**Chemistry of Metals and Alloys**

*Chem. Met. Alloys* 4 (2011) 94-97
Ivan Franko National University of Lviv
www.chemetal-journal.org

# Phase relations in the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ quasiternary system

A.A. KOZMA[1]*, I.E. BARCHIY[1], E.Yu. PERESH[1]

[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: Anton_Kozma@yahoo.com*

Received June 30, 2010; accepted May 18, 2011; available on-line November 8, 2011

**The quasiternary system $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ was investigated by DTA and X-ray diffraction in combination with mathematical modeling. Perspective views of the phase interactions and a projection of the liquidus surface were constructed. No quaternary compounds were observed. The system is of the invariant eutectic type. The three-dimensional one-, two- and three-phase regions present in the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system are described.**

**Phase diagram / Thermal analysis / X-ray diffraction**

## Introduction

Thallium compounds have recently attracted interest as promising thermoelectric materials [1]. There are two reasons for this. Firstly, thallium is similar in crystal chemical behavior to some of the alkali metals. It preferentially forms 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 increase the electrical conductivity of a compound, as a result of substantial reduction of the ionicity of the chemical bonds. Secondly, thallium is a heavy element and its introduction into a semiconductor will lead to a decrease of the thermal conductivity. One of the trends in semiconductor materials science in developing new functional materials is the increasing complexity of the investigated systems and of the compounds that form in these systems.

The $Tl_2Se$–$SnSe_2$–$Bi_2Se_3$ system is interesting due to the formation of ternary compounds that exhibit thermoelectric properties and have wide practical application. The phase diagram of the $Tl_2Se$–$SnSe_2$ boundary system is characterized by the formation of the ternary compounds $Tl_4SnSe_4$ and $Tl_2SnSe_3$, which melt congruently at 718 K and 738 K, respectively, and $Tl_2Sn_2Se_5$, which melts incongruently at 732 K [2,3]. At low temperature (655 K) the latter decomposes, $Tl_2Sn_2Se_5 \leftrightarrow Tl_2SnSe_3 + SnSe_2$. The ternary compound $Tl_2SnSe_3$ has two polymorphic modifications [4]. Two phases form in the $Tl_2Se$–$Bi_2Se_3$ system: $Tl_9BiSe_6$ (795 K) and $TlBiSe_2$ (990 K) [5,6]. The $SnSe_2$–$Bi_2Se_3$ system is of the eutectic type [7]. The $Tl_2Se$–$SnSe_2$–$Bi_2Se_3$ system is divided into the five subsystems $SnSe_2$–$TlBiSe_2$–$Bi_2Se_3$, $SnSe_2$–$Tl_2SnSe_3$–$TlBiSe_2$, $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$, $Tl_4SnSe_4$–$TlBiSe_2$–$Tl_9BiSe_6$, $Tl_2Se$–$Tl_4SnSe_4$–$Tl_9BiSe_6$, separated by the four quasibinary sections $SnSe_2$–$TlBiSe_2$, $Tl_2SnSe_3$–$TlBiSe_2$, $Tl_4SnSe_4$–$TlBiSe_2$ and $Tl_4SnSe_4$–$Tl_9BiSe_6$ [7,8]. Investigation of the ternary compounds, limited solid solutions and eutectic complex alloys in the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ subsystem is an important step in the search for new materials for semiconductor technology.

## Experimental

The synthesis of the thallium(I), tin(IV) and bismuth(III) binary selenides ($Tl_2Se$, $SnSe_2$, $Bi_2Se_3$) was carried out with high-purity elements (better than 99.99 wt.%). The 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 the zone crystallization method. The purity was controlled by chemical-spectral analysis with a quartz spectrograph ISP-30. The impurity contents (Si, Fe, Mg, Al, Cd, Sn, Cu, Ag, Bi, Pb) of the initial binary compounds were $2.1\times10^{-4}\div3.4\times10^{-5}$ wt.%. The ternary compounds $Tl_2SnSe_3$, $Tl_4SnSe_4$ and $TlBiSe_2$ were obtained from stoichiometric amounts of the binary selenides. Identification of the binary and ternary compounds was done by DTA and X-ray analysis.

