Accepted Manuscript

Phase diagrams of novel Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 quasi-ternary system following DTA and X-ray diffraction

I.E. Barchiy, A.R. Tatzkar, A.O. Fedorchuk, K. Plucinski

PII: S0925-8388(16)30347-4

DOI: 10.1016/j.jallcom.2016.02.078

Reference: JALCOM 36689

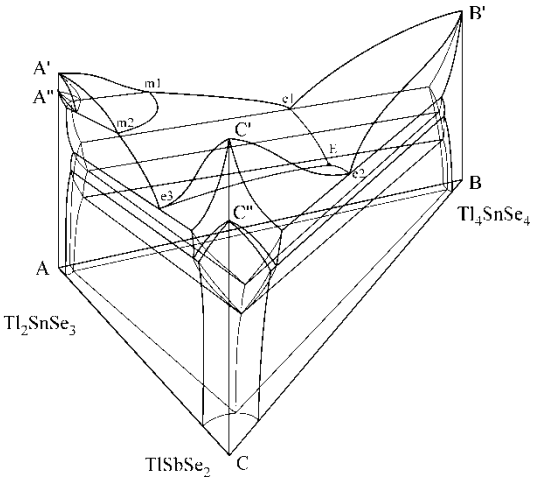
To appear in: *Journal of Alloys and Compounds*

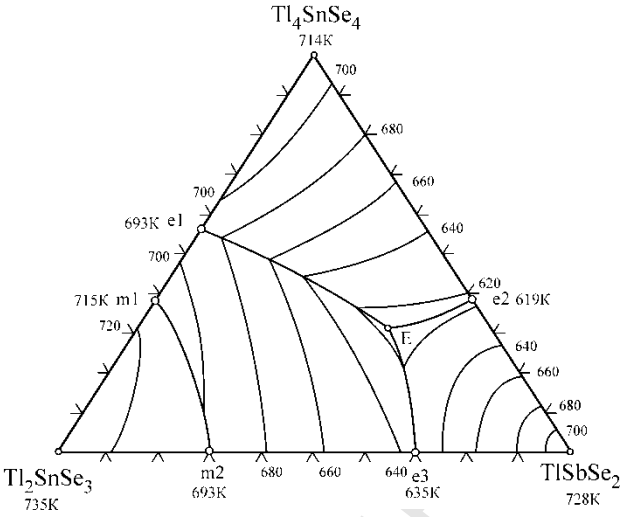
Received Date: 12 November 2015

Revised Date: 6 February 2016

Accepted Date: 8 February 2016

Please cite this article as: I.E. Barchiy, A.R. Tatzkar, A.O. Fedorchuk, K. Plucinski, Phase diagrams of novel Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 quasi-ternary system following DTA and X-ray diffraction, *Journal of Alloys and Compounds* (2016), doi: 10.1016/j.jallcom.2016.02.078.





Phase diagrams of novel Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 quasi-ternary system following DTA and X-ray diffraction

I.E. Barchiy[1], A.R. Tatzkar[1], A.O. Fedorchuk[2], K.Plucinski[3*]

[1]*Department of chemistry, Uzhgorod national university, Pidgirna St,. 46, Uzhgorod 88000, Ukraine*
[2]*Department of Inorganic and Organic Chemistry, Lviv National University of Veterinary Medicine and Biotechnologies, Pekarska St., 50, Lviv 79010, Ukraine*
[3]*IMUT Warsaw, Kaliskiego 2, 00-908, Warsaw, Poland*

** Corresponding author. e-mail: kpluc2006@wp.pl*

Abstract

Phase relation in the Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 quasiternary system were studied by the DTA and X-ray diffraction in combination with mathematical modeling. The phase diagrams of the Tl_4SnSe_4–$TlSbSe_2$ and Tl_2SnSe_3–$TlSbSe_2$ systems, the perspective views of the phase interaction in the ternary system, the liquidus surface projection, the isothermal section at 423 K were built for the first time. The Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 system is of the invariant eutectic type and is characterized by the formation of limited solid solutions following initial ternary compounds. New complex compounds are not formed.

