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The Tl_2Se–HgSe–$GeSe_2$ system and the crystal structure of $Tl_2HgGeSe_4$

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The phase equilibria in the quasi-ternary system Tl_2Se–HgSe–$GeSe_2$ were investigated by differential-thermal analysis and X-ray diffraction. Phase diagrams of the Tl_2Se–HgSe and Tl_2GeSe_3–HgSe systems were constructed, as well as the isothermal section of the Tl_2Se–HgSe–$GeSe_2$ system at 520 K. Two intermediate quaternary compounds, $Tl_2HgGeSe_4$ and $Tl_2HgGe_2Se_6$, exist at this temperature. $Tl_2HgGeSe_4$ crystallizes in the non-centrosymmetric space group *I*-42*m* with the unit cell parameters a = 0.79947(4) nm, c = 0.67617(4) nm.

Chalcogenides / Semiconductors / X-ray diffraction / Crystal structure

1. Introduction

Quaternary chalcogenides I_2-II-IV-VI_4 have been extensively studied because these compounds exhibit properties that are promising for applications in non-linear optics, detection of γ-radiation, solar energy conversion, *etc.* [1-6]. Available information on quaternary phases of this type that form in the quasi-ternary systems A^I_2X–$B^{II}X$–$D^{IV}X_2$ (A^I = Cu, Ag; B^{II} = Zn, Cd, Hg, Mn, Pb; D^{IV} = Si, Ge, Sn; X = S, Se, Te) was summarized by us in [7]. Compounds form in all possible combinations of the systems with A^I = Cu; for the silver-containing systems, they exist only for X = S [1,7-12] and some systems with Se [7], but do not form in tellurium-containing systems.

The search for new quaternary compounds was extended to the thallium-containing systems Tl_2X–$B^{II}X$–$D^{IV}X_2$, which are analogous to the Cu- and Ag-containing systems, but are sparsely investigated. The formation of the quaternary compound Tl_2PbGeS_4, which crystallizes in a monoclinic structure (space group $P2_1/a$), is known [13]. The authors of [14] report the crystal structure, electronic structure and thermoelectric properties of several telluride compounds $Tl_2B^{II}D^{IV}Te_4$ (B^{II} = Cd, Hg, Mn; D^{IV} = Ge, Sn). All of these compounds are isostructural and crystallize in the tetragonal space group *I*-42*m*.

Here, we report an investigation of the phase equilibria in one of the above-mentioned systems, namely Tl_2Se–HgSe–$GeSe_2$, and the crystal structure of a new quaternary compound that forms in the quasi-binary section Tl_2GeSe_3–HgSe at the equimolar ratio of the components.

The compounds Tl_2Se, HgSe and $GeSe_2$ melt congruently at 663 [15], 1073 [16] and 1050 K [17], respectively. Tl_2Se crystallizes in a tetragonal structure (space group *P*4/*ncc*, a = 0.852 nm, c = 1.268 nm) [18]. The crystal structure of HgSe is cubic (space group *F*-43*m*, a = 0.6460 nm) [16]. $GeSe_2$ has a monoclinic structure (space group $P2_1/c$) with the lattice parameters a = 0.7016(3) nm, b = 1.6796(8) nm, c = 1.1831(5) nm, β = 90.65(5)° [19].

The phase diagrams of the boundary quasi-binary systems are known. According to [20], the Tl_2Se–HgSe system features a ternary compound, $Hg_3Tl_2Se_4$, which melts incongruently at 691 K and has a polymorphous transition at 568 K. One of the modifications crystallizes in a monoclinic structure, space group *C*2/*c*, a = 1.1977(2) nm, b = 0.69264(14) nm, c = 1.3203(3) nm, β = 116.36(3)° [21]. Three compounds were found in the Tl_2Se–$GeSe_2$ system: Tl_4GeSe_4 and Tl_2GeSe_3 melt congruently at 661 and 706 K, respectively, with Tl_2GeSe_3 melting at the transition point; $Tl_2Ge_2Se_5$ melts incongruently at 778 K [22]. Tl_4GeSe_4 has a monoclinic structure (space group *C*2/*c*, a = 1.16700(2) nm, b = 0.73170(1) nm, c = 2.56030(10) nm, β = 106.54(1)°) [23]. Tl_2GeSe_3 crystallizes in a triclinic structure (space group *P*-1) with the unit cell parameters a = 1.5602 nm,

