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Quaternary Chalcogenide Semiconductors $Tl_2M^{II}M^{IV}{}_3Se_8$ and $Tl_2M^{II}M^{IV}X_4$

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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.

Results and Discussion

Phase equilibria

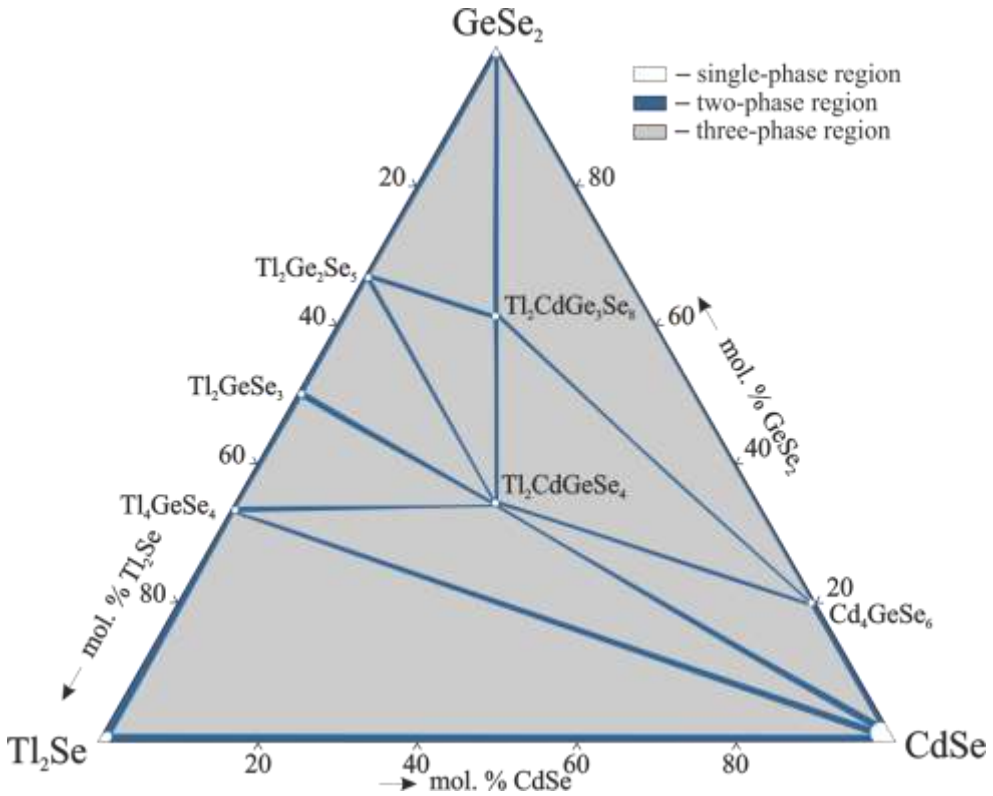

Fig. 1. Isothermal section of the quasi-ternary system Tl_2Se–CdSe–$GeSe_2$ at 570 K.