Keywords: Thallium, Tin, Stibium, Selenide, phase diagrams, thermal analysis, X-ray diffraction, solid state reaction

1. Introduction

The one of the main tasks for the semiconductor materials science and engineering consists the development of new functional materials. Particular interest present complex Tl chalcogenide crystals and their alloy derivatives. Among them particular interest is attracted to the Tl_2Se–$SnSe_2$–Sb_2Se_3 ternary system. These ternary system are interesting for investigation due to formation of ternary compounds which reveal unusual optical, thermoelectric and photoelectrical behaviors. They have broad practical application in infrared optoelectronics, thermoelectricity, pirometry, optical triggering, gratings etc. Tl-containing structures are expected to possess low thermal conductivity due to effective scattering of phonons that are responsible for the transfer of heat in the materials. Thallium complex compounds have recently attracted interest as promising thermoelectric materials [1,2]. Thallium is similar in crystal chemical behavior to some of the alkali metals. It forms preferentially compounds in oxidation state +1 and its ionic radius is very close to the ionic radius of potassium, however the electronegativity is higher. Replacement of potassium by thallium may enhance the electrical conductivity of a compound, as a result of substantial reduction of the ionicity of the chemical bonds. Also, thallium is a heavy element and its introduction into a semiconductor will lead to a decrease of the thermal conductivity.

The Tl_2Se–$SnSe_2$ system is characterized by the formations of Tl_4SnSe_4, Tl_2SnSe_3 ternary compounds, which congruently melt at 718 K and 738 K [3-6], respectively. In the Tl_2Se–Sb_2Se_3 system there are formed two congruently melting compounds: Tl_9SbSe_6 (743 K) and $TlSb_2Se_2$ (730 K) [7-9]. The $SnSe_2$–Sb_2Se_3 system is of the eutectic type [10]. The Tl_2Se–$SnSe_2$–Sb_2Se_3 ternary system is divided into the five separate secondary subsystems Tl_2Se–Tl_4SnSe_4–Tl_9SbSe_6, Tl_4SnSe_4–$TlSbSe_2$–Tl_9SbSe_6, Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$, Tl_2SnSe_3–$TlSbSe_2$–$SnSe_2$, $SnSe_2$–$TlSbSe_2$–Sb_2Se_3 with the four quasi-binary sections Tl_4SnSe_4–Tl_9SbSe_6, Tl_4SnSe_4–$TlSbSe_2$, Tl_2SnSe_3–$TlSbSe_2$

and $SnSe_2$–$TlSbSe_2$ [12]. The knowledge of the structure plays a crucial role for the design of crystals with advanced optoelectronic features [12-17] including infrared photo-transparency, multi-photon excitation, optical modulators in the Ir spectral range. In the present work we will present the data of the DTA and X-ray diffraction studies in combination with mathematical modeling of the phase diagrams for the Tl_4SnSe_4–$TlSbSe_2$ and Tl_2SnSe_3–$TlSbSe_2$ systems. Furthermore, the perspective views of the phase interaction in the ternary system, the liquidus surface projection, the isothermal section will be explored.

2. Materials and methods

As educts we used thallium (I), tin (IV) and stibium (III) selenides. Synthesis of these binary compounds was carried out with high-purity elements (better than 99.99 wt.%). $T1_2Se$, $SnSe_2$ and Sb_2Se_3 binary compounds were prepared by the single-temperature method from stoichiometric amounts of the initial elements in evacuated quartz containers. The binary compounds were purified by zone crystallization methods. The Tl_4SnSe_4, Tl_2SnSe_3 and $TlSbSe_2$ ternary compounds were obtained from stoichiometric amounts of initial binary selenides. Identification of binary and ternary compounds was done by the DTA and X-ray analysis.

The multicomponent alloys were synthesized from ternary complex selenides in quartz ampoules evacuated to a residual pressure of 0.13 Pa. After thermal treatment at highest temperature (823 K) for 24 h the samples were slowly cooled (25-30 K per hour) down to 423 K and homogenized at this temperature for 336 hours. Subsequently the ampoules were quenched into cold water.

The phase equilibria in the ternary system were investigated by the differential thermal (DTA), X-ray powder diffraction, microstructure (MSA) analyses. More details about the performed DTA, XRD diffraction and microstructure are given in the Supplement 1. The classical methods of physico-chemical analysis were used in combination with the simplex method of mathematical modeling of phase equilibria in multicomponent systems [18]. More details about this modeling approach are given in the Supplement 2. The differential thermal analysis was carried out by means of a device including an *x-y* recorder PDA-1 and a chromelalumel thermocouple, with an accuracy of ±5 K. The samples were heated and cooled in a furnace using an RIF-101 programmer, which provided a linear temperature variation. X-ray powder diffraction was carried out on a DRON-3-13 diffractometer (Cu Kα radiation, Ni filter). Rietveld refinements of X-ray powder diffraction data were performed by using the WinCSD program [19]. The microstructure analysis was carried out with a metallographic microscope Lomo Metam R1.

