

Physico-chemical interaction in the $Tl_2Se-SnSe-PbSe$ quasiternary system

M.J. FILEP^{1*}, M.Yu. SABOV¹, I.E. BARCHIY¹

¹ Department of Chemistry, Uzhgorod National University,
Pidgirna St. 46, 88000 Uzhgorod, Ukraine

* Corresponding author. Tel.: +380-3122-37163; fax: +380-3122-35091; e-mail: mfilep23@mail.ru

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The physico-chemical interaction in the $Tl_2Se-SnSe-PbSe$ quasiternary system was investigated by differential thermal analysis and X-ray diffraction in combination with mathematical modeling. Diagrams of the phase interaction, the projection of the liquidus surface and an isothermal section (520 K) were constructed. The quasiternary system is of the invariant eutectic type. The three-dimensional one-, two- and three-phase regions present in the $Tl_2Se-SnSe-PbSe$ system are described.

Triangulation / Thermal analysis / X-ray diffraction/ Phase diagram / Isothermal section

Introduction

The $Tl_2Se-SnSe-PbSe$ quasiternary system was investigated by Guseinov *et al.* [1]. However, the authors did not take into consideration the formation in the $Tl_2Se-Sn(Pb)Se$ system of the ternary compounds Tl_4SnSe_3 and Tl_4PbSe_3 , which melt congruently [2-6]. The two ternary compounds are isostructural, which indicates high probability of formation of a solid solution. The good thermoelectric properties of Tl_4SnSe_3 and Tl_4PbSe_3 provide the motivation for an investigation of the character of the physico-chemical interaction in the $Tl_2Se-SnSe-PbSe$ quasiternary system.

Experimental

Binary thallium(I), tin(II) and lead(II) selenides were prepared from stoichiometric amounts of high-purity elements (99.99 wt.%) in evacuated quartz containers. The ternary compounds Tl_4SnSe_3 and Tl_4PbSe_3 were obtained from stoichiometric amounts of binary Tl_2Se , $SnSe$ and $PbSe$. The multicomponent alloys were synthesized by the direct single-temperature method from binary and ternary selenides in quartz ampoules, which were evacuated to a residual pressure of 0.13 Pa. The highest synthesis temperature was 1023 K. After thermal treatment at the highest temperature for 24-36 h the samples were slowly cooled down (20-30 K per hour) to 520 K and homogenized at this temperature for 168 h. Subsequently the ampoules were quenched in cold water. The phase equilibria were studied by

differential thermal analysis (DTA) and X-ray powder diffraction in combination with the simplex method of mathematical modeling of phase equilibria in multicomponent systems. The differential thermal analysis was carried out by means of a device that includes an x-y recorder PDA-1 and a chromel-alumel combined thermocouple (the linearity of heating and cooling was controlled by a RIF-101 programmer) with an accuracy of ± 5 K. X-ray powder diffraction was carried out on a DRON-4 diffractometer (Cu $K\alpha$ radiation, Ni filter). The simplex method of computer simulation of phase equilibria has been described by Barchiy [7].

Results and discussion

Initially, we carried out a triangulation of the $Tl_2Se-SnSe-PbSe$ quasiternary system [8,9] on the basis of literature data [10]. The $SnSe-PbSe$ system is characterized by a eutectic invariant interaction. Ternary complex compounds form in the $Tl_2Se-SnSe(PbSe)$ binary systems: the phases Tl_4SnSe_3 and Tl_4PbSe_3 melt congruently at 708 K and 808 K, respectively, $Tl_2Sn_2Se_3$ melts incongruently at 683 K by the reaction $L + It-SnSe \leftrightarrow Tl_2Sn_2Se_3$, and decomposes according to $Tl_2Sn_2Se_3 \leftrightarrow Tl_4SnSe_3 + It-SnSe_2$ at low temperature (640 K) [3,5]. Using the results of XRD and the method developed by Gurtler we conclude that $Tl_4SnSe_3-Tl_4PbSe_3$ and $PbSe-Tl_4SnSe_3$ are quasibinary sections, which divide the $Tl_2Se-SnSe-PbSe$ system into separate subsystems.