b = 1.5549(5) nm, c = 0.9052(3) nm, α = 90.55(7)°, β = 111.42(6)°, γ = 114.45(7)° [24]. $Tl_2Ge_2Se_5$ also has a monoclinic structure (space group $C2/c$), with the lattice parameters a = 0.8481(2) nm, b = 0.8411(2) nm, c = 1.5800(5) nm, β = 107.10(3)° [25]. An investigation of the HgSe–$GeSe_2$ system [26] showed the existence of the ternary compound Hg_2GeSe_4, which forms in a peritectic reaction at 893 K and has a polymorphous transition at 830 K. Its low-temperature modification has a tetragonal cadmium thiogallate-type structure (space group I-4) with the lattice parameters a = 0.5672 nm, c = 1.1322 nm [26] (or a = 0.56786 nm, c = 1.12579 nm [27]; a = 0.56741 nm, c = 1.1249 nm [28]).

2. Experimental

A total of 50 samples were prepared for the investigation of the phase equilibria in the quasi-ternary system Tl_2Se–HgSe–$GeSe_2$. The alloys were synthesized from elementary Tl, Ge, Se (purity at least 99.99 wt.%) and previously prepared HgSe (Hg 99.999 wt.%). The synthesis was performed using the single-temperature method in evacuated quartz ampoules that were placed in a shaft-type furnace and heated to 870 K at the rate of 30 K/h. The melts were held at this temperature for 6 h with periodic vibration, and then cooled to 520 K at the rate of 10 K/h. The alloys were annealed at this temperature for 250 h, and then quenched into cold water. The obtained alloys were compact, black ingots with a characteristic luster.

XRD spectra were recorded on a DRON 4-13 diffractometer, using Cu K_α radiation with Ni filter ($10^\circ \le 2\theta \le 90^\circ$, scan step 0.05° and 2 s exposure at each point, for phase analysis; $10^\circ \le 2\theta \le 100^\circ$, 0.02°, 28 s exposure, for the structure refinement). The XRD sets were processed using PDWin2 and CSD software [29].

Thermal analysis was performed using a Paulik-Paulik-Erdey derivatograph, with the temperature measured by a Pt/Pt-Rh thermocouple.

3. Results and discussion

3.1. Phase diagram of the Tl_2Se–HgSe system

The existence of all previously known ternary compounds in the boundary systems of the Tl_2Se–HgSe–$GeSe_2$ system was confirmed.

The re-investigation of the phase diagram of the Tl_2Se–HgSe system confirmed the formation of the ternary compound $Tl_2Hg_3Se_4$, as reported in [20]. The temperatures of the physico-chemical processes, however, were different. $Tl_2Hg_3Se_4$ forms in a peritectic reaction, L+HgSe↔β-$Tl_2Hg_3Se_4$, at 602 K and has a polymorphous transition, α-$Tl_2Hg_3Se_4$↔β-$Tl_2Hg_3Se_4$, at 540 K. A eutectic point occurs at 28 mol.% HgSe and 560 K. The constructed phase diagram of the system is shown in Fig. 1.

