



Proceedings New Quaternary Chalcogenides Tl₂M^{II}M^{IV}₃Se₈ and Tl₂M^{II}M^{IV}X₄ ⁺

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Abstract: New quaternary thallium-containing chalcogenides Tl₂M^{II}M^{IV}₃X₈ and Tl₂M^{II}M^{IV}X₄ were synthesized, and their crystal structure was determined by XRD. Three Tl₂M^{II}M^{IV}₃X₈ chalcogenides crystallize in orthorhombic symmetry (S.G. *P*₂1₂1₂1; Tl₂CdGe₃Se₈ lattice parameters *a* = 0.76023(9), *b* = 1.2071(2), *c* = 1.7474(2) nm), eight isostructural Tl₂B^{II}D^{IV}X₄ compounds crystallize in tetragonal symmetry, S.G. *I*-42*m*. These compounds form in the quasi-ternary systems Tl₂X–M^{II}X–M^{IV}X₂ (X–S, Se, Te) at the component ratio 1:1:1 and 1:1:3 at the sections Tl₂M^{II}VX₃–B^{II}X and Tl₂M^{II}M^{IV}X₄–M^{IV}X₂, respectively. The composition of the Tl₂CdGe₃Se₈ compound was additionally confirmed by SEM and EDS.

Keywords: crystal structure; thallium-containing chalcogenides; phase equilibria; powder X-ray diffraction

1. Introduction

The formation of 12 new quaternary compounds, Tl₂HgSi(Ge,Sn)S₄, Tl₂PbSi(Ge)S₄, Tl₂CdSi(Ge,Sn)Se₄, Tl₂HgSi(Ge,Sn)Se₄, Tl₂PbSi(Ge)Se₄, was found in the investigation of sulfur- and selenium-containing quasi-ternary systems Tl₂X–M^{II}X–M^{II}X₂ by XRD and differential thermal analysis (DTA) along the Tl₂M^{II}X₃–M^{II}X sections. The structure of six of them (Tl₂HgSi(Ge, Sn)Se₄, Tl₂HgSnS₄, Tl₂CdGe(Sn)Se₄) and their two analogs Tl₂Cd(Hg)SiTe₄ was determined in the isotropic approximation within the Tl₂HgGeTe₄ structure (S.G. *I*-42*m*) as a model. Along with five other tellurides Tl₂M^{II}M^{II}VTe₄ (M^{II}–Mn, Cd, Hg; M^{IIV}–Si, Ge, Sn), these were reported in [1]. Pb-containing compounds Tl₂PbSiS₄ and Tl₂PbGeS₄ are isostructural and crystallize in the monoclinic structure, S.G. *P*₂₁/*a*).

A large number of the compounds of this type with Cu, Ag, and alkali metals are known, e.g., Li₂CdGeSe₄, Li₂CdSnSe₄, Cu₂CdSnS₄, Cu₂CdGeSe₄, Ag₂FeSnS₄. They belong to diamond-like semiconductors and have already found applications in non-linear optics and other fields of semiconductor technology, high thermal stability, and other important optical and thermoelectric properties [1–3].

The compounds of the 2-1-3-8 composition are known with alkali metals and Cu. They crystallize in the orthorhombic (S.G. $P2_{1}2_{1}2_{1}$: Ta Cs₂ZnGe₃Te₈, Cs₂CdGe₃Se₈, Cs₂CdGe₃Se₈ [4]), monoclinic (S.G. $P2_{1}/a$: Cs₂ZnGe₃Se₈, α -K₂ZnSn₃Se₈, [4–6]), and tetragonal structure (S.G. $I4_{1}/a$: Cu₂FeSn₃Se₈, Cu₂CdSn₃Se₈ [7]).

2. Materials and Methods

Three new quaternary selenides of the general formula $Tl_2M^{II}Ge_3Se_8$ (M^{II} = Zn, Cd, Hg) were obtained by direct high-temperature synthesis. The method consisted of co-melting high-purity elements thallium, zinc, cadmium, germanium, and selenium (at least 99.99 wt.% purity) and mercury selenide in evacuated to 1 × 10⁻³ torr and soldered quartz ampoules. The synthesis involved heating to 673 K at the rate of 20 K/h, 12 h exposure; heating to 1333 K at the rate of 10 K/h, 7 h exposure; cooling to 773 K at the rate of 6 K/h; homogenizing annealing at this temperature for 350 h. Finally, the ampoules were quenched into 20% aqueous saline solution.

Powder patterns for the determination of the phase composition of the synthesized samples Tl₂ZnGe₃Se₈, Tl₂CdGe₃Se₈, and Tl₂HgGe₃Se₈ were recorded at a DRON 4–13 diffractometer, Cu K α radiation, 2θ range $10^{\circ} \le 2\theta \le 80^{\circ}$, scan step 0.05° , 5 s exposure in each point. Datasets for structure computation were recorded in the 2θ range of $10^{\circ} \le 2\theta \le 100^{\circ}$, scan step 0.05° , 20 s exposure in each point. The crystal structure of new quaternary chalcogenides was determined by Rietveld method realized in WinCSD software package [8]. Visualization of the crystal structure elements utilized Diamond software.