The $Tl_4SnSe_3-Tl_4PbSe_3$ system belongs to the Roozeboom type IV (Fig. 1). The lines of primary

crystallization of the alloys on the bases of ε (Tl_4SnSe_3) and η (Tl_4PbSe_3) crystals cross at an invariant point with the coordinates 62 mol.% Tl_4PbSe_3 , 754 K (peritectic process $\text{L} + \eta \leftrightarrow \varepsilon$). Limited solid solutions ε (based on Tl_4SnSe_3) and η (based on Tl_4PbSe_3) are formed in the system. At the temperature of 520 K the regions of the ε - and η -solid solutions do not exceed 48 and 15 mol.%, respectively.

The $\text{PbSe}-\text{Tl}_4\text{SnSe}_3$ system belongs to the Roozeboom type V (Fig. 2) and is characterized by the formation of limited solid solutions δ (based on PbSe) and ε (based on Tl_4SnSe_3). The liquidus of the quasibinary system consists of two lines of primary crystallization, which intersect at an invariant point

with the coordinates: 12 mol.% PbSe , 690 K (eutectic process $\text{L} \leftrightarrow \delta + \varepsilon$). The extents of the δ - and ε -solid solutions at the eutectic temperature are 9 and 22 mol.% respectively; at the temperature 520 K they are 7 and 15 mol.% respectively.

Forty-two alloys were prepared for the investigation of the $\text{Tl}_2\text{Se}-\text{SnSe}-\text{PbSe}$ quasiternary system. The compositions of the alloys were selected so that they are located along the quasibinary sections $\text{Tl}_4\text{SnSe}_3-\text{Tl}_4\text{PbSe}_3$, $\text{PbSe}-\text{Tl}_4\text{SnSe}_3$, in the homogeneity regions of the binary and ternary compounds (for plotting the isothermal section), and on the simplex points (for the mathematical computer simulation of the projection of the liquidus surface on the concentration triangle).

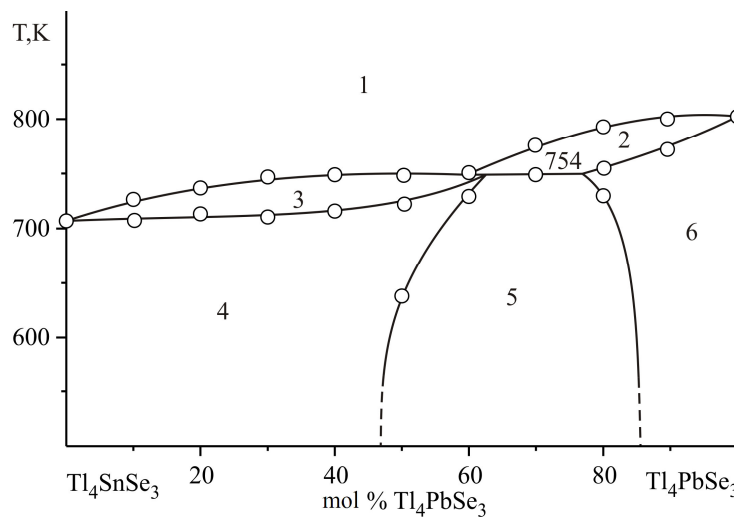


Fig. 1 Phase diagram of the $\text{Tl}_4\text{SnSe}_3-\text{Tl}_4\text{PbSe}_3$ system: 1 - L, 2 - L + η , 3 - L + ε , 4 - ε , 5 - $\varepsilon + \eta$, 6 - η .

