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# Crystal structure of quaternary selenides $Tl_2CdSi(Ge)_3Se_8$

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**Abstract:** Quaternary compounds $Tl_2CdSi_3Se_8$ and $Tl_2CdGe_3Se_8$ were found at the $Tl_2CdSi(Ge)Se_4$–$Si(Ge)Se_2$ sections of the quasi-ternary systems $Tl_2Se$–$CdSe$–$Si(Ge)Se_2$ at 570 K by XRD and microstructure analysis methods. Similar quaternary chalcogenides $A_{I2}B_{II}D_{IV3}X_8$ were reported earlier with alkaline elements ($A^I$ = Cs, Rb, K, Na; $B^{II}$ = Mg, Mn, Zn, Cd, Hg; $D^{IV}$ = Ge, Sn; X = S, Se, Te. Several types of crystal structures were observed in this family of compounds, orthorhombic (*S.G.* $P2_12_12_1$), monoclinic (*S.G.* $P2_1/c$ or $P2_1/n$), cubic $Pa$-3. Additionally, similar compositions $Cu(Ag)_2CdSn_3S_8$ were found in the $Cu(Ag)_2S$–$CdS$–$SnS_2$ systems. The $Cu_2CdSn_3S_8$ compound is a synthetic analoque of the natural mineral rhodostannite $Cu_2FeSn_3S_8$ and crystallizes in the tetragonal *S.G.* $I4_1/a$. The $Ag_2CdSn_3S_8$ crystal structure refines well in both tetragonal rhodostannite type (*S.G.* $I4_1/a$, $R_I$=0.0750) and cubic chalcospinel type (*S.G.* $Fd$–$3m$; $a$=1.07635(2) *nm*, $R_I$=0.0781). The $Tl_2CdD^{IV}{}_3X_8$ compounds ($M^{IV}$ = Si, Ge; X = Se) are closer to the quaternary phases with alkaline metals with orthorhombic structure. Their structure was determined in the isotropic approximation using the $Cs_2CdGe_3Se_8$ structure as a model, *S.G.* $P2_12_12_1$ with the lattice parameters $a$=0.7485(1), $b$=1.2117(3), $c$=1.7134(3) *nm*, $R_I$= 0.0953 ($Tl_2CdSi_3Se_8$) and $a$=0.7602(3), $b$=1.2071(2), $c$=1.7474(2) nm, $R_I$=0.1204 ($Tl_2CdGe_3Se_8$). Each layer $2/_\infty[CdD^{IV}{}_3Se_8]^{2-}$ consists of chains $1/_\infty[CdD^{IV}Se_6]^{6-}$ that are linked by alternating $[CdSe_4]$ and $[D^{IV}Se_4]$ tetrahedra by corner sharing along the direction $a$. Moreover, the adjacent chains are connected into a layer by $[D^{IV}{}_2Se_6]^{4-}$ dimers by corner sharing along the direction $c$.

**Keywords:** quaternary chalcogenides; SEM/EDX; crystal structure, phase equilibria.

# 3. Results and Discussion

*3.1. Phase equilibria in the $Tl_2Se$–CdSe–$SiSe_2$ system*

Isothermal section of the $Tl_2Se$–CdSe–$SiSe_2$ system at 570 K was investigated by X-ray diffraction and microstructure analysis (Figure 1). The section consists of 9 single-phase, 16 two-phase and 9 three-phase fields. The studied isothermal section is similar to that of the germanium-containing $Tl_2Se$–CdSe–$GeSe_2$ system [1] due to the presence of analogous compounds.

Each system features two quaternary compounds of the compositions 2-1-1-4 and 2-1-3-8. $Tl_2CdSi_3Se_8$ and $Tl_2CdGe_3Se_8$ form at the $Tl_2CdSi(Ge)Se_4$–$Si(Ge)Se_2$ sections.