3. Results and discussion

3.1. Tl_4SnSe_4–$TlSbSe_2$ quasibinary system

Tl_4SnSe_4–$TlSbSe_2$ quasibinary system is characterized by the eutectic processes $L \leftrightarrow Tl_4SnSe_4 + htm TlSbSe_2$ (see Fig.1). The lines of primary crystallization are intersected in the invariant point with coordinates 62 mol./% $TlSbSe_2$, 619K. Limited solid solutions are formed in the system: β on the base of Tl_4SnSe_4 and δ, δ' following low-, high-temperature polymorphic modification of $TlSbSe_2$, respectively. Eutectical processes $\delta' \leftrightarrow \beta + \delta$ is observed at 595 K. The solid solution range based on $TlSbSe_2$ do not exceed 14 mol.% at 423 K.

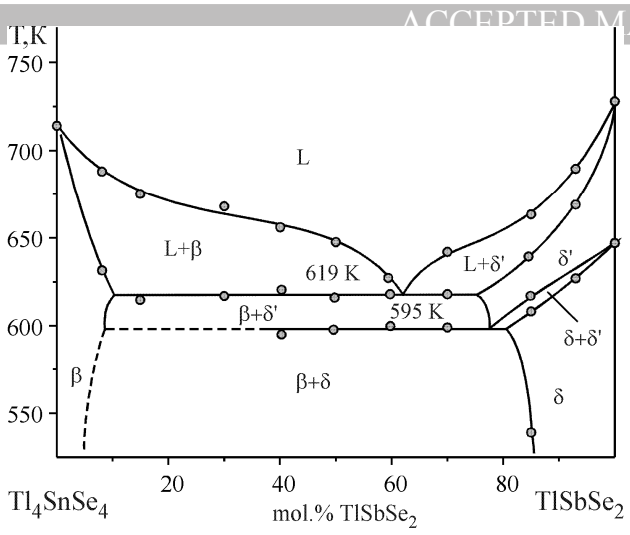


Fig.1. Phase diagram of the Tl_4SnSe_4–$TlSbSe_2$ system (the accuracy of the points corresponds to 5 K)

3.2. Tl_2SnSe_3–$TlSbSe_2$ quasibinary system

The phase diagram of the Tl_2SnSe_3–$TlSbSe_2$ system is presented in Fig.2. This system belongs to the Rozeboom type V and is characterized by the invariant eutectic processes L↔ltmTl_2SnSe_3+htm$TlSbSe_2$. The coordinates of the eutectic point correspond to 70 mol.% $TlSbSe_2$ at 635K. In this system are formed ε, ε' solid solutions based on low-, high-temperature polymorphic modifications of Tl_2SnSe_3 and δ, δ' solid solutions based on low-, high-temperature polymorphic modifications of $TlSbSe_2$, respectively. The metatectic processes ε'↔L+ε based on the polymorphic transformation of the ternary compound Tl_2SnSe_3 is observed at 693 K, eutectic processes δ'↔ε+δ based on the polymorphic transformation of $TlSbSe_2$ takes place at 597 K. At 423 K the existence of the solid solution range of low-temperature polymorphic modification of $TlSbSe_2$ is less than 11 mol.%. The lattice parameters of initial ternary compounds and solid solutions based on $TlSbSe_2$ are shown in Table 1.

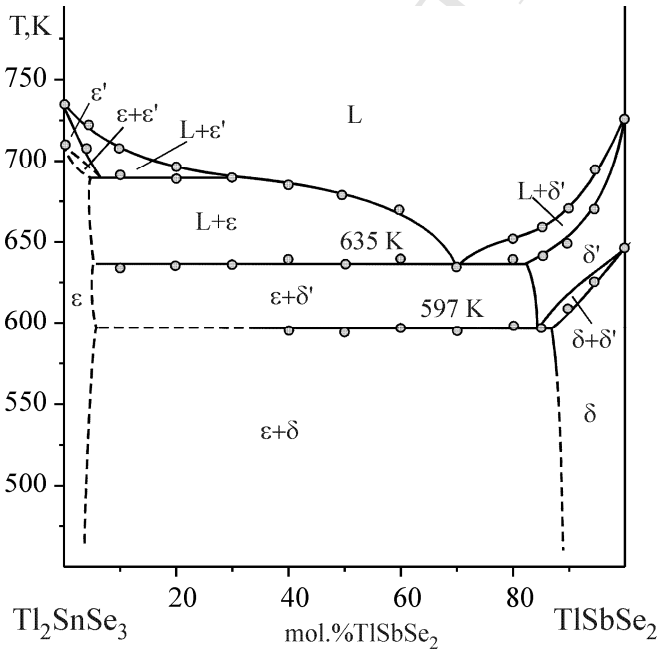


Fig.2. Phase diagram of the Tl_2SnSe_3–$TlSbSe_2$ system (the accuracy of the points corresponds to 5 K)