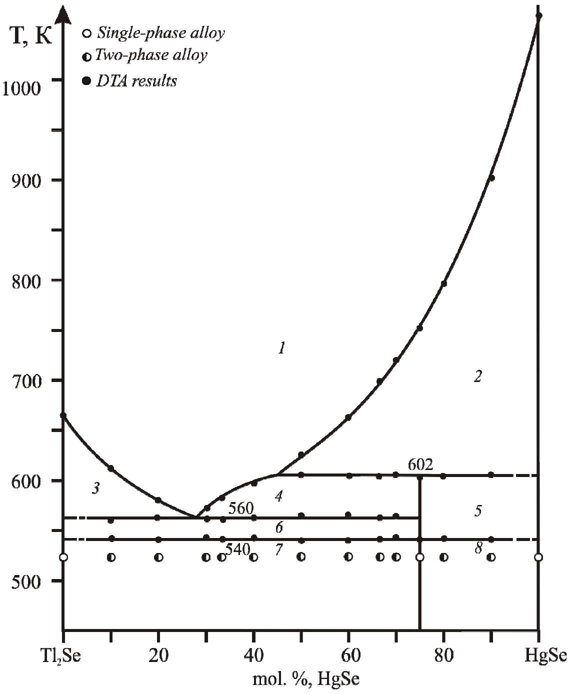


Fig. 1 Phase diagram of the Tl_2Se–HgSe system:
1 – L; 2 – L+HgSe; 3 – L+Tl_2Se;
4 – L+β-$Tl_2Hg_3Se_4$; 5 – β-$Tl_2Hg_3Se_4$+HgSe;
6 – Tl_2Se+β-$Tl_2Hg_3Se_4$;
7 – α-$Tl_2Hg_3Se_4$+Tl_2Se; 8 – α-$Tl_2Hg_3Se_4$+HgSe.

3.2. Phase diagram of the Tl_2GeSe_3–HgSe system

The Tl_2GeSe_3–HgSe system is a quasi-binary section, which triangulates the quasi-ternary system Tl_2Se–HgSe–$GeSe_2$ into two sub-systems, Tl_2Se–Tl_2GeSe_3–HgSe and $GeSe_2$–Tl_2GeSe_3–HgSe. The investigated Tl_2GeSe_3–HgSe section features one quaternary compound, $Tl_2HgGeSe_4$, which melts congruently at 762 K (Fig. 2). The interactions in the partial systems Tl_2GeSe_3–$Tl_2HgGeSe_4$ and $Tl_2HgGeSe_4$–HgSe are eutectic in nature. The curves of primary crystallization cross at eutectic points at 14 and 60 mol.% HgSe at 663 and 740 K, respectively. The solid solution ranges of the section components are smaller than 2 mol.% Tl_2GeSe_3 and 5 mol.% HgSe at the annealing temperature. Representative diffraction patterns of alloys from the investigated system confirm the DTA results, and are presented in Fig. 3. The diffraction patterns of the alloys with 0, 50, 100 mol.% HgSe content correspond to the quaternary and the two boundary compounds. The diffraction patterns of the intermediate alloys with 10, 30, 60, 80, 95 mol.% HgSe content contain two sets of reflections of the system components with gradually changing intensities.

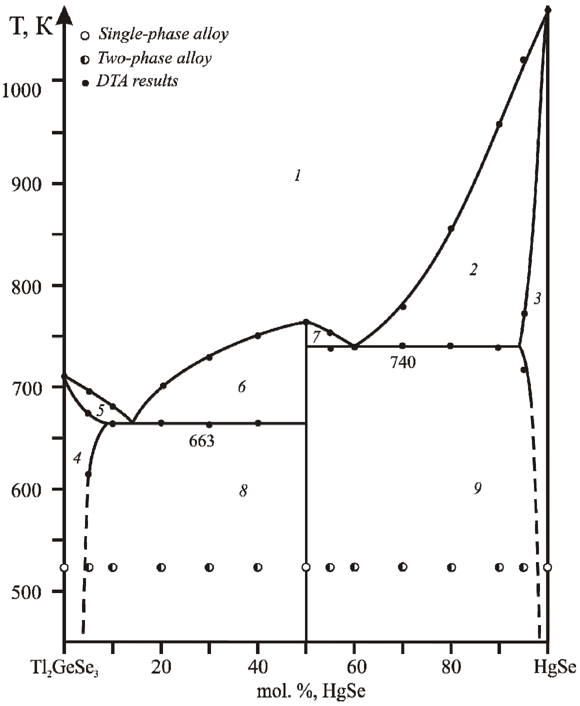


Fig. 2 Phase diagram of the quasi-binary system Tl_2GeSe_3–HgSe:
1 – L; 2 – L+HgSe; 3 – HgSe; 4 – Tl_2GeSe_3;
5 – L+Tl_2GeSe_3; 6, 7 – L+$Tl_2HgGeSe_4$;
8 – Tl_2GeSe_3+$Tl_2HgGeSe_4$;
9 – HgSe+$Tl_2HgGeSe_4$.

3.3. *Isothermal section of the Tl_2Se–HgSe–$GeSe_2$ system at 520 K*

The isothermal section of the quasi-ternary Tl_2Se–HgSe–$GeSe_2$ system at 520 K was constructed from the results of the XRD phase analysis (Fig. 4).