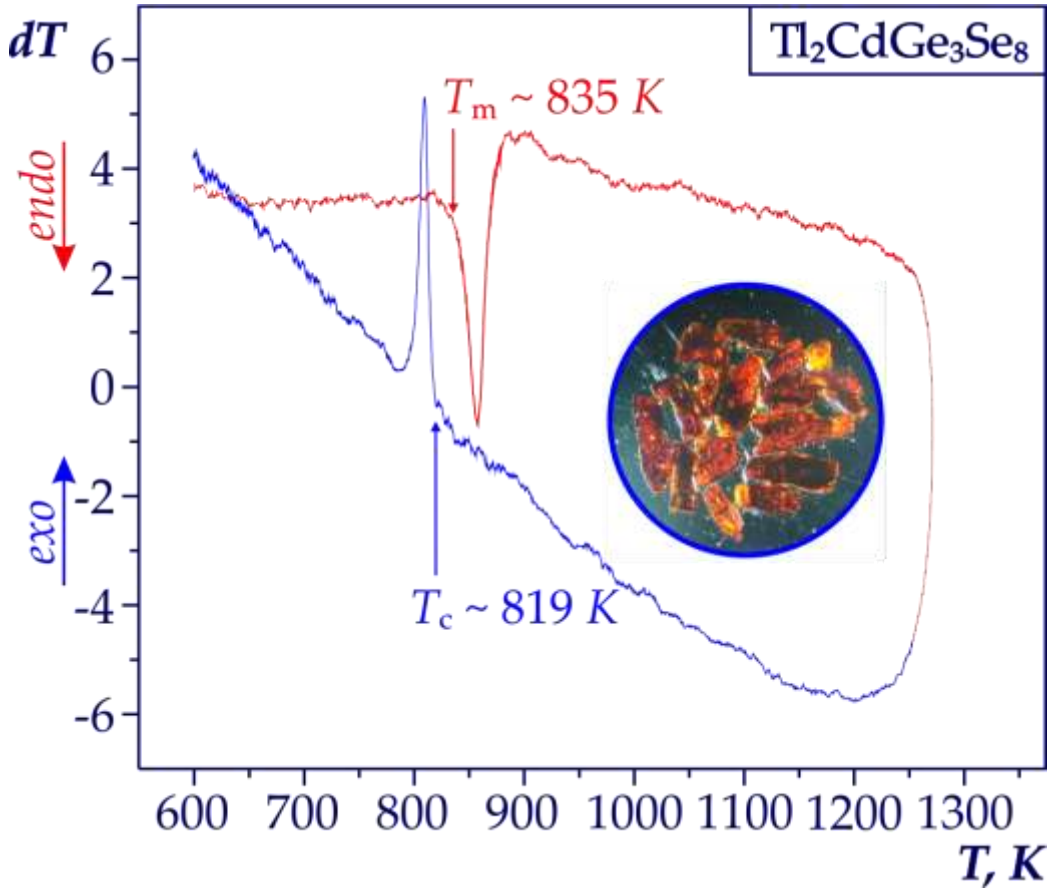

Fig. 2. DTA curve of the $Tl_2CdGe_3Se_8$ compound and photo of this compound

EDS analysis

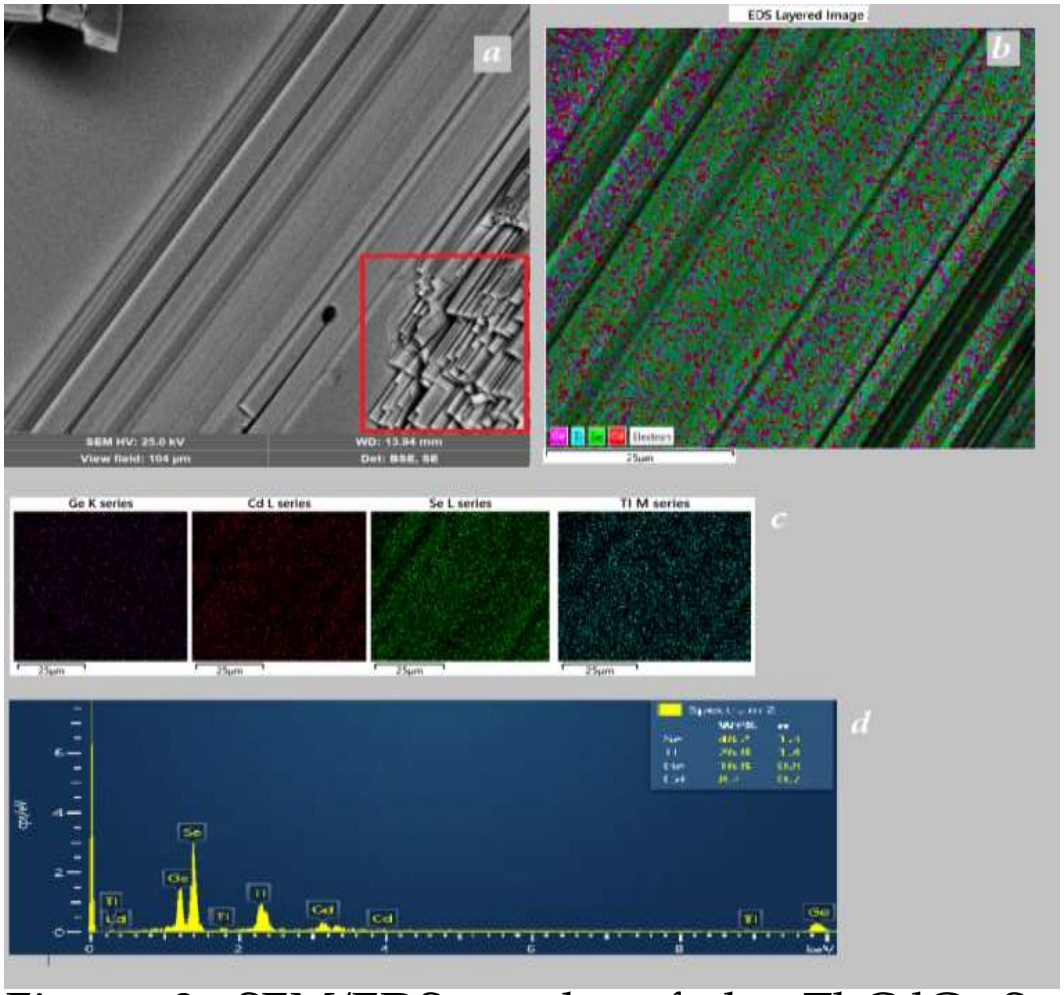

Figure 3. SEM/EDS results of the $Tl_2CdGe_3Se_8$ sample: microphotograph of the sample chip (***a***), EDS results with general mapping, element mapping, elemental composition (***b, c, d***)

Averaged formula of the investigation of 6 probes is $Tl_{1.79}Cd_{1.00}Ge_{2.99}Se_{7.83}$, which is fairly close to $Tl_2CdGe_3Se_8$.

Red square in Figure 3a shows the region where the formation of the layered structure is observed.

Crystal structure

Empirical formula	$Tl_2CdGe_3Se_8$
Space group	$P2_12_12_1$
Unit cell dimensions:	
a (nm)	0.76023(9)
b (nm)	1.2071(2)
c (nm)	1.7474(2)
V (nm^3)	1.6036(6)
F(000) (electrons)	2312.0
Number of atoms in cell	56.0
Calculated density (g/cm^3)	5.676(2)
Absorption coefficient (1/cm)	794.03
Radiation and wavelenght	CuK_α 1.54185
Diffractometer	Powder
Mode of refinement	Full profile
Number of atom sites	14
Number of free parameters	58
2θ and sinθ/l (max)	100.05 0.497
h(min), k(min), l(min)	0 0 0
h(max), k(max), l(max)	7 11 17
Number of atom sites	14
R_I	0.1204
R_P	0.2783
Scale factor	1.98(6)
Texture axis and parameter	58
Number of free parameters	[0 1 0] 0.134(5)

