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New Quaternary Chalcogenides $Tl_2M^{II}M^{IV}_3Se_8$ and $Tl_2M^{II}M^{IV}X_4$

Hadj Bellagra[1], Oksana Nyhmatullina[2], Yuri Kogut[1], Halyna Myronchuk[2], Lyudmyla Piskach[1]*

[1] Eastern European National University, Department of Chemistry, Voli Ave. 13, Lutsk 43025, Ukraine;
[2] Eastern European National University, Department of Ecology, Voli Ave. 13, Lutsk 43025, Ukraine;
* Correspondence: lyuda0760@ukr.net ; Tel.: +380-50-911-1265
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Abstract: New quaternary thallium-containing chalcogenides $Tl_2M^{II}M^{IV}_3X_8$ and $Tl_2M^{II}M^{IV}X_4$ were synthesized, and their crystal structure was determined by XRD. Three $Tl_2M^{II}M^{IV}_3X_8$ chalcogenides crystallize in orthorhombic symmetry (S.G. $P2_12_12_1$; $Tl_2CdGe_3Se_8$ lattice parameters a=0.76023(9), b=1.2071(2), c=1.7474(2) nm), eight isostructural $Tl_2B^{II}D^{IV}X_4$ compounds crystallize in tetragonal symmetry, S.G. I-42m. These compounds form in the quasi-ternary systems Tl_2X–$M^{II}X$–$M^{IV}X_2$ (X – S, Se, Te) at the component ratio 1:1:1 and 1:1:3 at the sections $Tl_2M^{IV}X_3$–$B^{II}X$ and $Tl_2M^{II}M^{IV}X_4$–$M^{IV}X_2$, respectively. The composition of the $Tl_2CdGe_3Se_8$ 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, $Tl_2HgSi(Ge,Sn)S_4$, $Tl_2PbSi(Ge)S_4$, $Tl_2CdSi(Ge,Sn)Se_4$, $Tl_2HgSi(Ge,Sn)Se_4$, $Tl_2PbSi(Ge)Se_4$, was found in the investigation of sulfur- and selenium-containing quasi-ternary systems Tl_2X–$M^{II}X$–$M^{IV}X_2$ by XRD and DTA methods along the $Tl_2M^{IV}X_3$–$M^{II}X$ sections. The structure of six of them ($Tl_2HgSi(Ge, Sn)Se_4$, Tl_2HgSnS_4, $Tl_2CdGe(Sn)Se_4$) and their two analogs $Tl_2Cd(Hg)SiTe_4$ was determined in the isotropic approximation within the $Tl_2HgGeTe_4$ structure (S.G. I-42m) as a model. Along with 5 other tellurides $Tl_2M^{II}M^{IV}Te_4$ (M^{II} – Mn, Cd, Hg; M^{IV} – Si, Ge, Sn), these were reported in [1]. Pb-containing compounds Tl_2PbSiS_4 and Tl_2PbGeS_4 are isostructural and crystallize in the monoclinic structure, S.G. $P2_1/a$).

A large number of the compounds of this type with Cu, Ag and alkali metals are known, e.g. $Li_2CdGeSe_4$, $Li_2CdSnSe_4$, Cu_2CdSnS_4, $Cu_2CdGeSe_4$, Ag_2FeSnS_4. They belong to diamond-like semiconductors and have already found applications in non-linear optics and other fields of semiconductor technology, have 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 (ПГ $P2_12_12_1$: та $Cs_2ZnGe_3Te_8$, $Cs_2CdGe_3S_8$, $Cs_2CdGe_3Se_8$ [4]), monoclinic (ПГ $P2_1/a$: $Cs_2ZnGe_3S_8$, α-$K_2ZnSn_3S_8$, [4-6]), and tetragonal structures (*ПГ* $I4_1/a$: $Cu_2FeSn_3S_8$, $Cu_2CdSn_3S_8$ [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/hr, 12 hr exposure; heating to 1333 K at the rate of 10 K/hr, 7 hr exposure; cooling to 773 K at the rate of 6 K/hr; homogenizing annealing at this temperature for 350 hrs. Finally, the ampoules were quenched into 20 % aqueous saline solution.

Powder patterns for the determination of the phase composition of the synthesized samples $Tl_2ZnGe_3Se_8$, $Tl_2CdGe_3Se_8$ and $Tl_2HgGe_3Se_8$ were recorded at a DRON 4-13 diffractometer, Cu Kα radiation, 2θ range 10°≤ 2θ ≤80°, scan step 0.05°, 5 s exposure in each point. Data sets for structure computation were recorded in the2θ range of 10°≤2θ≤100°, 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 $Tl_2CdGe_3Se_8$ compound was additionally confirmed by SEM and EDS at a Tescan Vega 3 LMU scanning microscope (Tescan Brno s.r.o., Czech Republic) equipped with Oxford Instruments Aztec ONE X-ray microanalyzer with X-Max^{N}20 deterctor (accelerating voltage 25 kV; K-, L- and M-lines of the spectrum; magnification x1000).