The sections Tl_2GeSe_3–HgSe and $Tl_2HgGeSe_4$–$GeSe_2$ are most interesting, as they feature quaternary phases. The former is described in detail above, and the determination of the crystal structure of $Tl_2HgGeSe_4$ is presented below (see Sect. *3.4*). A quaternary phase with unknown structure was found in the $Tl_2HgGeSe_4$–$GeSe_2$ section. The best diffraction pattern of this phase was obtained for the alloy with the composition 25 mol.% Tl_2Se, 25 mol.% HgSe, 50 mol.% $GeSe_2$, which corresponds to the formula $Tl_2HgGe_2Se_6$. Its crystal structure is currently under investigation.

3.4. *Crystal structure of the quaternary compound $Tl_2HgGeSe_4$*

The crystal structure of $Tl_2HgGeSe_4$ was determined by X-ray powder diffraction. The experimental conditions and the crystallographic parameters of the $Tl_2HgGeSe_4$ structure are listed in Table 1. The structure was refined by the Rietveld method, using $Tl_2HgGeTe_4$ as starting model [14]. The original article reports the $Tl_2HgGeTe_4$ structure as a superstructure of Tl_2Se_2 in the non-centrosymmetric space group I-42m. Experimental and theoretical diffraction patterns of $Tl_2HgGeSe_4$ and their difference are plotted in Fig. 5.

A new approach to the representation of the crystal structure was proposed in [30], focusing on the stacking of hexagonal (wurtzite type) and cubic (sphalerite type) layers. Using this approach, the second coordination surrounding (SCS) in $Tl_2HgGeSe_4$ can be presented as a defective (–1) hexagonal analog of a cuboctahedron, obtained by the substitution of one selenium atom for two. The metal atoms (Tl, Hg) form a trigonal-prismatic surrounding around the selenium atoms, as shown in Fig. 6. The location of the chalcogen atoms within the SCS

Table 1 Investigation of the $Tl_2HgGeSe_4$ crystal structure.

Space group	I-42m
a, nm	0.79947(4)
c, nm	0.67617(4)
V, nm^3	0.43217(7)
Number of atoms per cell	16
Radiation	Cu K_α
wavelength, nm	0.154185
Diffractometer	DRON 4-13
Calculation method	Full profile
Calculated density D_x, $g\cdot cm^{-3}$	7.716(1)
Absorption coefficient μ, cm^{-1}	1313.73
Number of atom sites	4
Number of refined parameters	16
2θ, °, and $\sin\theta/\lambda_{max}$, nm^{-1}	119.66 and 5.61
Texture axis and parameter	[0 0 1] and 1.6513
R_I and R_p	0.0677 and 0.1185