Table 1. Lattice parameters of $TlSbSe_2$, Tl_4SnSe_4, Tl_2SnSe_3 ternary compounds and solid solutions based on $TlSbSe_2$.

Phase	Lattice parameters
Tl_4SnSe_4 [20]	SG $P12_11$, a = 8.481, b = 8.411, c = 15.800 (Å), β = 102.39°, V = 1108.82 Å^3
ltm-Tl_2SnSe_3 [21]	SG $Pnam$, a = 8.051, b = 8.169, c = 21.240 (Å), V = 1396.93 Å^3
ht-$TlSbSe_2$ [22]	SG $Cmcm$, a = 4.514, b = 11.958, c = 4.211 (Å), V = 227.3 Å^3
ltm-$TlSbSe_2$ [23]	SG $P12_11$, a = 9.137, b = 4.097, c = 12.765 (Å), β = 111.75°, V = 443.83 Å^3
ltm-$TlSbSe_2$ (this work)	SG $P12_11$, a = 9.112(3), b = 4.100(2), c = 12.633(5) (Å), β = 110.64(1)°, V = 441.67 Å^3
$(TlSbSe_2)_{0.95}(Tl_4SnSe_4)_{0.05}$	SG $P12_11$, a = 9.105(3), b = 4.104(2), c = 12.645(5) (Å), β = 110.68(2)°, V = 442.06 Å^3
$(TlSbSe_2)_{0.95}(Tl_2SnSe_3)_{0.05}$	SG $P12_11$, a = 9.114(2), b = 4.107(2), c = 12.645(4) (Å), □ = 110.72(1)°, V = 442.7 Å^3

The solid solutions $(TlSbSe_2)_{0.95}(Tl_4SnSe_4)_{0.05}$ and $(TlSbSe_2)_{0.95}(Tl_2SnSe_3)_{0.05}$ have chemical compositions $Tl_{1.095}Sb_{0.905}Sn_{0.048}Se_2$, $Tl_{1.024}Sb_{0.927}Sn_{0.049}Se_2$, respectively.

3.3. Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ quasiternary system

A perspective view and the projection of the liquidus surface of the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ system are shown in Fig.3 and Fig.4, respectively. The points A', B' and C', which are located on the edges of triangular prism, represent the melting temperature of the ternary selenides Tl_2SnSe_3 (735 K), Tl_4SnSe_4 (714 K), $TlSbSe_2$ (728 K). The liquidus of the ternary system consists of four primary crystallization areas: Tl_4SnSe_4(B')–e1–E–e2–Tl_4SnSe_4(B') (β-phase), $TlSbSe_2$(C')–e2–E–e3–$TlSbSe_2$(C') (δ'-phase), Tl_2SnSe_3(A')–m1–m2–Tl_2SnSe_3(A') (ε'-phase) and m1–e1–E–e3–m2–m1 (ε-phase). The fields of primary crystallization are divided by monovariant lines e1–E (process L↔β+ε), e2–E (process L↔β+δ'), e3–E (process L↔β+ε), m2–m1 (process ε'↔L+ε), which cross at the ternary invariant points E (20 mol.% Tl_2SnSe_3, 32 mol.% Tl_4SnSe_4, 48 mol.% $TlSbSe_2$, 614 K). In the sub-liquidus part three surfaces depict the monovariant metatectic processes ε'↔L+ε based on the polymorphic transformation between the low– and high–temperature modifications of the ternary compound Tl_2SnSe_3 (715–693 K), invariant eutectic processes L↔β+δ'+ε (at 614 K) and invariant eutectoid processes δ'↔β+δ+ε (at 587 K). At temperature 616 K all alloys possess solid state phase.

The isothermal section at 423 K of the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ system is shown in Fig.5. New complex compounds were not observed in the ternary system. The types and temperature of the processes in the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ quasiternary system are shown in Table 2.