3. Results and discussion

3.1. Phase equilibria in the Tl_2Se–CdSe– $GeSe_2$ system

Isothermal sections of 14 quasi-ternary systems Tl_2X–$M^{II}X$–$M^{IV}X_2$ (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, $Tl_2HgSi(Ge,Sn)S_4$, $Tl_2PbSi(Ge)S_4$, $Tl_2CdGe(Sn)Se_4$, $Tl_2HgSi(Ge,Sn)Se_4$, $Tl_2PbSi(Ge)Se_4$. According to DTA results, they all form incongruently (formation temperatures are listed in Table 1). Additionally, 7 compounds of the 2-1-3-8 composition were found, $Tl_2CdGe_3Se_8$, $Tl_2HgSi(Ge)_3S_8$, $Tl_2HgSi(Ge)_3Se_8$ $Tl_2PbSi(Ge)_3S_8$. Two analogous quaternary tellurides $Tl_2Cd(Hg)SiTe_4$ were also obtained.

Isothermal section of the Tl_2Se–CdSe–$GeSe_2$ system at 570 K is shown in Figure 1. The system at the annealing temperature features in the state of thermodynamic equilibrium 9 single-phase, 17 two-phase and 9 three-phase fields. Like other thallium-containing systems, two sections are quasi-binary in the entire temperature and concentration range, Tl_2GeSe_3–CdSe where the quaternary compound $Tl_2CdGeSe_4$ forms, and Tl_4GeSe_4–CdSe where no new compounds were found. Investigation of the vertical section $Tl_2CdGeSe_4$–$GeSe_2$ found the formation of a new quaternary compound of approximate composition ~ $Tl_2CdGe_3Se_8$. According to DTA data, its melting point is 835 K as seen in the respective endothermal effect (Figure 2).

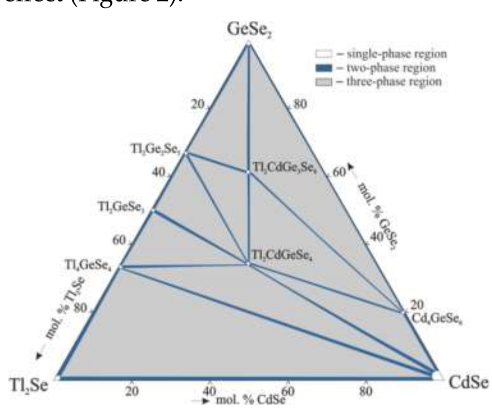

Figure 1. Isothermal section of the quasi-ternary system Tl_2Se–CdSe–$GeSe_2$ at 570 K [9].

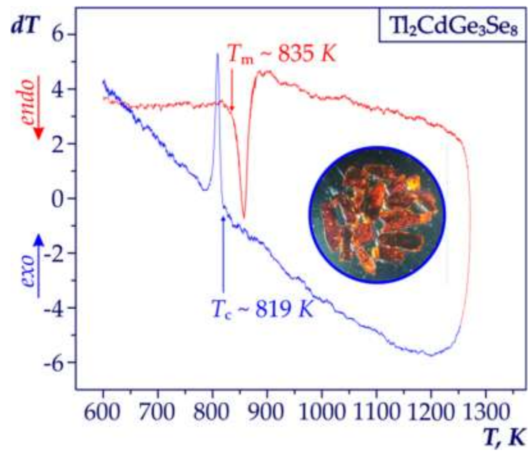

Figure 2. DTA curve of the $Tl_2CdGe_3Se_8$ compound and photo of this compound.

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

Compound	Temperature, K	Compound	Temperature, K
Tl2HgSiS4	654	Tl2PbSiS4	818
Tl2HgSiSe4	703	Tl2PbSiSe4	788
Tl2HgGeS4	698	Tl2HgSnS4	718
Tl2HgGeSe4	764 (congruent)	Tl2HgSnSe4	883
Tl2PbGeS4	781	Tl2CdGeSe4	809
Tl2PbGeSe4	710	Tl2CdSnSe4	860

3.2. EDS analysis

The chemical composition of the quaternary compound $Tl_2CdGe_3Se_8$ that forms at the $Tl_2CdGeSe_4$–$GeSe_2$ 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, c, d. Averaged formula of the investigation of 6 probes is $Tl_{1.79}Cd_{1.00}Ge_{2.99}Se_{7.83}$, which indicates the uniformity of the sample over its surface and the composition close to $Tl_2CdGe_3Se_8$ (Table 2). Red square in Figure 3a shows the region where the formation of the layered structure is observed. The sample was cleaved along ***c*** axis**.**