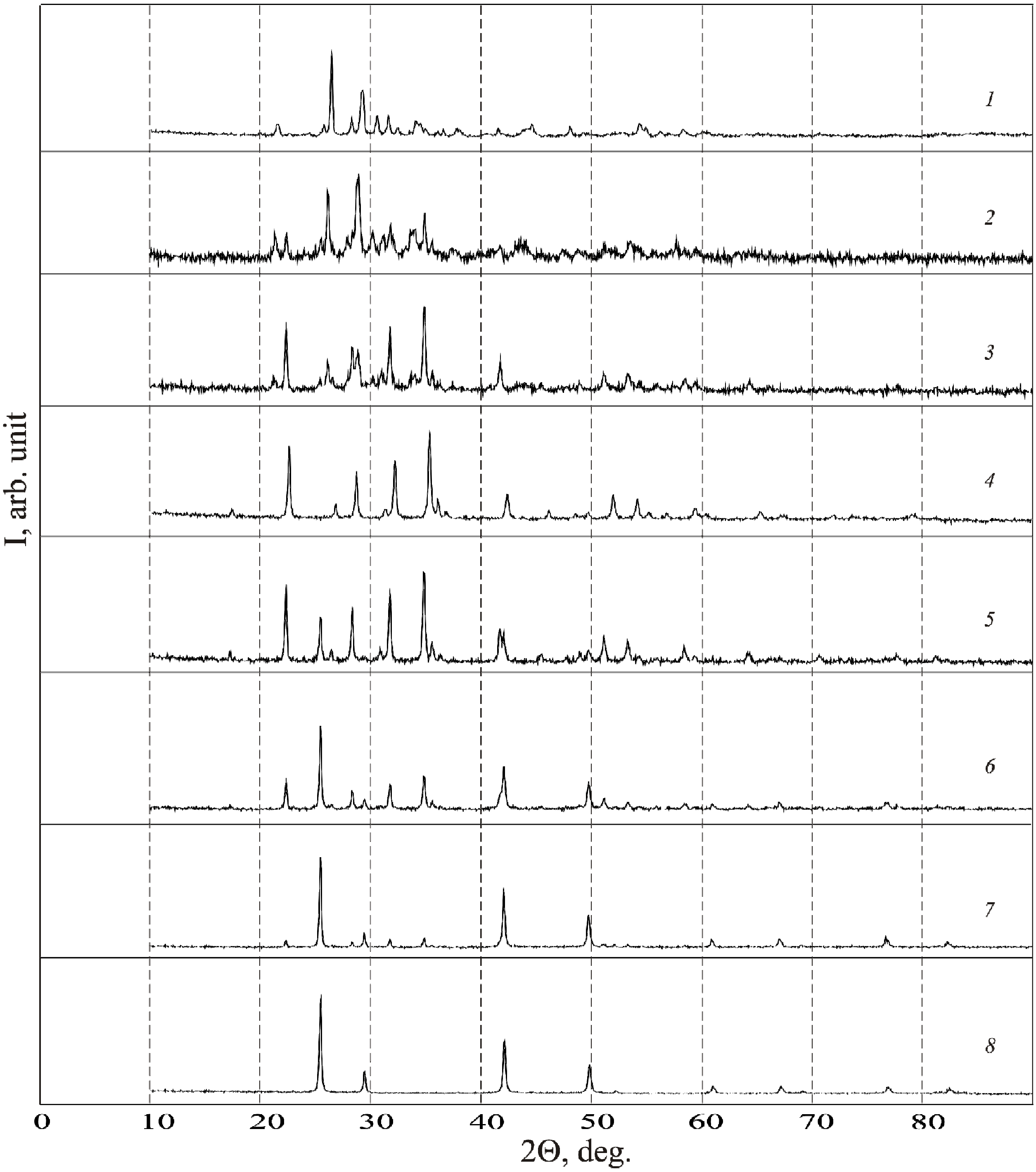


Fig. 3 Diffraction patterns of Tl_2GeSe_3–HgSe alloys annealed at 520 K (mol.% HgSe): 1 – 0; 2 – 10; 3 – 30; 4 – 50; 5 – 60; 6 – 80; 7 – 95; 8 – 100.

is similar to that in the Tl_2Se_2 structure, or its superstructure, $TlInSe_2$ [31], which have the same anion sub-lattice, where the atoms of mono- and trivalent thallium (or thallium and indium in $TlInSe_2$) occupy analogous sites .

The $Tl_2HgGeSe_4$ structure features germanium-centered tetrahedra of selenium atoms at the points of a body-centered cubic sub-lattice. Six cations form octahedra around these tetrahedra, as shown in Fig. 7.

No strongly pronounced layers are seen in the structure, but a 3D framework may be pointed out, which can be described as an intersection of layers of chalcogen atoms (Fig. 8). The shortest distances between selenium atoms are shown, and the mercury

