

PHYSICOCHEMICAL ANALYSIS
OF INORGANIC SYSTEMS

Interaction in the Systems $\text{TlBiSe}_2\text{–Tl}_9\text{BiSe}_6\text{–PbSe}$
and $\text{Tl}_9\text{BiSe}_6\text{–Tl}_4\text{PbSe}_3\text{–PbSe}$

E. E. Masalovich^a, M. Yu. Sabov^a, I. E. Barchii^a, and A. M. Solomon^b

^aChair of Inorganic Chemistry, Chemical Faculty, Uzhgorod National University, vul. Pidgirna 46, Uzhgorod, 88000 Ukraine

^bInstitute of Electron Physics, National Academy of Sciences, Universitetska vul. 21, Uzhgorod, 880017 Ukraine

e-mail: omelian.masalovich@gmail.ru

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Abstract—Phase equilibria in the systems $\text{TlBiSe}_2\text{–Tl}_9\text{BiSe}_6\text{–PbSe}$ and $\text{Tl}_9\text{BiSe}_6\text{–Tl}_4\text{PbSe}_3\text{–PbSe}$ were studied by differential thermal, X-ray powder diffraction, and microstructural analyses. State diagrams of the quasi-binary sections $\text{Tl}_9\text{BiSe}_6\text{–Tl}_4\text{PbSe}_3$, $\text{TlBiSe}_2\text{–PbSe}$, and $\text{Tl}_9\text{BiSe}_6\text{–PbSe}$ were constructed, and so were projections of liquidus surfaces and isothermal sections at 600 K for the secondary quasi-ternary systems $\text{TlBiSe}_2\text{–Tl}_9\text{BiSe}_6\text{–PbSe}$ and $\text{Tl}_4\text{PbSe}_3\text{–Tl}_9\text{BiSe}_6\text{–PbSe}$. The coordinates of invariant points and the boundaries of solid solutions were determined.

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Triangulation of the $\text{Tl}_2\text{Se–PbSe–Bi}_2\text{Se}_3$ system showed that the quasi-binary sections $\text{TlBiSe}_2\text{–PbSe}$, $\text{Tl}_9\text{BiSe}_6\text{–Tl}_4\text{PbSe}_3$ and $\text{Tl}_9\text{BiSe}_6\text{–PbSe}$ partition it into four quasi-ternary systems [1], among which are $\text{Tl}_9\text{BiSe}_6\text{–Tl}_4\text{PbSe}_3\text{–PbSe}$ (**I**) and $\text{TlBiSe}_2\text{–Tl}_9\text{BiSe}_6\text{–PbSe}$ (**II**).

The systems $\text{Tl}_4\text{PbSe}_3\text{–PbSe}$ and $\text{TlBiSe}_2\text{–Tl}_9\text{BiSe}_6$ are of the eutectic type and are parts of the quasi-binary sections $\text{Tl}_2\text{Se–PbSe}$ and $\text{Tl}_2\text{Se–Bi}_2\text{Se}_3$, respectively [2, 3]. In the $\text{Tl}_9\text{BiSe}_6\text{–Tl}_4\text{PbSe}_3$ system, continuous series of solid solutions form [4]. Continuous series of solid solutions also form in the $\text{TlBiSe}_2\text{–PbSe}$ system; however, within the concentration range 20–40 mol % 2PbSe at temperatures below 500°C, they are unstable [5]. The differences in unit cell structure and parameters between the compounds TlBiSe_2 (space group $R\bar{3}m$, $a = 0.85346$ nm, $c = 2.233$ nm, $Z = 3$ [6]) and PbSe (space group $Fm\bar{3}m$, $a = 0.6105$ nm [7]) cast doubt on the possibility of the formation of continuous series of solid solutions between them. Therefore, it was necessary to investigate this possibility again. We failed to find data on phase equilibria in the $\text{Tl}_9\text{BiSe}_6\text{–PbSe}$ system, which is common for ternary systems **I** and **II**. In this context, in studying phase equilibria in systems **I** and **II**, it was necessary to initially investigate the systems $\text{Tl}_9\text{BiSe}_6\text{–PbSe}$ and $\text{TlBiSe}_2\text{–PbSe}$.

EXPERIMENTAL

To study features of the physicochemical interaction in the quasi-ternary systems, alloys were synthe-

sized in the quasi-binary sections $\text{Tl}_9\text{BiSe}_6\text{–PbSe}$ and $\text{TlBiSe}_2\text{–PbSe}$, and also within the ternary systems. The compositions of the alloys within the systems being studied were chosen so that they corresponded to nodes of the simplex lattice for mathematical modeling of phase equilibria [8] and also allowed one to identify the regions of the existence of individual phases.