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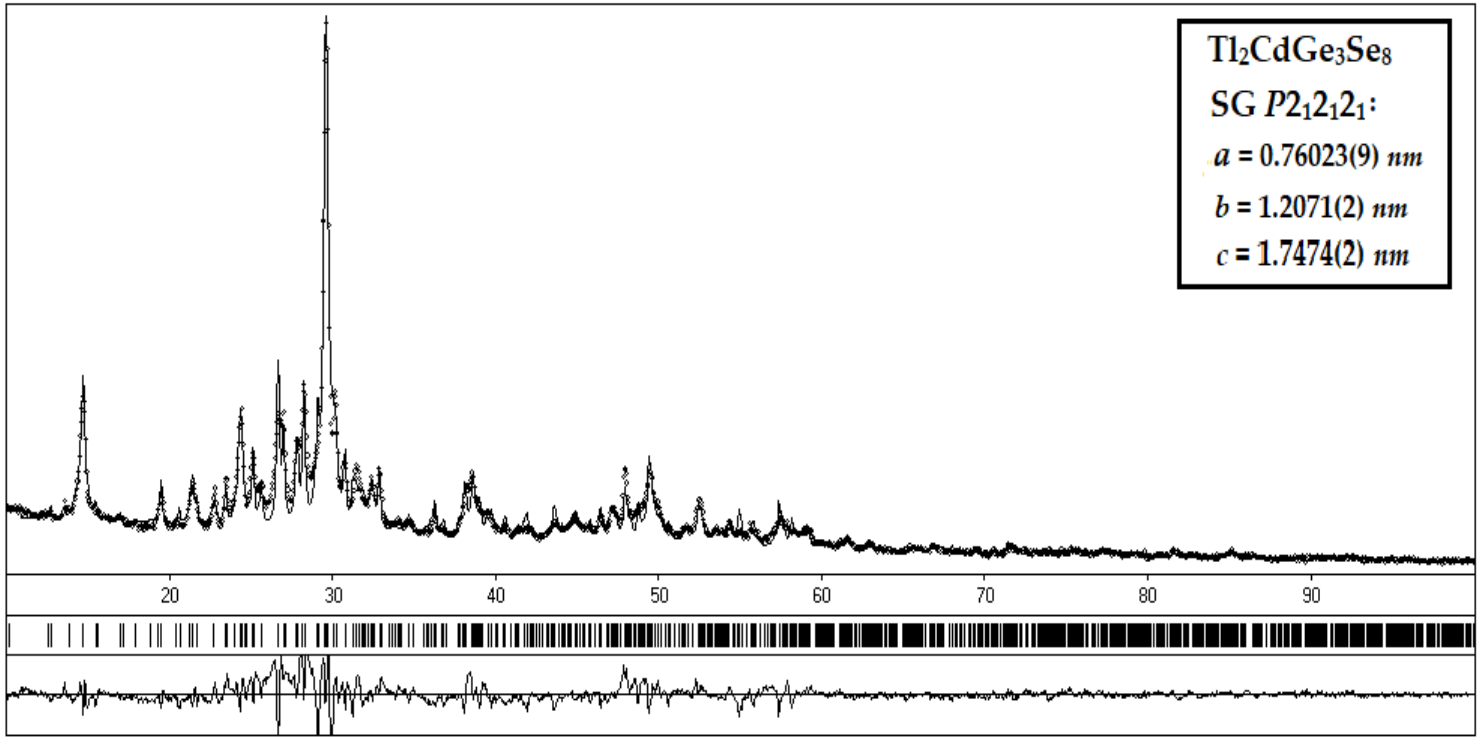
Atoms coordinates and isotropic temperature displacement parameters in the $Tl_2CdGe_3Se_8$ structure