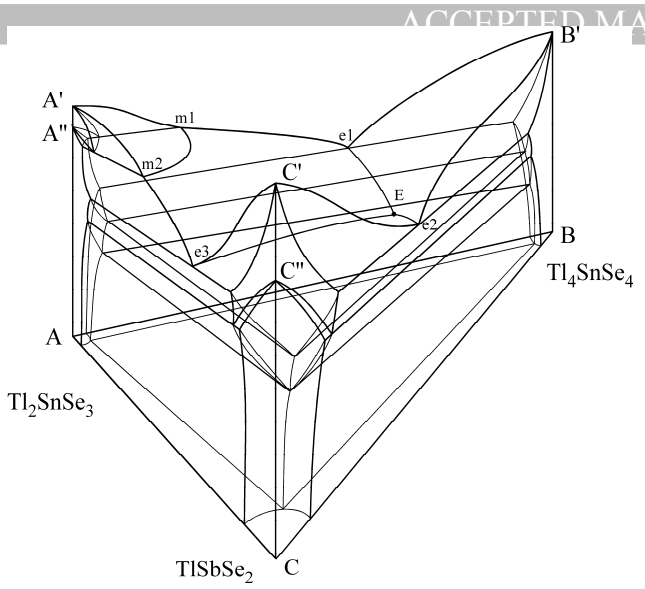


Fig.3. Perspective view of the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ system

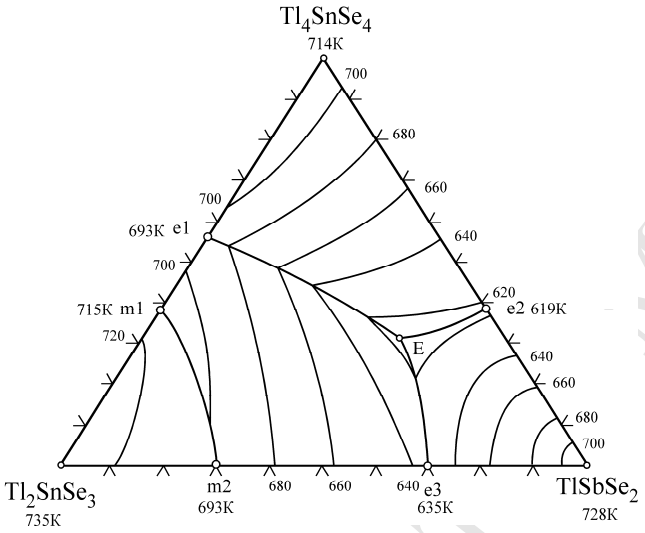


Fig.4. Liquidus surface of the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ system

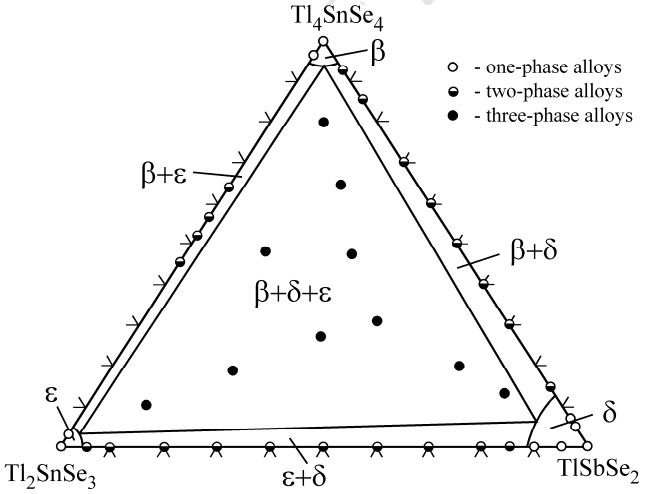


Fig.5. Isothermal section at 423 K of the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ system

Table 2. Types, temperature of the processes in the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ system