Multicomponent alloys were synthesized from the ternary selenides in quartz ampoules evacuated to a residual pressure of 0.13 Pa. The highest synthesis temperature was 1023 K. After thermal treatment at the highest temperature for 10-12 h the samples

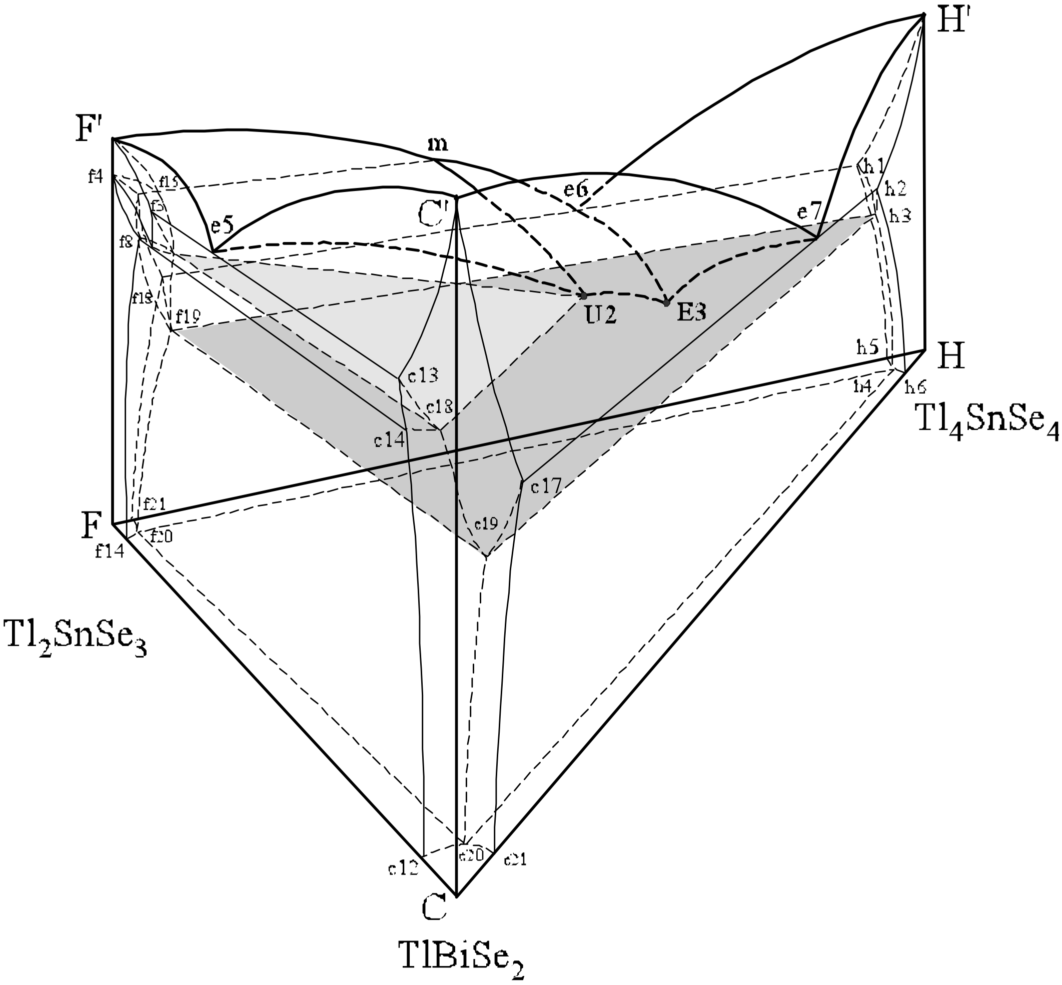


**Fig. 1** Perspective view of the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ quasiternary system.

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 in cold water.

The phase equilibria in the ternary system were studied by classical methods of physico-chemical analysis, such as differential thermal analysis (DTA) and X-ray powder diffraction, in combination with the simplex method of mathematical modeling of phase equilibria in multicomponent systems. For the DTA analysis the samples were heated and cooled in a furnace using an RIF-101 programmer that provided a linear temperature variation. The heating rate was 250-320 K/h. The temperature was measured with an accuracy of ±5 K, using a Chromel-Alumel thermocouple. X-ray powder diffraction was carried out on a DRON-3 diffractometer (Cu Kα radiation, Ni filter). The peak intensities were estimated from the peak area and normalized to a 100-point scale. The method used for the computer simulation of the phase equilibria has been described by Barchiy [9]. This method provides good results and allows reducing the number of alloys.