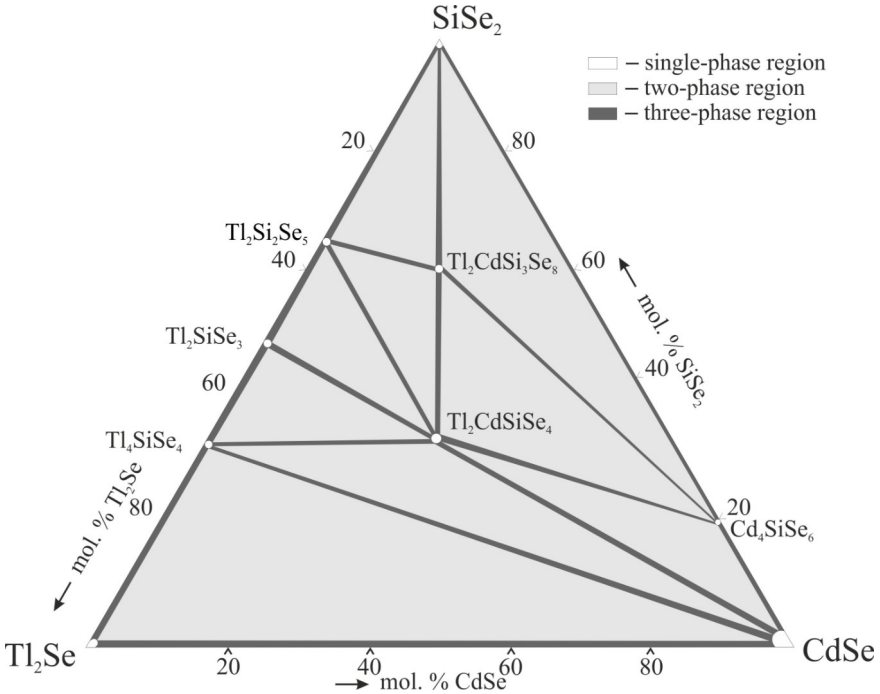



**Figure 1.** Isothermal section of the $Tl_2Se$–CdSe–$SiSe_2$ system at 570 K


[1] Selezen A.O., Olekseyuk I.D., Myronchuk G.L., Smitiukh O.V., Piskach L.V., Synthesis and structure of the new semiconductor compounds $Tl_2B^{II}D^{IV}X_4$ ($B^{II}$ – Cd, Hg; $D^{IV}$– Si, Ge; X – Se, Te) and isothermal sections of the $Tl_2Se$–CdSe-Ge(Sn)$Se_2$ systems at 570 K. *J. Solid State Chem.* 2020, 289, 121422. doi: 10.1016/j.jssc.2020.121422

### *3.2. Crystal structure of the $Tl_2CdSi(Ge)_3Se_8$ compounds*

According to XRD results (Figure 2), $Tl_2CdSi(Ge)_3Se_8$ crystallize in non-centrosymmetric space group $P2_12_12_1$ (№ 19), structure type $Cs_2HgGe_3Se_8$, with the lattice parameters $a$=0.7485(1), $b$=1.2117(3), $c$=1.7134(3) *nm* ($Tl_2CdSi_3Se_8$) and $a$=0.7602(3), $b$=1.2071(2), $c$=1.7474(2) *nm* ($Tl_2CdGe_3Se_8$).

The $Tl_2CdSi_3Se_8$ crystals are yellow (Figure 3, *a*) and $Tl_2CdGe_3Se_8$ are red (Figure 3, *b*).