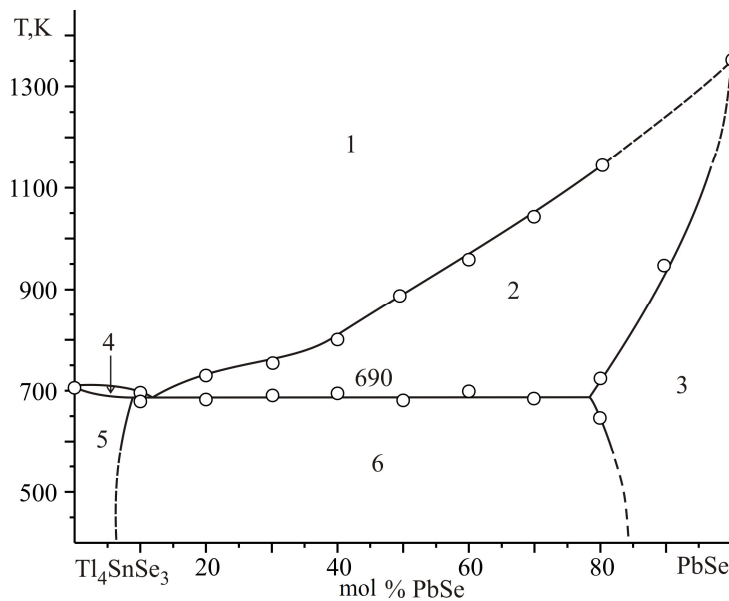


Fig. 2 Phase diagram of the $\text{PbSe}-\text{Tl}_4\text{SnSe}_3$ system: 1 - L, 2 - L + δ , 3 - δ , 4 - L + ε , 5 - ε , 6 - $\delta + \varepsilon$.

Based on the XRD results the isothermal section at 520 K of the Tl₂Se–SnSe–PbSe quasiternary system was plotted (Fig. 3). Limited solid solutions are formed in the ternary system: γ based on *lt*-SnSe, δ based on PbSe, η based on Tl₄PbSe₃, ε based on Tl₄SnSe₃. Due to the solid-phase decomposition of Tl₂Sn₂Se₃ at 640 K, only reflections of the δ -, ε -, and γ -phases are present in the diffraction patterns of the alloys in the PbSe–Tl₄SnSe₃–SnSe subsystem at 520 K.

The width of the solid solution on the basis of *lt*-SnSe (γ -phase) does not exceed 3 mol.% along the Tl₂Se–SnSe section and 18 mol.% in the SnSe–PbSe system. The largest areas of homogeneity correspond to the solid solutions ε based on Tl₄SnSe₃ and Tl₂Se (to 37 mol.% in the Tl₂Se–SnSe system, to 48 mol.% along the Tl₄SnSe₃–Tl₄PbSe₃ section, and to 7 mol.% along the PbSe–Tl₄SnSe₃ section), η based on Tl₄PbSe₃ and Tl₂Se (to 35 mol.% in the Tl₂Se–PbSe system and to 15 mol.% along the Tl₄SnSe₃–Tl₄PbSe₃ section), and δ on the basis of binary PbSe (to 10 mol.% in the Tl₂Se–PbSe system, to 23 mol.% in the SnSe–PbSe system, and to 15 mol.% along the PbSe–Tl₄SnSe₃ section).

The projection of the liquidus surface of the Tl₂Se–SnSe–PbSe quasiternary system (Fig. 4) on the concentration triangle was constructed according to

the results of the DTA investigation and computer simulation of the phase equilibria in multicomponent systems by the simplex triangle. It consists of six fields of primary crystallization: δ -crystals (PbSe–*e1*–*E1*–*e4*–*E2*–*U2*–*U1*–*e3*–PbSe), η -crystals (Tl₄PbSe₃–Tl₂Se–*p2*–*E1*–*e1*–Tl₄PbSe₃), ε -crystals (Tl₄SnSe₃–*e2*–*E2*–*e4*–*E1*–*p2*–Tl₂Se–Tl₄SnSe₃), θ -crystals on the basis of Tl₂Sn₂Se₃ (*p1*–*U2*–*E2*–*e2*–*p1*), γ -crystals on the basis of *lt*-SnSe (*m*–*U1*–*U2*–*p1*–*m*) and β -crystals on the basis of *ht*-SnSe (SnSe–*e3*–*U1*–*m*–SnSe). The fields of primary crystallization are delimited by 11 monovariant eutectic and peritectic lines. The types and temperatures of the processes in the Tl₂Se–SnSe–PbSe quasiternary system are listed in Table 1. The monovariant lines cross at two invariant peritectic and two invariant eutectic points:

U1: L + *ht*-SnSe \leftrightarrow PbSe + *lt*-SnSe, 39 mol.% Tl₂Se, 50 mol.% SnSe, 11 mol.% PbSe, 725 K;

U2: L + *lt*-SnSe \leftrightarrow Tl₂Sn₂Se₃ + PbSe, 44 mol.% Tl₂Se, 12 mol.% SnSe, 42 mol.% PbSe, 673 K;

E1: L \leftrightarrow Tl₄SnSe₃ + PbSe + Tl₂Sn₂Se₃, 60 mol.% Tl₂Se, 15 mol.% SnSe, 25 mol.% PbSe, 657 K;

E2: L \leftrightarrow Tl₄SnSe₃ + PbSe + Tl₂Sn₂Se₃, 48 mol.% Tl₂Se, 38 mol.% SnSe, 14 mol.% PbSe, 647 K.