**Results and discussion**

The quasiternary system $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ is formed by three eutectic-type systems: $Tl_2SnSe_3$–$TlBiSe_2$ and $TlBiSe_2$–$Tl_4SnSe_4$, which are characterized by the invariant eutectics processes L↔μ'+σ (eutectic point e5 – 15 mol.% $TlBiSe_2$, 724 K) and L↔σ+η (eutectic point e7 – 20 mol.% $TlBiSe_2$, 674 K) [7], and the quasibinary subsystem $Tl_2SnSe_3$–$Tl_4SnSe_4$, which is characterized by two invariant processes: the eutectic L↔μ+η (eutectic point e6 – 60 mol.% $Tl_4SnSe_4$, 693 K) and the metatectic μ'↔L+μ based on the polymorphic transformation of the ternary compound $Tl_2SnSe_3$ (metatectic point m – 42 mol.% $Tl_4SnSe_4$, 710 K) [2,4]. Limited solid solutions based on the ternary compounds are formed in the system: σ-phase based on $TlBiSe_2$, μ- and μ'-phases based on the low- and high-temperature polymorphic modifications of $Tl_2SnSe_3$, η-phase based on $Tl_4SnSe_4$.

A perspective view of the system is shown in Fig. 1. The points C', F' and H', which are located on the edges of a triangular prism, represent the melting temperatures of the three ternary selenides ($Tl_2SnSe_3$ – 732 K, $TlBiSe_2$ – 990 K, $Tl_4SnSe_4$ – 715 K, respectively).

The liquidus of the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system consists of four primary crystallization areas: C'e5U2E3e7C' (σ-phase), F'e5U2mF' (μ'-phase), mU2E3e6m (μ-phase) and H'e6E3e7H' (η-phase). The fields of primary crystallization are divided by five monovariant lines: e5–U2 (process L↔μ'+σ), m–U2 (process L↔μ'+μ), e6–E3 (process L↔μ+η),e7–E3 (process L↔σ+η), U2–E3 (process L↔μ+σ), which intersect at two ternary invariant points: U2 (29 mol.% $Tl_2SnSe_3$, 59 mol.% $Tl_4SnSe_4$, 12 mol.% $TlBiSe_2$, 677 K) and E3 (14 mol.% $Tl_2SnSe_3$, 75 mol.% $Tl_4SnSe_4$, 11 mol.% $TlBiSe_2$, 622 K). The solidus consists of the surfaces F'f15f17f13F' (end of the μ'-phase crystallization), f8f17f19f18f8 (end of the μ-phase crystallization), H'h1h3h2H' (end of the η-phase crystallization), C'c13c18c19c17C' (end of the σ-phase crystallization), the two-phase crystallization surfaces f18h1h3f19f18 (μ+η), f17c18c19f19f17 (μ+σ), h2c17c19h3h2 (σ+η) and the eutectic surface a19p3c19a19.

The invariant surface f17U2c18f17 represents the polymorphic interaction at 677 K between the high- and low-temperature modifications of $Tl_2SnSe_3$. Two monovariant processes on the base of this interaction take place in the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system (Fig. 2): the monovariant metatectic μ'↔L+μ (temperature range 710-677 K) and the monovariant eutectoid μ'↔μ+σ (temperature range 702-677 K). The 3D-region μ'+μ+σ is bordered by the surfaces f8c14c18f17f8, f8f17f7f8, c14f7f17c18c14, and L+μ'+μ by f16f15mU2f17f7f16, f16f15f17f7f16, f15mU2f17f15. All the alloys in the subsolidus part below 622 K are in the solid state and represent a mixture of μ+η+σ crystals.

The homogeneity region of the ternary compound $Tl_4SnSe_4$ is limited by the surfaces H'h1h3h2H', H'h1h5HH', H'h2h6HH', h1h2h4h5h1, h2h3h4h6h2, and that of the ternary compound $TlBiSe_2$ by C'c13c18c19c17C', C'c13c14c12CC', C'c17c21CC', c13c14c18c13, c14c18c19c20c12c14, c17c19c20c21c17. The homogeneity region of the ternary selenide $Tl_2SnSe_3$ consists of three areas: μ, μ', μ'+μ. The μ'-phase based on the high-temperature modification is bordered by the surfaces F'f15f4F', F'f3f7f4F', F'f15f17f7f3F', f4f15f17f7f4, that of the μ-phase based on the low-temperature modification by f4f8f14Ff4, f4f16f18f21Ff4, f8f17f19f20f14f8, f16f17f19f20f21f18f16, f8f16f15f17f8, f8f17f19f18f16f8. The area of the mixture μ'+μ is limited by the surfaces f4f15f16f4, f4f7f8f4, f4f8f16f4, f4f7f17f15f4, f8f16f15f17f8, f8f7f17f8.