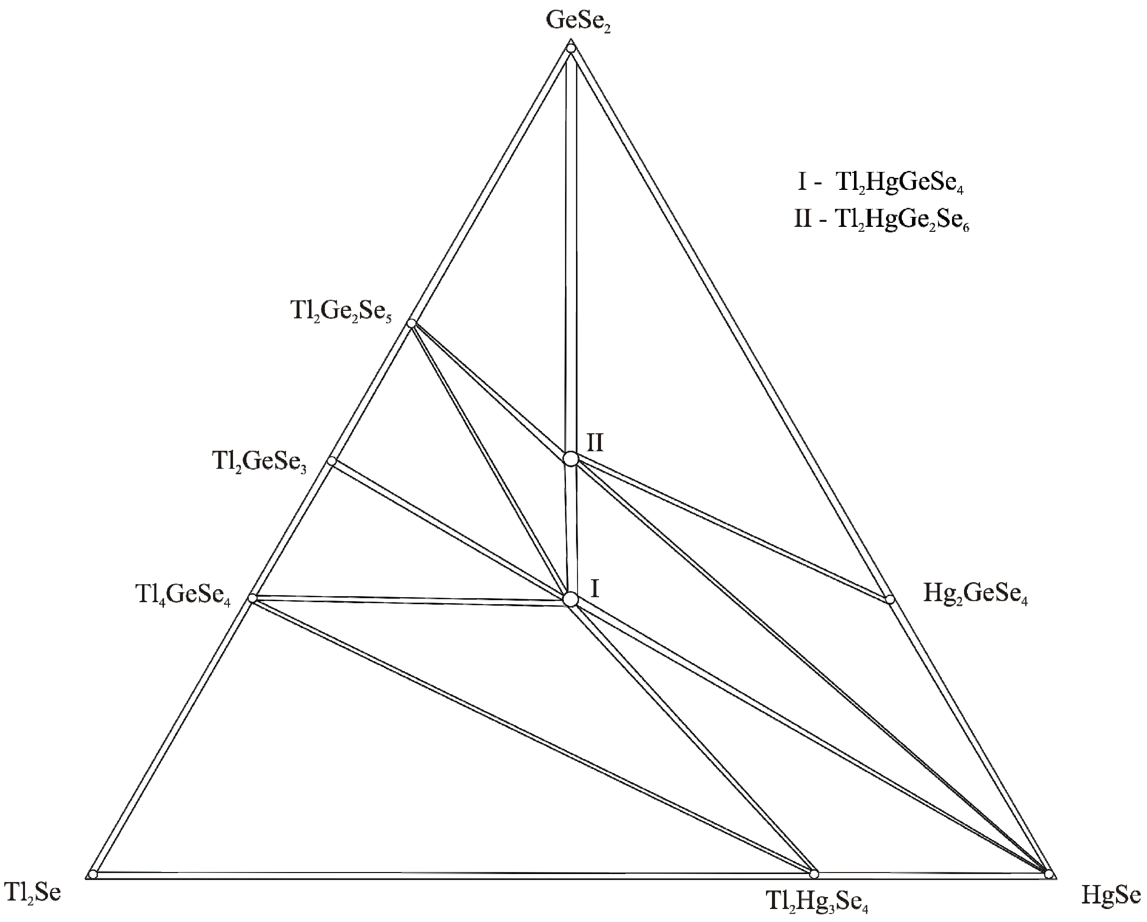


Fig. 4 Isothermal section of the Tl_2Se–HgSe–$GeSe_2$ system at 520 K.