No new compounds were observed in the Tl₂Se–SnSe–PbSe quasiternary system.

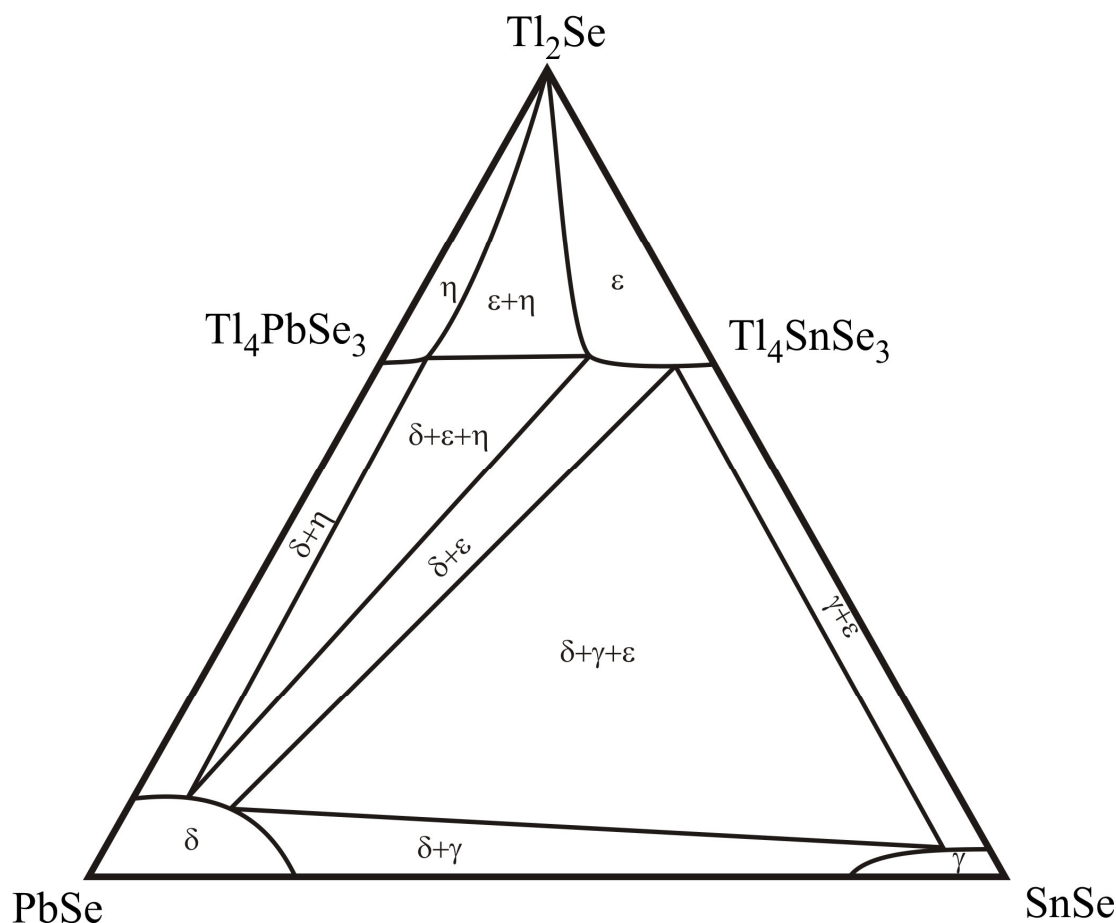


Fig. 3 Isothermal section at 520 K of the Tl₂Se–SnSe–PbSe system.