The projection of the liquidus surface of the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system (Fig. 3) onto the concentration triangle was constructed according to the results of the present investigation. It consists of four fields of primary crystallization: σ-crystals ($TlBiSe_2$–e5–U2–E3–e7–$TlBiSe_2$), μ'-crystals ($Tl_2SnSe_3$–e5–U2–m–$Tl_2SnSe_3$), μ-crystals (m–U2–E3–e6–m), and η-crystals ($Tl_4SnSe_4$–e6–E3–e7–$Tl_4SnSe_4$). The fields of primary crystallization are divided by five monovariant lines: e5–U2, m–U2, U2–E3, e6–E3, e7–E3. The types and temperatures of the processes in the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ quasiternary system are listed in Table 1.

No new compounds were observed in the system.

## Conclusions

Differential thermal, X-ray phase and mathematical modeling of the phase equilibria by the simplex method were used to construct for the first time a perspective representation of the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system and the liquidus projection for the same system. The character of the monovariant processes, the temperatures and coordinates of the invariant processes in this quasiternary system were determined. Two invariant processes take place in the system: U2 – μ'+σ↔L+μ (29 mol.% $Tl_2SnSe_3$,

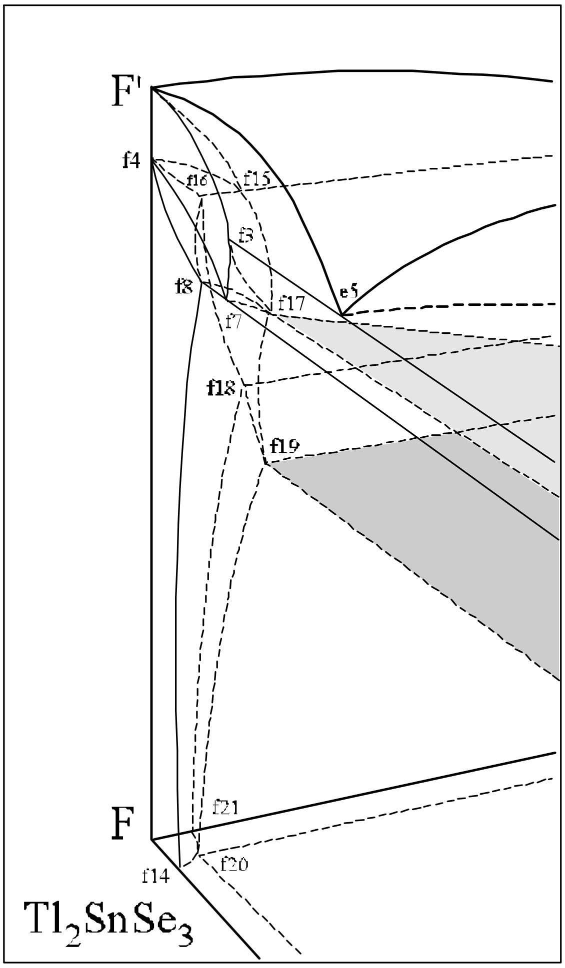


**Fig. 2** Perspective view of the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system in the region of the ternary compound $Tl_2SnSe_3$.