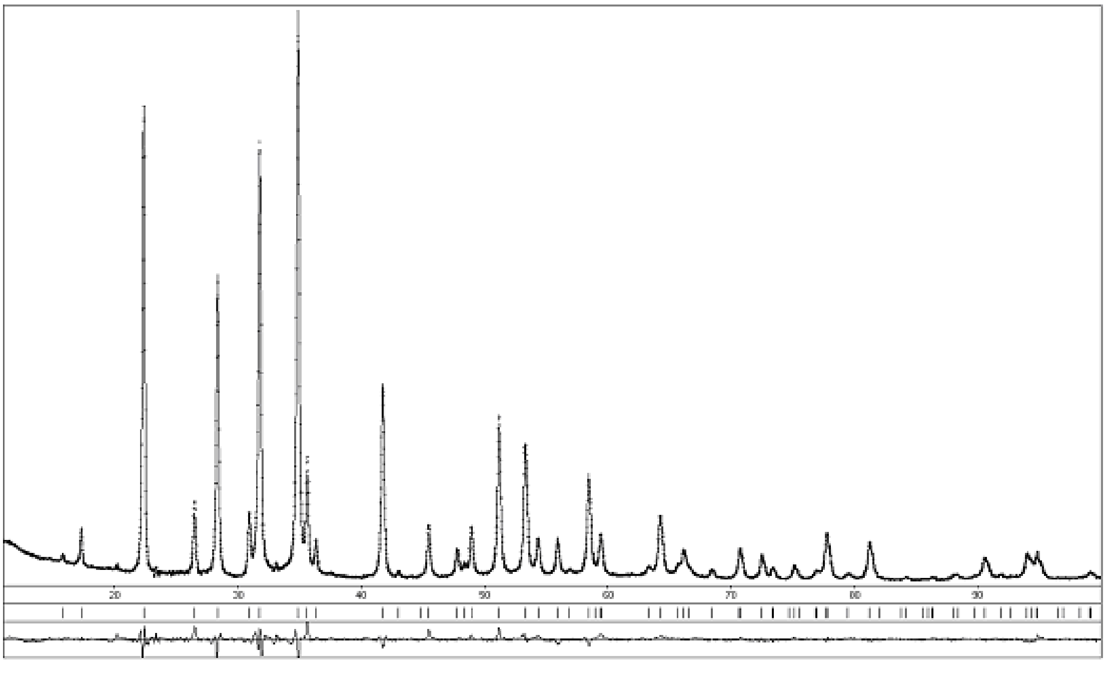
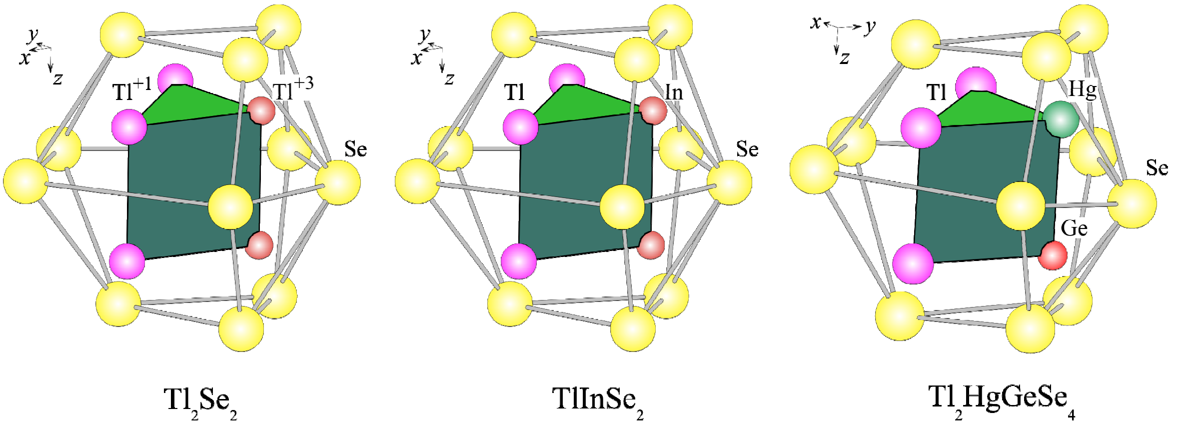


Fig. 5 Experimental and theoretical diffraction patterns of $Tl_2HgGeSe_4$, and their difference.



Tl_2Se_2 $TlInSe_2$ $Tl_2HgGeSe_4$

Fig. 6 Location of the metal atoms within the defect Se sub-lattice in the structures of Tl_2Se_2, $TlInSe_2$ and $Tl_2HgGeSe_4$.

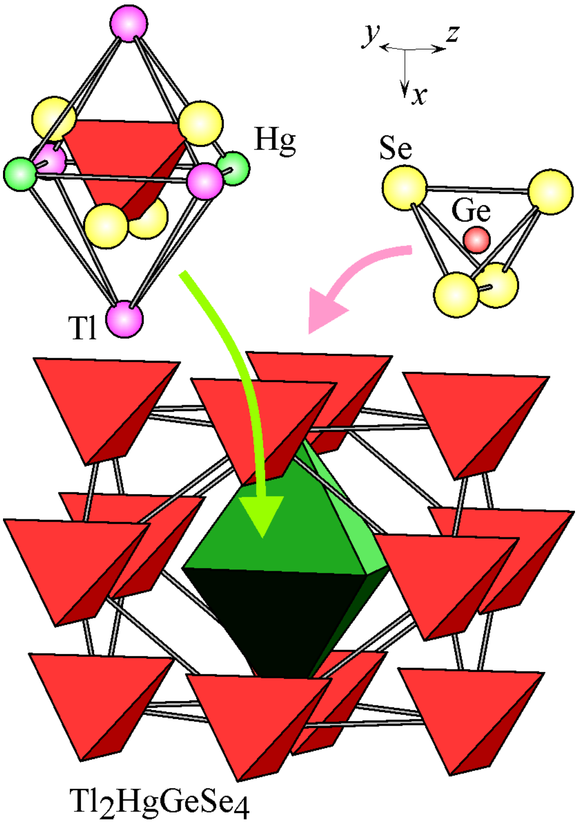


Fig. 7 Location of metal atoms within the cubic anionic sub-lattice formed by germanium-centered tetrahedra of selenium atoms in the $Tl_2HgGeSe_4$ structure.