Alloys were produced by alloying preliminarily synthesized compounds Tl_9BiSe_6 , Tl_4PbSe_3 , TlBiSe_2 , and PbSe . Ternary compounds and lead selenide were obtained from elemental substances (Tl-000 grade thallium, 11-4 special-purity grade bismuth, OVCh-000 grade lead, and 17-3 special-purity grade selenium). Necessary weighed samples of the initial substances were placed in quartz ampoules, which were evacuated to 0.13 Pa and sealed. The contents of the ampoules were heated at a rate of 40–60 deg/h to the maximum synthesis temperature, which was 40–60 K higher than the melting point of the higher-melting component, and were kept for 24 h. Homogenizing annealing was carried out at 600 K for 336 h. Then the ampoules were quenched in ice water.

Identification of the initial compounds and also analysis of ternary alloys based on them were performed by differential thermal analysis (PDA-01 X–Y recorder, chromel–alumel thermocouple, linearity of heating and cooling was controlled by RIF-101 programmer) and X-ray powder diffraction analysis (DRON-4 diffractometer, $\text{CuK}\alpha$ radiation). Binary and ternary alloys were also studied by microstructural analysis (Lomo Metam-1 metallographic microscope).

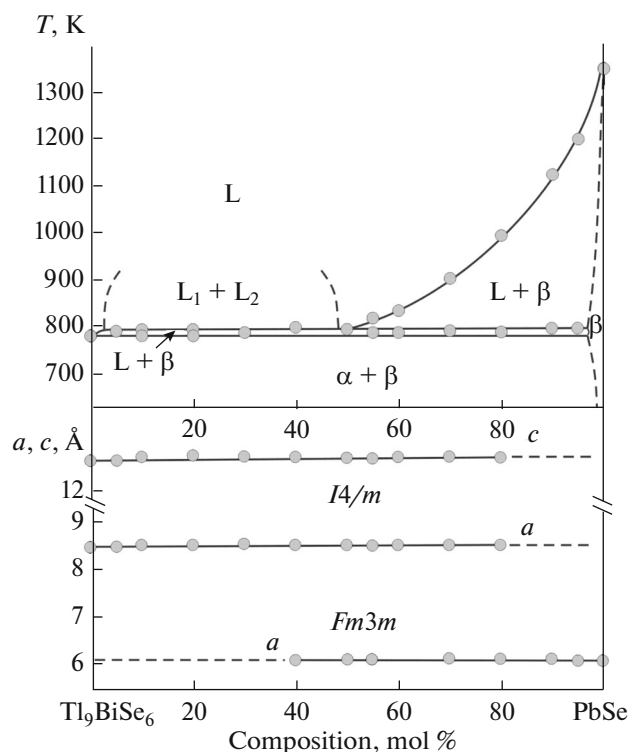


Fig. 1. State diagram of the Tl_9BiSe_6 -PbSe system.

RESULTS AND DISCUSSION

To investigate each of the quasi-binary systems Tl_9BiSe_6 -PbSe and TlBiSe_2 -PbSe, 12 samples were synthesized, which were examined by differential thermal, X-ray powder diffraction, and microstructural analyses. Based on the obtained data, the corresponding state diagrams were constructed.

It was determined that, in the Tl_9BiSe_6 -PbSe system, two invariant equilibrium processes occur. One of them is eutectic and occurs at the Tl_9BiSe_6 melting point (785 K), which is indicative of the degeneracy of the eutectic on the Tl_9BiSe_6 side. The other process is monotectic and occurs at 798 K. Within the concentration range 4–48 mol % PbSe, there is phase separation in the liquid phase. Calculated from the X-ray powder diffraction data, the unit cell parameters of the initial components remain virtually unchanged throughout the concentration range and showed that the boundary solid solutions are based on Tl_9BiSe_6 (α -phase) and PbSe (β -phase) does not exceed 5 mol % (Fig. 1).

The state diagram of the TlBiSe_2 -PbSe system is of the eutectic type and has a wide (>55 mol %) range of solid solutions based on PbSe (β -phase). The extent of the γ -boundary solution based on TlBiSe_2 does not exceed 5 mol %. The eutectic process $L \leftrightarrow \gamma + \beta$ occurs at 950 K; the coordinates of the invariant point are (950 K, 23 mol % PbSe) (Fig. 2).