Types	Processes	Temperature, K
melting of Tl_2SnSe_3	A': $Tl_2SnSe_{3(sol)} \leftrightarrow Tl_2SnSe_{3(liq)}$	735
polymorphic transformation of Tl_2SnSe_3	A": $Tl_2SnSe_{3(high)} \leftrightarrow Tl_2SnSe_{3(low)}$	710
melting of Tl_4SnSe_4	B': $Tl_4SnSe_{4(sol)} \leftrightarrow Tl_4SnSe_{4(liq)}$	714
melting of $TlSbSe_2$	C': $TlSbSe_{2(sol)} \leftrightarrow TlSbSe_{2(liq)}$	728
polymorphic transformation of $TlSbSe_2$	C": $TlSbSe_{2(high)} \leftrightarrow TlSbSe_{2(low)}$	647
binary invariant eutectic	e1: $L \leftrightarrow \beta+\varepsilon$	693
binary invariant eutectic	e2: $L \leftrightarrow \beta+\delta'$	619
binary invariant eutectic	e3: $L \leftrightarrow \beta+\varepsilon$	635
binary invariant metatectic	m1: $\varepsilon' \leftrightarrow L+\varepsilon$	715
binary invariant metatectic	m2: $\varepsilon' \leftrightarrow L+\varepsilon$	693
binary invariant eutectoid	$\delta' \leftrightarrow \beta+\delta$	595
binary invariant eutectoid	$\delta' \leftrightarrow \varepsilon+\delta$	597
monovariant eutectic	e1–E: $L \leftrightarrow \mu+\eta$	693–622
monovariant eutectic	e2–E: $L \leftrightarrow \sigma+\eta$	674–622
monovariant eutectic	e3–E: $L \leftrightarrow \mu'+\sigma$	724–677
monovariant metatectic	m1–m2: $\varepsilon' \leftrightarrow L+\varepsilon$	715–693
ternary invariant eutectic	E: $L \leftrightarrow \beta+\delta'+\varepsilon$	614

4. Crystallochemistry of the compound $TlSbSe_2$ and their solid state alloys derivatives

According to Fig. 1,2,3 and 5, the most prolonged solid solutions for the titled compounds formed by $TlSbSe_2$. The crystallochemistry analysis of $TlSbSe_2$ has shown presence interatomic distances Se-Se (Fig.6a) at the border of sum of ionic radiuses (for atomas Se^{-2} r=1.91 Å). This fact does not exclude a possibility to existence of the pairs Se-Se. Localization of electrons for these pairs could favor a deficiency by cations for the such kind of materials. For the system $TlSbSe_2$–Tl_2SnSe_3, formation of solid solutions on the basis of $TlSbSe_2$ occurs at a fixed number of cationic atoms for the existed solid alloys. So here we have a coexistence of cations which may favor a shortening of chemical bonds Se-Se (see Fig. 6b). For the system $TlSbSe_2$–Tl_4SnSe_4, formation of solid solutions is increasing number of cationic atoms for the existed solid alloys. This can cause defects on anions in the materials on the basis of $TlSbSe_2$ solid solutions. Following Fig. 6c, such substitution may lead to a further decrease of Se-Se bond lengths. So depending on the synthesis conditions and thermal treatment of the materials for the entire existed solid solutions range one can obtain the materials with a variable number of defects. However, the defects may cause to favorable changes of these compounds. More details about the solution forming are given in the Supplement 3.