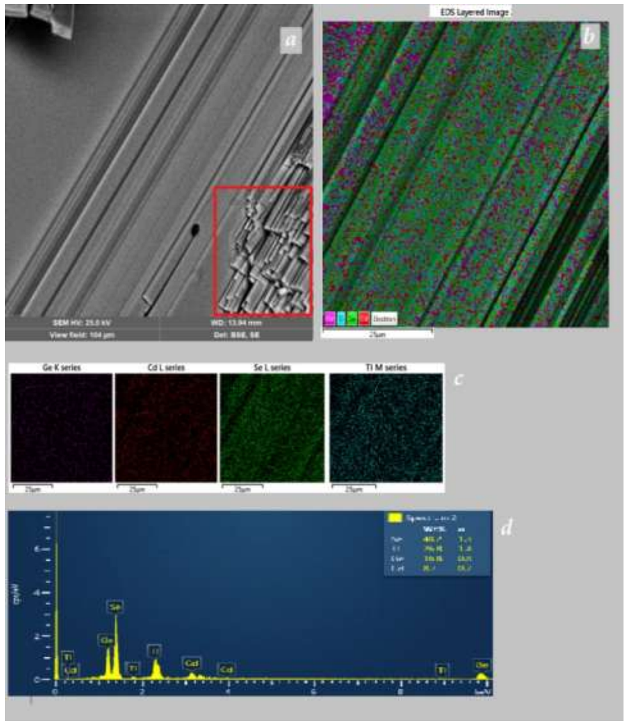

Figure 3. SEM/EDS results of the $Tl_2CdGe_3Se_8$ sample: microphotograph of the sample chip (***a***), EDS results with general mapping, element mapping, elemental composition (***b, c, d***).

Table 2. SEM/EDS results of the $Tl_2CdGe_3Se_8$ sample.

Parameter	**Atom**	**Number_2**	**Number_3**	**Number_4**	**Number_5**	**Number_6**	**Number_7**	**Number_1_SUM**
Wt.%	Tl	26.8	27.3	27.8	28.7	29	27.6	**27.8667**
	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**
At.%, n	Tl	1.7975	1.7063	1.9857	1.6616	1.9216	1.6682	**1.7901**
	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**

Supplementary

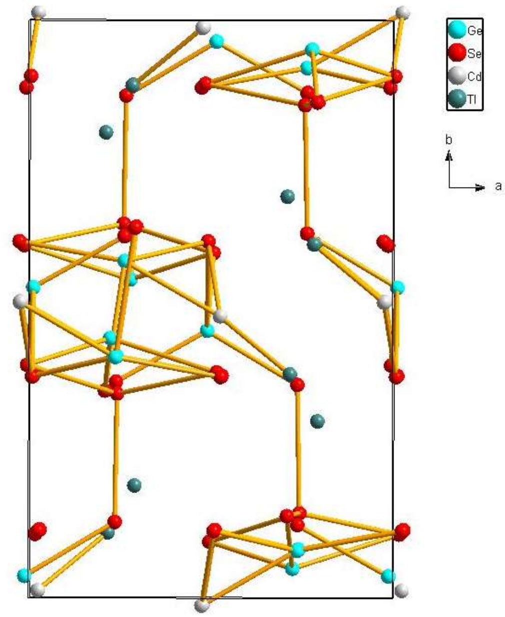

Figure 4. Crystal structure of the $Tl_2CdGe_3Se_8$ compound along ***0z*** axis.

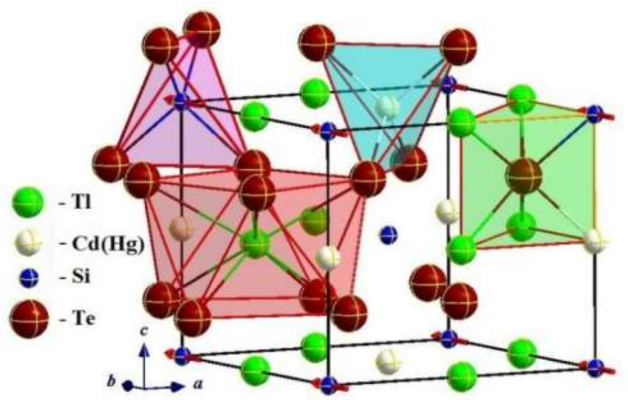

Figure 5. Coordination polyhedra of atoms in the $Tl_2M^{II} M^{IV}X_4$ structure.

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 of the atomic number and consequently mass of the compound components is accompanied by the increase of atom size and compound density. The calculated density increases substantially with the molar mass in all cases of the substitution of either two-, four-, or six-valent element.

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