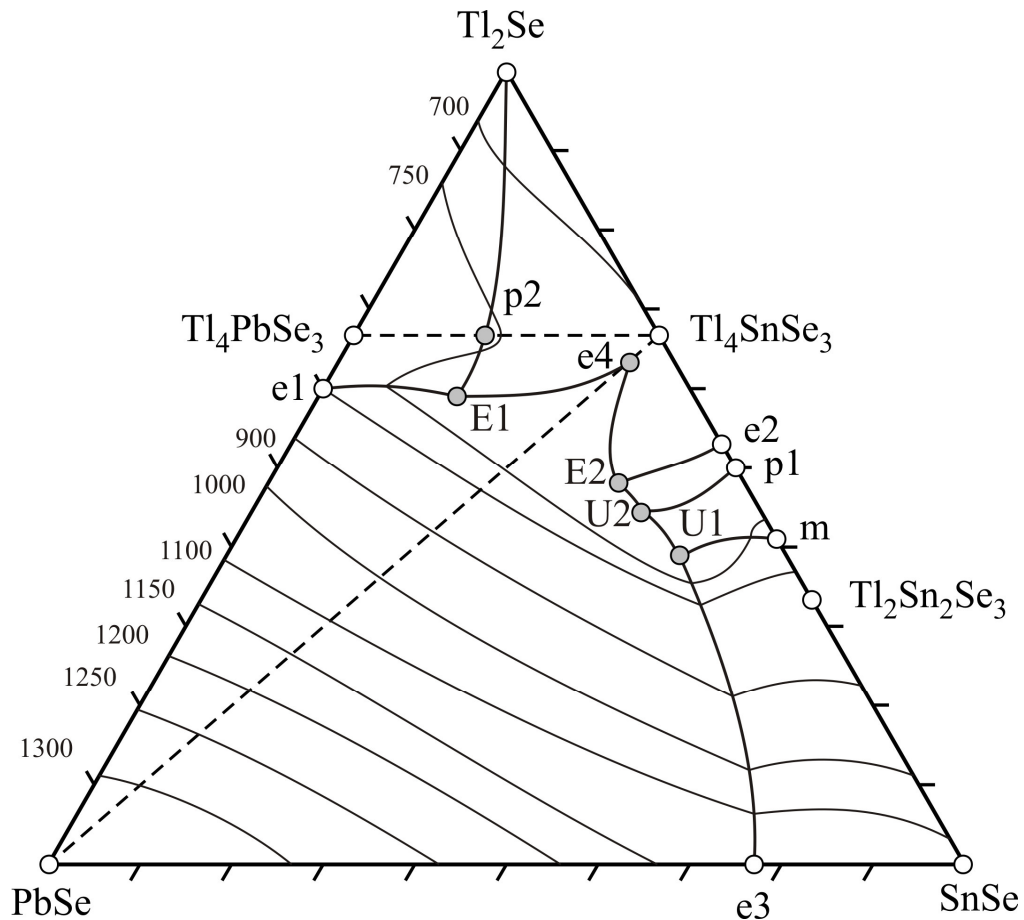


Fig. 4 Liquidus surface projection of the Tl_2Se – SnSe – PbSe system.

Table 1 Type and temperature of the processes in the system Tl_2Se – SnSe – PbSe .

Monovariant line	Process	Temperature, K
Tl_2Se -p2	$L+\eta\leftrightarrow\varepsilon$	651-754
p2-E1	$L+\eta\leftrightarrow\varepsilon$	754-657
e1-E1	$L\leftrightarrow\delta+\eta$	800-657
e4-E1	$L\leftrightarrow\delta+\varepsilon$	690-657
e4-E2	$L\leftrightarrow\delta+\varepsilon$	690-647
e2-E2	$L\leftrightarrow\varepsilon+\theta$	663-647
U2-E2	$L+\delta\leftrightarrow\gamma+\theta$	673-647
p1-U2	$L+\gamma\leftrightarrow\theta$	683-673
U1-U2	$L+\delta\leftrightarrow\gamma$	725-673
m-U1	$\beta\leftrightarrow L+\gamma$	764-725
e3-U1	$L\leftrightarrow\beta+\delta$	1131-725

Conclusions

Differential thermal analysis, X-ray diffraction and mathematical simulation of phase equilibria in multicomponent systems by the simplex method were

used to investigate the physico-chemical interaction in the Tl_2Se – SnSe – PbSe system for the first time. The character of the monovariant processes and the coordinates of the invariant processes were determined. The existence of solid solutions of the ternary compounds Tl_4SnSe_3 and Tl_4PbSe_3 was established. No new compounds were observed in the quasiternary system. The results of the investigation may be used for the synthesis of new thermoelectric materials for semiconductor technology.

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