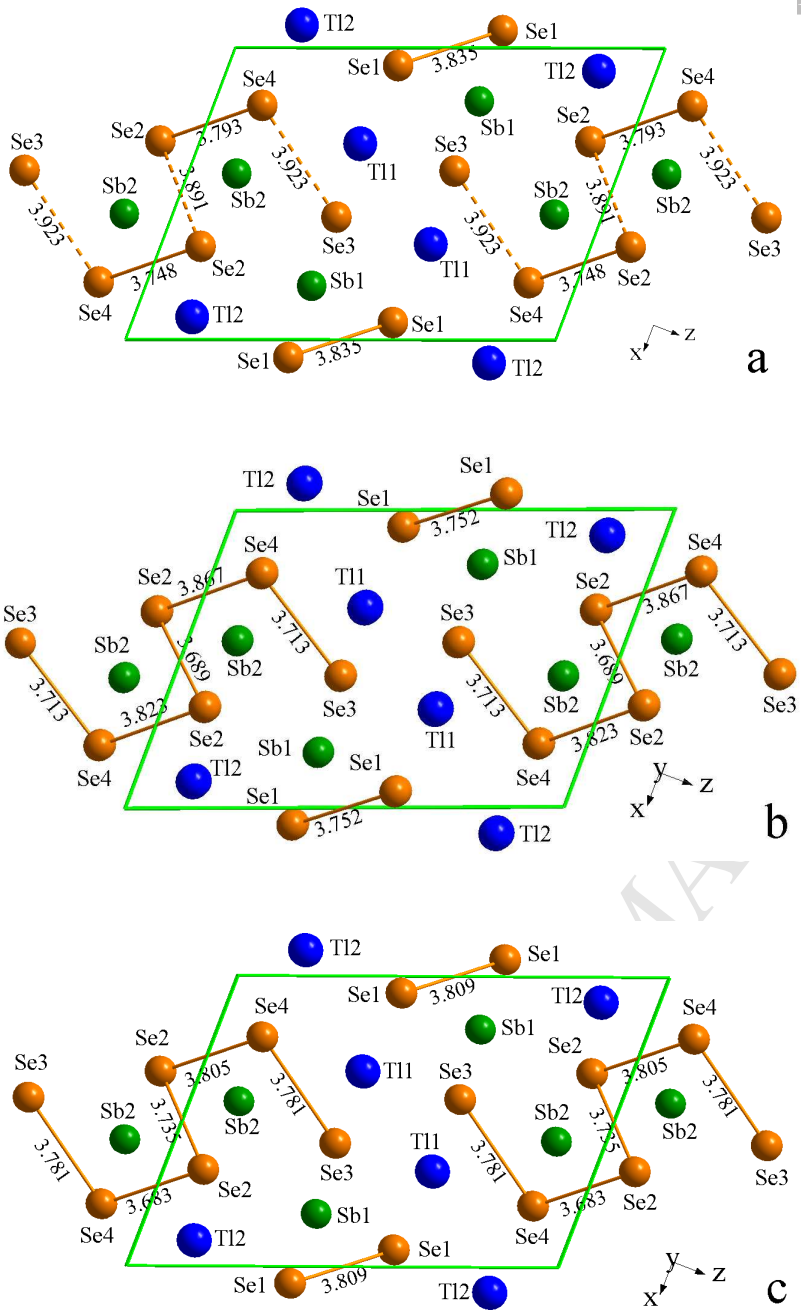


Fig.6. Chemical bond distances Se-Se (Å) for structure of ltm-$TlSbSe_2$ compounds: (**a**) solid state alloys $(TlSbSe_2)_{0.95}(Tl_2SnSe_3)_{0.05}$ (**b**) and $(TlSbSe_2)_{0.95}(Tl_4SnSe_4)_{0.05}$ (**c**).

5. Conclusions

Differential thermal, X-ray phase, microstructure analyses and mathematical modeling of phase equilibria in the multi-component systems were used to construct the two quasibinary sections of the systems Tl_4SnSe_4–$TlSbSe_2$, Tl_2SnSe_3–$TlSbSe_2$, perspective view of the Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$ system, the liquidus surface projection and isothermal section at 423 K. The character of the monovariant processes, the temperatures and coordinate of the invariant processes in the ternary system were determined. In this system there exists one invariant processes: E – L↔β+δ'+ε (20 mol.% Tl_2SnSe_3, 32 mol.% Tl_4SnSe_4, 48 mol.% $TlSbSe_2$, 614 K). The existence of solid solutions of the ternary compounds Tl_2SnSe_3, Tl_4SnSe_4, $TlSbSe_2$ was established. New complex compounds were not formed in the ternary system.

References

[1] M.G. Kanadzidis, The Role of Solid State Chemistry in the Discovery of New Thermoelectric Materials, in: Terry M. Tritt (Eds.), Semiconductors and Semimetals, Academ. Press, San Diego, San Francisco, N.Y., 2001, p.p.51-98.

[2] A.V. Shevelkov, Chemical aspects of creation of thermoelectric materials, Usp. Khim. **77 (1)** (2008) 3–21.

[3] P. Houenou, R. Eholie, Etude du systeme $SnSe_2$–Tl_2Se, C.R. Acad. Sci., Paris **C283** (1976) 731–733.

[4] P. Houenou, R. Eholie, J. Flahaut, Étude du diagramme ternaire Tl-Sn-Se: Description du quadrilatère $SnSe_2$–Tl_2SnSe_3–TlSe-Se, J. Less Common Met. **81** (1981) 181–197.

[5] V.B. Lazarev, E.Yu. Peresh, V.I. Starosta, V.V. Mudriy, Phase relations and properties of compounds in the $Tl_2S(Se)$–$SnS_2(Se_2)$ systems, Zh. Neorg. Khim. **30**,(1985) 1502–1506.

[6] I.E. Barchii, O.S. Glukh, E.Yu. Peresh, V.V. Tsigika, Tl_4GeSe_4–Tl_2Se–Tl_4SnSe_4 system, Zh. Neorg. Khim. **50** (2005) 835–837.