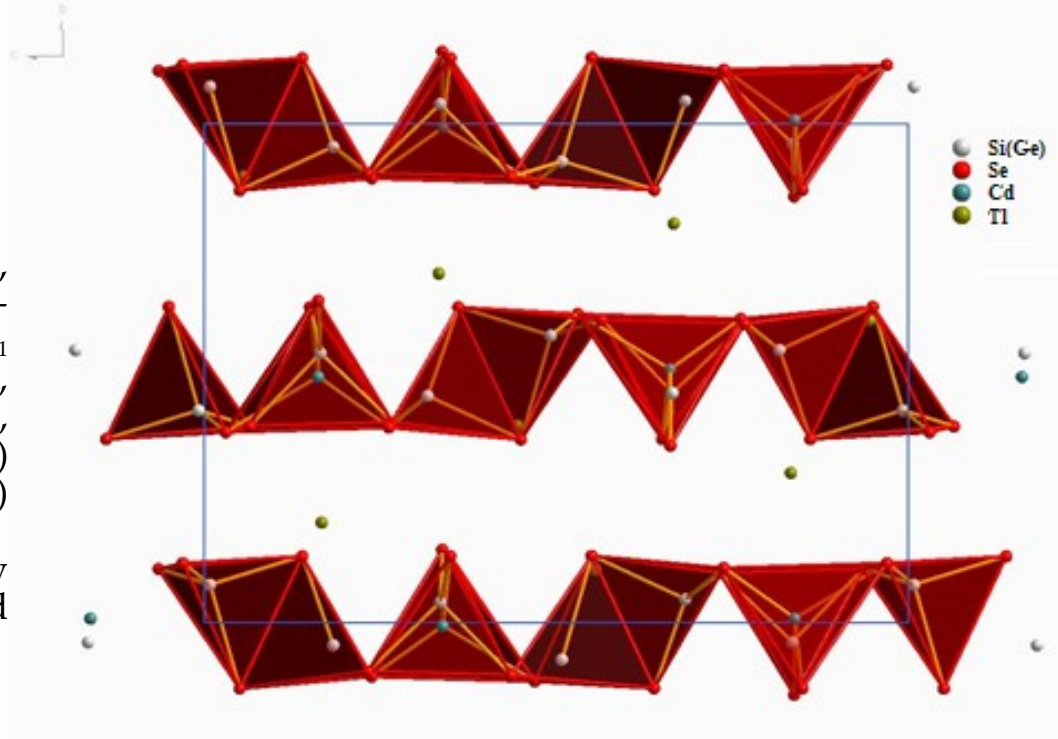
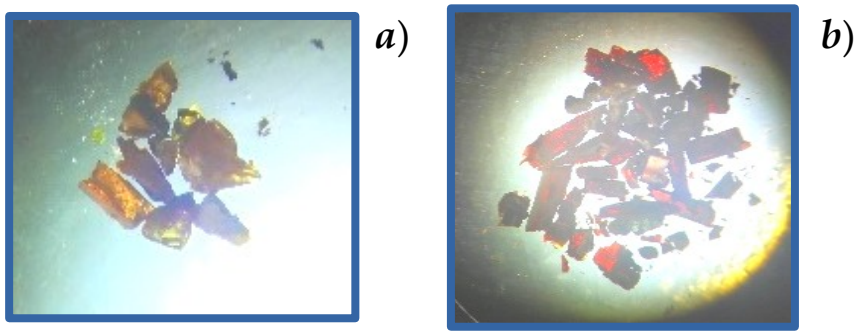



**Figure 2.** Кристалічна структура сполук $Tl_2CdSi(Ge)_3Se_8$



***a***) ***b***)

**Figure 3.** Photo of the crystals of $Tl_2CdSi_3Se_8$ (***a***) and $Tl_2CdGe_3Se_8$ (***b***) compounds.

*3.3. EDS analysis*

Microphotograph of the $Tl_2CdSi_3Se_8$ *and* $Tl_2CdGe_3Se_8$ crystals used for quantitative elemental analysis and EDS results are shown in Figures 3, 4. The composition averaged over six samples is $Tl_2Cd_{1.2}Si_{3.17}Se_{8.4}$ which indicates the uniformity of the sample over its surface and is close to $Tl_2CdSi_3Se_8$ and $Tl_{1.79}Cd_{1.00}Ge_{2.99}Se_{7.83}$ for $Tl_2CdGe_3Se_8$ [2].