The investigation of the composition of the Tl₂CdGe₃Se₈ compound was additionally confirmed by SEM and EDS at a Tescan Vega 3 LMU scanning microscope (Tescan Brno s.r.o., Brno, Czech Republic) equipped with Oxford Instruments Aztec ONE X-ray microanalyzer with X-Max^N20 detector (accelerating voltage 25 kV; K-, L- and M-lines of the spectrum; magnification ×1000).

3. Results and Discussion

3.1. Phase Equilibria in the Tl₂Se–CdSe–GeSe₂ System

Isothermal sections of 14 quasi-ternary systems Tl₂X–M^{II}X–M^{II}X2 (X–S, Se) at 570 K were plotted from the X-ray phase analysis results. Twelve compounds of the 2-1-1-4 type were found, Tl₂HgSi(Ge,Sn)S₄, Tl₂PbSi(Ge)S₄, Tl₂CdGe(Sn)Se₄, Tl₂HgSi(Ge,Sn)Se₄, Tl₂PbSi(Ge)Se₄. According to DTA results, they all form incongruently (formation temperatures are listed in Table 1). Additionally, seven compounds of the 2-1-3-8 composition were found, Tl₂CdGe₃Se₈, Tl₂HgSi(Ge)₃Se₈, Tl₂HgSi(Ge)₃Se₈ Tl₂PbSi(Ge)₃Se₈ Tl₂PbSi(Ge)₃Se₈

Isothermal section of the Tl₂Se–CdSe–GeSe₂ system at 570 K is shown in Figure 1. The system at the annealing temperature features in the state of thermodynamic equilibrium nine single-phase, 17 two-phase, and nine three-phase fields. Like other thallium-containing systems, two sections are quasi-binary in the entire temperature and concentration range–Tl₂GeSe₃–CdSe where the quaternary compound Tl₂CdGeSe₄ forms, and Tl₄GeSe₄–CdSe where no new compounds were found. Investigation of the vertical section Tl₂CdGeSe₄–GeSe₂ found the formation of a new quaternary compound of approximate composition Tl₂CdGe₃Se₈. According to DTA data, its melting point is 835 K as seen in the respective endothermal effect (Figure 2).



Figure 1. Isothermal section of the quasi-ternary system Tl₂Se–CdSe–GeSe₂ at 570 K [9].



Figure 2. DTA curve of the Tl₂CdGe₃Se₈ compound and photo of this compound.

Table 1. Peritectic formation temperatures of the 2-1-1-4 compounds.

Compound	Temperature, K	Compound	Temperature, K
Tl2HgSiS4	654	Tl ₂ PbSiS ₄	818
Tl2HgSiSe4	703	Tl ₂ PbSiSe ₄	788
Tl2HgGeS4	698	Tl2HgSnS4	718
Tl2HgGeSe4	764 (congruent)	Tl ₂ HgSnSe ₄	883
Tl2PbGeS4	781	Tl2CdGeSe4	809
Tl2PbGeSe4	710	Tl ₂ CdSnSe ₄	860

3.2. EDS Analysis

The chemical composition of the quaternary compound Tl2CdGe3Se8 that forms at the Tl₂CdGeSe₄-GeSe₂ section (1:2) was confirmed by SEM/EDS analysis of the surface of the studied sample (Figure 3). Electron photograph of the crystal chip that was used for quantitative elemental analysis is shown in Figure 3a, and EDS results are shown in Figure 3b-d. Averaged formula of the investigation of six probes is Tl1.79Cd1.00Ge2.99Se7.83, which indicates the uniformity of the sample over its surface and the composition close to Tl₂CdGe₃Se₈ (Table 2). The red square in Figure 3a shows the region where the formation of the layered structure is observed. The sample was cleaved along the *c* axis.

Unit cell parameters of the $Tl_2B^{II}D^{IV}X_4$ compounds (S.G. *I*-42*m*) on the whole agree with well-known trends and depend on the nature of constituent atoms. In the majority of cases, the increase in the atomic number and, consequently, the mass of the compound components is accompanied by the increase in atom size and compound density. The calculated density increases substantially with the molar mass in all cases of the substitution of either a two-, four-, or six-valent element.

om	Number_2	Number_3	Number_4	Number_5	Number_6	Number_7	
Гl	26.8	27.3	27.8	28.7	29	27.6	

Table 2. SEM/EDS results of the Tl₂CdGe₃Se₈ sample.

Parameter	Atom	Number_2	Number_3	Number_4	Number_5	Number_6	Number_7	Number_1_SUM
	Tl	26.8	27.3	27.8	28.7	29	27.6	27.8667
Wt.%	Cd	8.2	8.8	7.7	9.5	8.3	9.1	8.6000
	Ge	16.8	15.8	17	16.9	15.9	16.7	16.5167
	Se	48.2	48.1	47.5	44.9	46.7	46.6	47.0000
	Tl	1.7975	1.7063	1.9857	1.6616	1.9216	1.6682	1.7901
At.%, n	Cd	1.0000	1.0001	1.0000	1.0000	0.9999	1.0000	1.0000
	Ge	3.1717	2.7798	3.4179	2.7541	2.9656	2.8412	2.9884
	Se	8.3679	7.7820	8.7820	6.7287	8.0097	7.2906	7.8268



Figure 3. SEM/EDS results of the Tl₂CdGe₃Se₈ sample: microphotograph of the sample chip (**a**), EDS results with general mapping, element mapping, elemental composition (**b**–**d**).

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