[7] Y.I. Jafarov, M.B. Babanly, A.A. Kuliev, Tl_2Se–Sb_2Se_3, TlSe–$TlSbSe_2$ (Tl_9SbSe_6) systems, Zh. Neorg. Khim. **45** (1998) 858-860.

[8] T.S. Boston, H.S. Whitfield, NQR study of thernary chalcogenides A_3BX_3, ABX_2 and ABX where A – Cu, Ag or Tl, B – As or Sb, X – S or Se, J. Solid State Chem. **10** (1981) 203–209.

[9] I. Mucha, Reinvestigation of phase equilibria in the thallium (I) selenide-antimony (III) selenide system, Thermochim. Acta. **563** (2013) 6–11.

[10] T.A. Ostapyuk, I.M. Yermiychuk, O.F. Zmiy, I.D. Olekseyuk, Phase equilibria in the quasiternary system Cu_2Se–$SnSe_2$–Sb_2Se_3, Chem. Met. Alloys. **2** (2009) 164–169.

[11] A.R. Tackar, A.A. Kozma, I.E. Barchiy, A.M. Solomon, V.V. Rekita, Triangulation of the Tl_2Se–$SnSe_2$–Sb_2Se_3 system, Nauch. Vestn. Uzhgorod. Univ. (Ser. Khim.). **29 (1)** (2013) 14–19.

[12] G.E.Davydyuk, M.Piasecki, O.V.Parasyuk, G.L.Myronchuk, A.O.Fedorchuk, S.P.Danylchuk, L.V.Piskach, M.Yu.Mozolyuk, N.AlZayed, Two-photon absorption of $Tl_{1-x}In_{1-x}Sn_xSe2$ (x=0, 0.1, 0.2, 0.25) single crystalline alloys and their nanocrystallites, Opt. Mater. **35** (2013) 2514–2518.

[13] N.S. AlZayed, J. Ebothé, J. Michel, I.V. Kityk, A.O. Fedorchuk, O.V. Parasyuk, G.L. Myronchuk, Optically stimulated IR non-linear optical effects in the Tl_3PbCl_5 nanocrystallites, Physica E: Low-dimensional Systems and Nanostructures. **65** (2015) 130–134.

[14] J.A. Peters, Z. Liu, J. Im, S. Nguyen, M. Sebastian, A.J. Freeman, M.G. Kanatzidis, B.W Wessels, Characterization of deep level defects in Tl_6I_4S single crystals by photo-induced current transient spectroscopy, J. Phys. D: Appl. Phys. **48** (2015) 075303

[15] K.J.Plucinski, M.Makowska-Janusik, A.Mefleh, V.G.Yushanin, SiO_N films deposited on Si(111) substrates - new promising materials for nonlinear optics, Mater. Sci. Eng. **B64** (1999) 88-98

[16] I.V.Kityk, J.Wasylak, J.Dorosz, J.Kucharski, Eu-doped glass materials for red luminescence, Opt. Lasers Technol. **33** (2001) 157-160.

[17] A.Majchrowski, I.V.Kityk, J.Ebothe. Phys.Status Solidi, **B241** (2004) 3047-3055.

[18] I.E. Barchiy, Mathematical design of phase equilibrium in the Tl_2S–Tl_2Se–Tl_5Se_2I system, Ukr. Khim. Zh. **67** (2001) 18–23.

[19] L. Akselrud, Yu. Grin, WinCSD: software package for crystallographic calculations, J. Appl. Crystallogr. **47** (2014) 803–805

[20] G. Akinocho, P. Houenou, S. Oyetola, R. Eholie, J. C. Jumas, J. Olivier-Fourcade, M. Maurin, Etude structurale de Tl_4SnSe_4, J. Solid State Chem. **93** (1991) 336-340

[21] S. Jaulmes, P. Houenou, Structure cristalline du seleniure d'etain(IV) et de thallium(I): Tl_2SnSe_3, Mater. Res. Bull. **15** (1980) 911-915

[22] K. Wacker, P. Buck X-ray investigations of thallium-antimony selenide $TlSbSe_2$ // Mater. Res. Bull. **15** (1980), 1105-1111

[23] K. Wacker, M. Salk, G. Decker Schultheiss, E. Keller, Die Kristallstruktur der geordneten Phase der Verbindung $TlSbSe_2$, Z. Anorg. Allg. Chem. **606** (1991) 51–58.

>Two Tl_4SnSe_4–$TlSbSe_2$,Tl_2SnSe_3–$TlSbSe_2$ systems were explored.

> Invariant processes in the ternary system were determined.

> New complex compounds were not observed in ternary system.