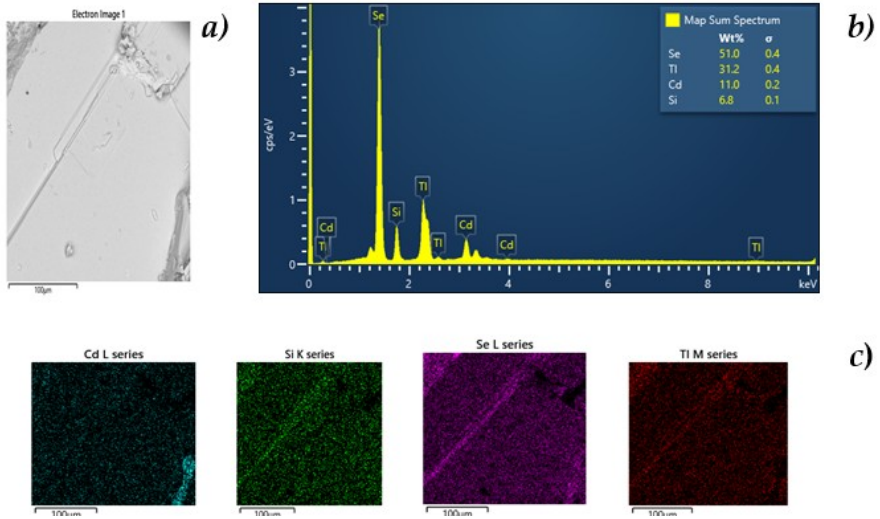



**Figure 3.** Microphotograph (*a*), EDS results (*b*) and mapping of elements (*c*) for the $Tl_2CdSi_3Se_8$ sample

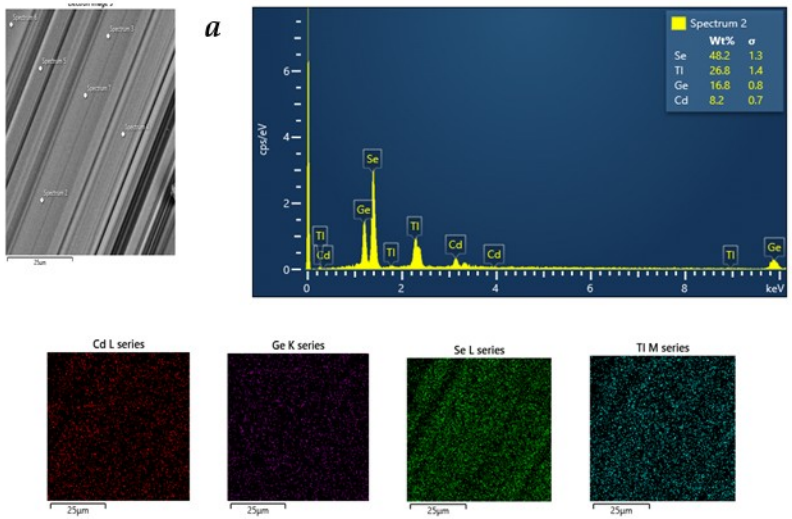



**Figure 4.** Microphotograph (*a*), EDS results (*b*) and mapping of elements (*c*) for the $Tl_2CdGe_3Se_8$ sample [2]


[2] Selezen A.O., Kogut Yu.M., Piskach L.V., Gulay L.D., New Quaternary Chalcogenides $Tl_2M^{II}M^{IV}{}_3Se_8$ and $Tl_2M^{II}M^{IV}X_4$. Presented at the 2nd International Electronic Conference on Crystals, 10–20 November 2020; Available online: https://iocc_2020.sciforum.net/.

# Conclusions

1. Isothermal section of the $Tl_2Se$–$CdSe$–$SiSe_2$ system at 570 K was investigated by X-ray diffraction and microstructure analysis.

2. Quaternary compounds $Tl_2CdSi_3Se_8$ and $Tl_2CdGe_3Se_8$ were found at the $Tl_2CdSi(Ge)Se_4$–$Si(Ge)Se_2$ sections of the quasi-ternary systems $Tl_2Se$–$CdSe$–$Si(Ge)Se_2$ at 570 K by XRD and microstructure analysis methods.

3. The $Tl_2CdD^{IV}{}_3X_8$ compounds ($M^{IV}$ = Si, Ge; X = Se) are closer to the quaternary phases with alkaline metals with orthorhombic structure. Their structure was determined in the isotropic approximation using the $Cs_2CdGe_3Se_8$ structure as a model, *S.G.* $P2_12_12_1$ with the lattice parameters $a$=0.7485(1), $b$=1.2117(3), $c$=1.7134(3) *nm*, $R_I$= 0.0953 ($Tl_2CdSi_3Se_8$) and $a$=0.7602(3), $b$=1.2071(2), $c$=1.7474(2) nm, $R_I$=0.1204 ($Tl_2CdGe_3Se_8$).

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