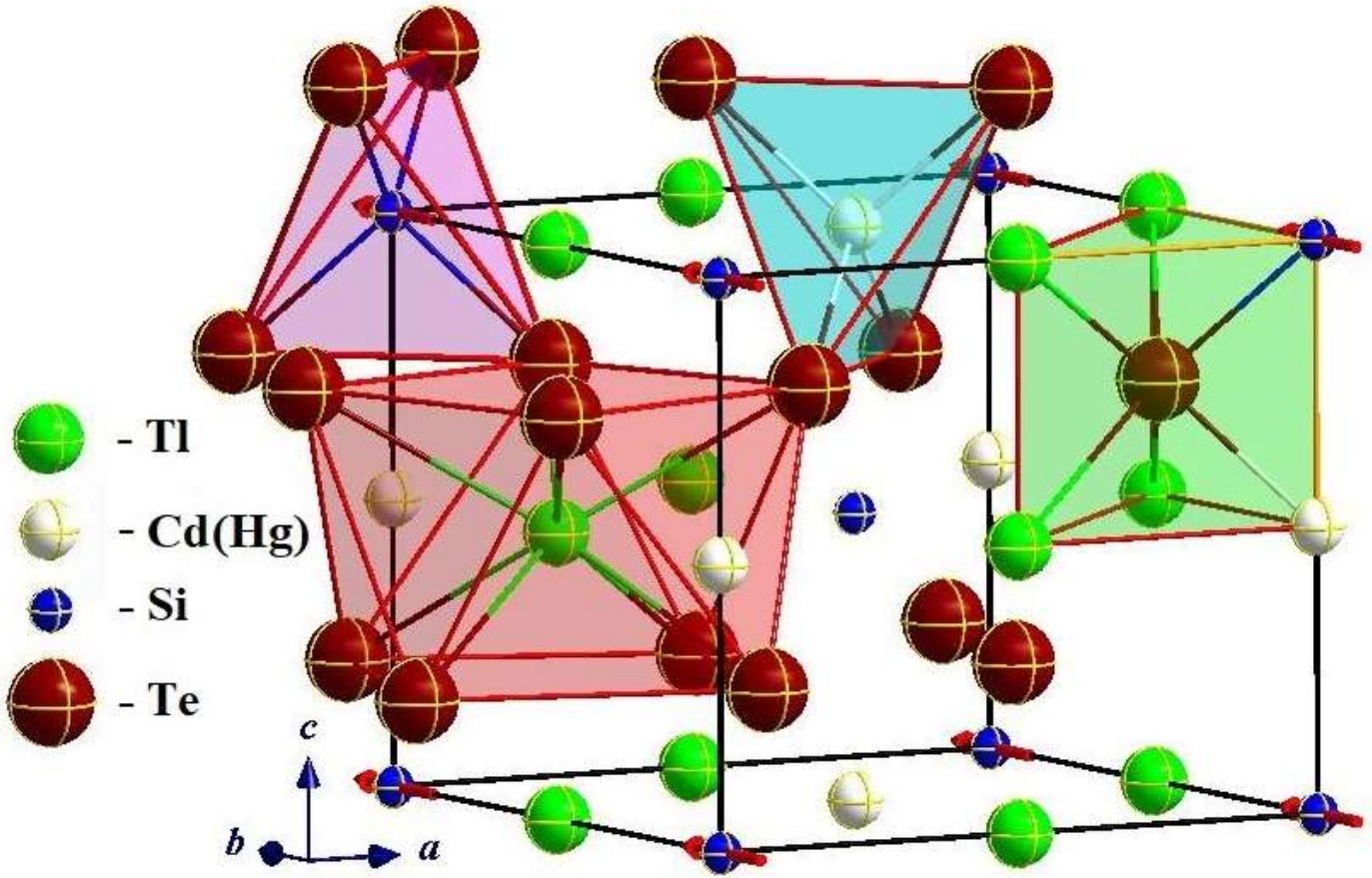
Atom	*x/a*	*y/b*	*z/c*	B(is/eq)×10², nm²	N
Ge1	0.512(4)	0.9622(12)	0.162(2)	1.37(8)	4
Ge2	0.762(5)	0.9173(11)	0.4877(12)	1.41(8)	4
Ge3	0.777(4)	0.9496(12)	0.8254(13)	1.57(8)	4
Se1	0.484(4)	0.8903(14)	0.7767(12)	1.75(8)	4
Se2	0.995(4)	0.4034(12)	0.7412(12)	1.87(8)	4
Se3	0.262(4)	0.6263(10)	0.8461(12)	1.20(8)	4
Se4	0.764(3)	0.6314(10)	0.8456(13)	1.43(8)	4
Se5	0.973(3)	0.6168(12)	0.4835(12)	0.88(8)	4
Se6	0.009(3)	0.3833(11)	0.9433(13	1.52(8)	4
Se7	0.792(3)	0.8585(11)	0.9563(12)	1.54(8)	4
Se8	0.758(4)	0.8535(10)	0.3510(14)	1.81(8)	4
Cd	0.476(3)	0.9874(9)	0.6677(10)	1.45(8)	4
Tl1	0.284(2)	0.8871(6)	0.9490(6)	3.30(8)	4
Tl2	0.7094(14)	0.6949(6)	0.6650(7)	2.39(7)	4

Experimental and calculated diffraction patterns and their difference for $Tl_2CdGe_3Se_8$



Crystal structure of the $Tl_2M^{II}M^{IV}X_4$ compounds

Obtained quaternary equimolar 2-1-1-4 compounds ($Tl_2CdGe(Sn)Se_4$, Tl_2HgSnS_4, $Tl_2HgSi(Ge, Sn)Se_4$ and $Tl_2Cd(Hg)SiTe_4$) are isostructural and crystallize in S.G. *I*-42*m*.



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