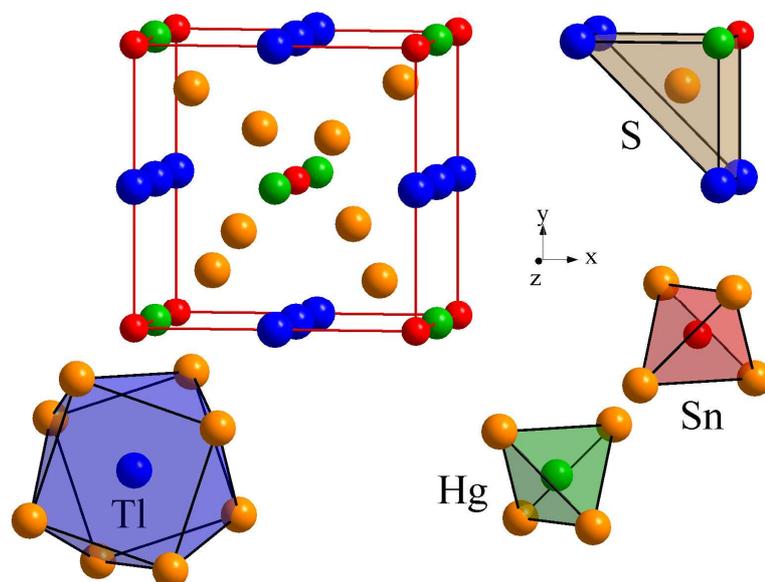

Fig. 3 Projection of the unit cell of Tl$_2$HgSnS$_4$ onto the *xy* plane and the coordination polyhedra of the atoms.
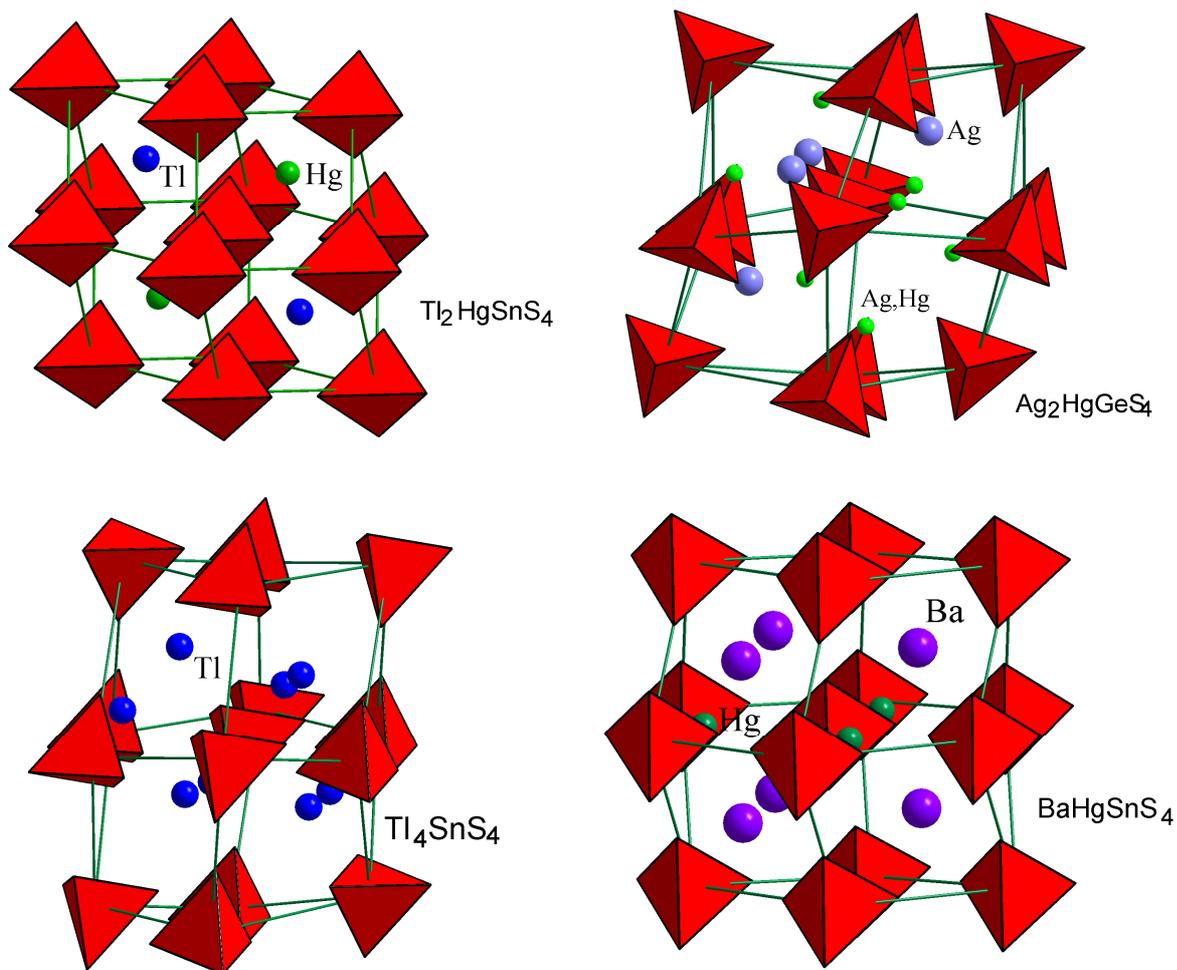
Fig. 4 First (metal atoms) and second (other complex anions) coordination surroundings of the SnS$_4^{4-}$ (GeS$_4^{4-}$) anions in the structures of Tl$_2$HgSnS$_4$, Ag$_2$HgGeS$_4$, Tl$_4$SnS$_4$, and BaHgSnS$_4$.
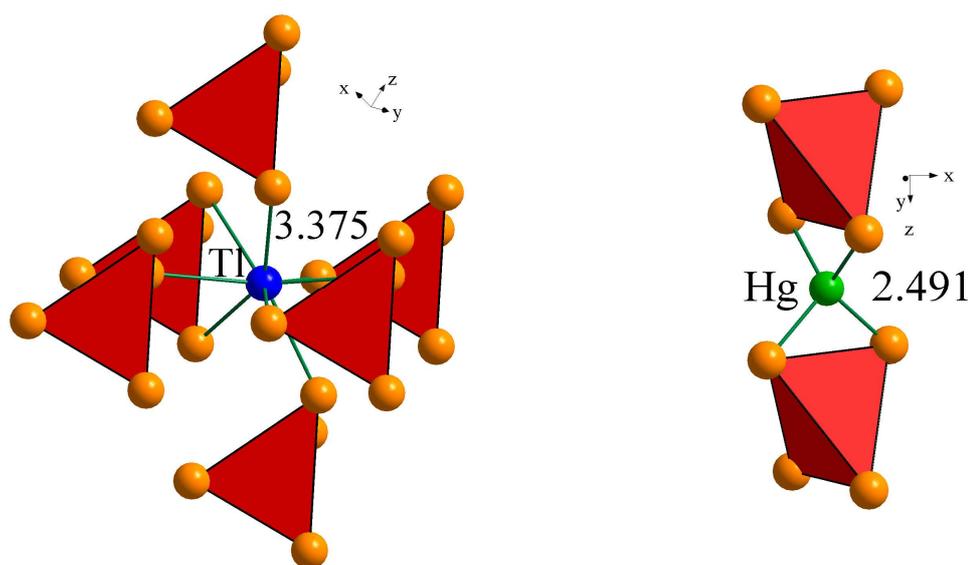

Fig. 5 Coordination surrounding of the Tl and Hg atoms by S atoms and by SnS$_4^{4-}$ tetrahedra in the structure of Tl$_2$HgSnS$_4$.

Conclusions

The isothermal section of the Tl$_2$S–HgS–SnS$_2$ system at 520 K was investigated by powder XRD. A new quaternary compound was found at the equimolar ratio of the binary components, which is described by the formula Tl$_2$HgSnS$_4$. It was found that the compound crystallizes in the non-centrosymmetric space group *I*-42*m* with the unit cell parameters a = 7.8571(6) Å, c = 6.6989(7) Å. The relationship to similar structures is discussed.

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