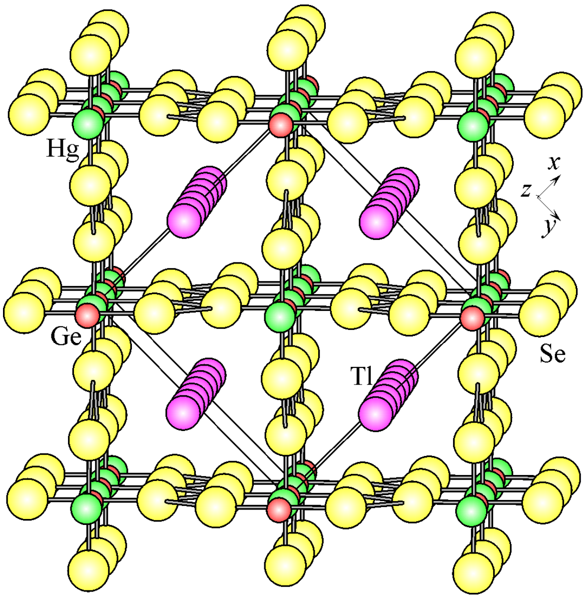


Fig. 8 Shortest Se–Se distances in the $Tl_2HgGeSe_4$ structure.

and germanium atoms are located in the voids at the intersections of the nets. The thallium atoms are located in the channels of the 3D framework.

The atom coordinates and isotropic displacement parameters are presented in Table 2, the interatomic distances are listed in Table 3. According to the obtained results, the refined formula of the quaternary compound $Tl_2HgGeSe_4$ corresponds to the stoichiometric one.

Table 2 Atom coordinates, site occupations and isotropic displacement parameters in the structure of $Tl_2HgGeSe_4$, space group I-4̄2m.

Atom	Wyckoff position	x	y	z	Site occupation	$B_{iso}\times10^2$, nm^2
Hg	2*b*	0	0	½	1.0	2.46(6)
Tl	4*c*	0	½	0	1.0	2.07(6)
Ge	2*a*	0	0	0	1.0	2.41(2)
Se	8*i*	0.1693(2)	0.1693(2)	0.2189(5)	1.0	1.17(6)

Table 3 Interatomic distances in the $Tl_2HgGeSe_4$ structure.

$Tl_2HgGeSe_4$	Distance, nm
Hg–Se	0.2688(3)×4
Tl–Se	0.3323(2)×4
	0.3523(2)×4
Ge–Se	0.2420(2)×4

The Tl–Se distances (Table 3) show good agreement with the sum of the ionic radii ($r(Tl^+)$ = 0.149 nm, $r(Se^{2-})$ = 0.191 nm [32]), whereas the distances Hg–Se and Ge–Se are somewhat shorter than the sum of the ionic radii ($r(Hg^{2+})$ = 0.112 nm, $r(Ge^{4+})$ = 0.272 nm [32]). Commonly, one of the reasons for such contraction is partially covalent bonding between the atoms. The Tl–Se distances (0.323(2) nm and 0.3523(2) nm) are commensurate with those in the '$Tl_3In_3SnSe_8$' structure [33]. The interatomic distances Hg–Se are close to those in Hg_4SiSe_6 (0.2501-0.2932 nm) [34] or Hg_2SnSe_4 (0.2636-0.2720 nm) [35]. The Ge–Se distances correlate well with those in Tl_4GeSe_4 (0.250-0.256 nm) [24], Tl_2GeSe_3 (0.229-0.260 nm) [25], and $Tl_2Ge_2Se_5$ (0.234-0.258 nm) [23].

4. Conclusions

The phase equilibria in the Tl_2Se–HgSe–$GeSe_2$ system were investigated, and two intermediate quaternary phases were found. The crystal structure of the compound of the equimolar composition $Tl_2HgGeSe_4$ was determined by X-ray powder diffraction (space group I-42m).

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