**Table 1** Type and temperatures of the processes in the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system.

| Type | Processes | Temperature, K |
|---|---|---|
| melting of $Tl_2SnSe_3$ | F’: $Tl_2SnSe_{3(sol)}\leftrightarrow Tl_2SnSe_{3(liq)}$ | 732 |
| polymorphic transformation of $Tl_2SnSe_3$ | f4: $Tl_2SnSe_{3(low)}\leftrightarrow Tl_2SnSe_{3(high)}$ | 718 |
| melting of $TlBiSe_2$ | C’: $TlBiSe_{2(sol)}\leftrightarrow TlBiSe_{2(liq)}$ | 990 |
| melting of $Tl_4SnSe_4$ | H’: $Tl_4SnSe_{4(sol)}\leftrightarrow Tl_4SnSe_{4(liq)}$ | 715 |
| ternary invariant eutectic | E3: $L\leftrightarrow\sigma+\mu'+\eta$ | 622 |
| ternary polymorphic transformation | U2: $\mu'+\sigma\leftrightarrow L+\mu$ | 677 |
| binary invariant eutectic | e5: $L\leftrightarrow\mu'+\sigma$ | 724 |
| binary invariant eutectic | e6:– $L\leftrightarrow\mu+\eta$ | 693 |
| binary invariant eutectic | e7: $L\leftrightarrow\sigma+\eta$ | 674 |
| binary invariant metatectic | f15: $\mu'\leftrightarrow L+\mu$ | 710 |
| binary invariant eutectoid | f7: $\mu'\leftrightarrow\mu+\sigma$ | 702 |
| monovariant eutectic | e6–E3: $L\leftrightarrow\mu+\eta$ | 693-622 |
| monovariant eutectic | e7–E3: $L\leftrightarrow\sigma+\eta$ | 674-622 |
| monovariant eutectic | e5–U2: $L\leftrightarrow\mu'+\sigma$ | 724-677 |
| monovariant eutectic | U2–E3: $L\leftrightarrow\mu+\sigma$ | 677-622 |
| monovariant metatectic | f15–f17: $\mu'\leftrightarrow L+\mu$ | 710-677 |
| monovariant eutectoid | f7–f17: $\mu'\leftrightarrow\mu+\sigma$ (702-677 K) | 702-677 |

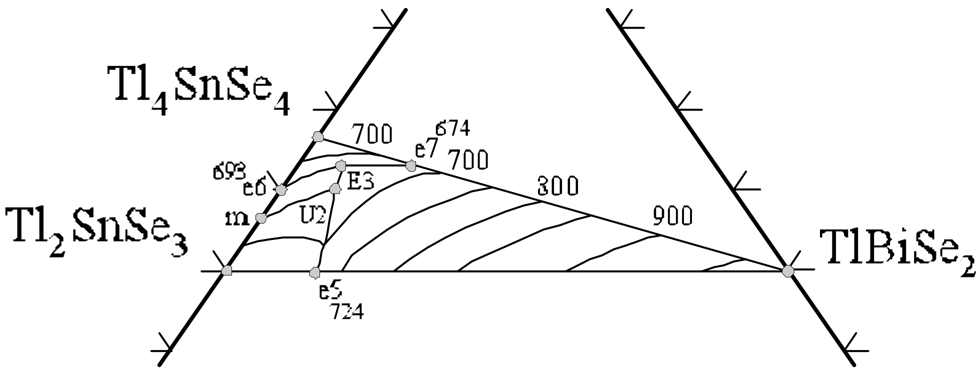


**Fig. 3** Liquidus projection of the $Tl_2SnSe_3$–$Tl_4SnSe_4$–$TlBiSe_2$ system.

59 mol.% $Tl_4SnSe_4$, 12 mol.% $TlBiSe_2$, 677 K) and E3 – $L\leftrightarrow\sigma+\mu'+\eta$ (14 mol.% $Tl_2SnSe_3$, 75 mol.% $Tl_4SnSe_4$, 11 mol.% $TlBiSe_2$, 622 K). The existence of solid solutions of the ternary compounds $Tl_2SnSe_3$, $Tl_4SnSe_4$, $TlBiSe_2$ was established. No quaternary compounds were observed.

## References

[1] A.V. Shevelkov, *Usp. Khim.* 77 (2008) 3.

[2] P. Houenou, R. Eholie, *C. R. Acad. Sci. Paris. C* 283 (1976) 731.

[3] A.A. Gatuk, M.B. Babanli, A.A. Kuliev, *Azerbaid. Khim. Zh.* 6 (1977) 128.

[4] S. Jaulmes, P. Houenou, *Mater. Res. Bull.* 15 (1980) 911.

[5] I.E. Barchiy, E.Yu. Peresh, V.B. Lazarev, Yu.V. Voroshilov, B.I. Tkachenko, *Zh. Neorg. Khim.* 24 (1988) 1791.

[6] I.E. Barchiy, O.S. Gluh, E.Yu. Peresh, V.V. Tsygyka, *Zh. Neorg. Khim.* 50 (2005) 835.

[7] A.A. Kozma, I.E. Barchiy, E.Yu. Peresh, V.V. Tsygyka, *Ukr. Khim. Zh.* 76 (2010) 80.

[8] A.A. Kozma, E.Yu. Peresh, I.E. Barchiy, V.V. Tsygyka, A.I. Barchiy, *Visn. Uzhgorod. Univ., Ser. Khim.* 20 (2008) 89.

[9] I.E. Barchiy, *Ukr. Khim. Zh.* 67 (2001) 18.