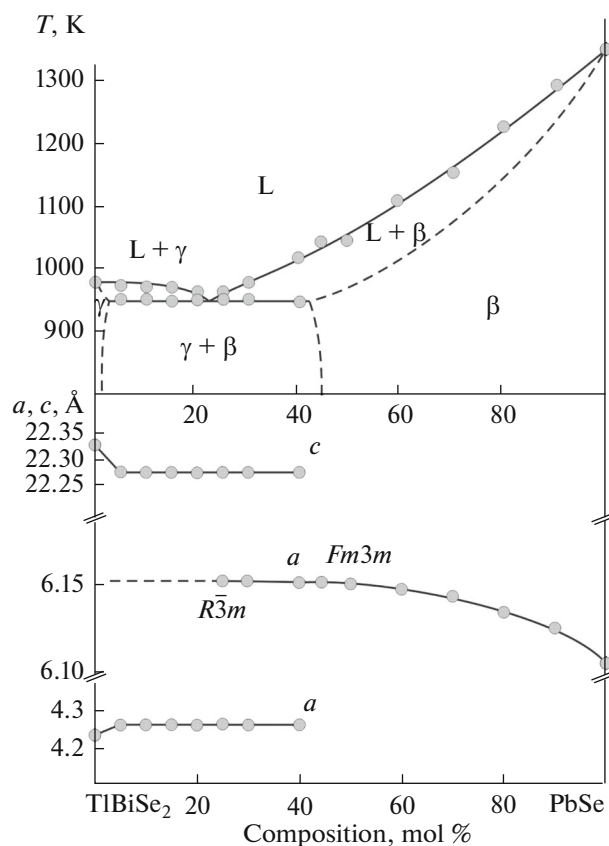


Fig. 2. State diagram of the TlBiSe_2 -PbSe system.

The calculated unit cell parameters of the β -phase (Fig. 2) in the PbSe homogeneity range are characterized by a positive deviation from Vegard's law, which suggests the presence of stresses in the structure and, correspondingly, the possibility of decomposition of solid solutions.

The X-ray powder diffraction data of the studied samples agree with the microstructural analysis data (Fig. 3).

Using the primary crystallization temperatures of alloys by mathematical modeling by the method of simplex triangles, projections of the liquidus surfaces of ternary systems I (Fig. 4) and II (Fig. 5) were constructed.

In system I, there occur monovariant eutectic process $L \leftrightarrow \alpha + \beta$ within the temperature range 800–785 K (line e- Tl_9BiSe_6) and monotectic process $L_1 \leftrightarrow L_2 + \beta$ in the region bounded by the line mkn; the coordinates of the point k are (~62 mol % Tl_9BiSe_6 , ~18 mol % Tl_4PbSe_3 , ~20 mol % PbSe, ~795 K).

The liquidus of system II is constituted by three surfaces of the beginning of crystallization of components, TlBiSe_2 -e₁-E-e₂- TlBiSe_2 , Tl_9BiSe_6 -e₁-E- Tl_9BiSe_6 , and PbSe-e₂-E- Tl_9BiSe_6 -PbSe, which are separated by the lines of monovariant eutectic pro-

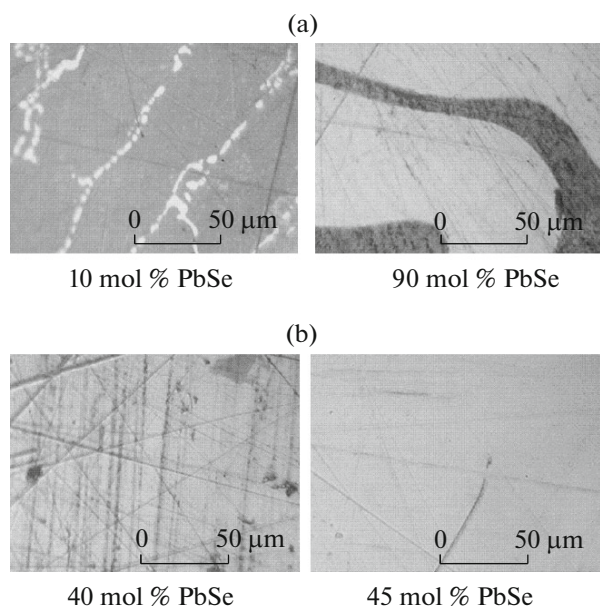


Fig. 3. Microstructure of some alloys in the systems (a) Tl_9BiSe_6 -PbSe and (b) TlBiSe_2 -PbSe systems.

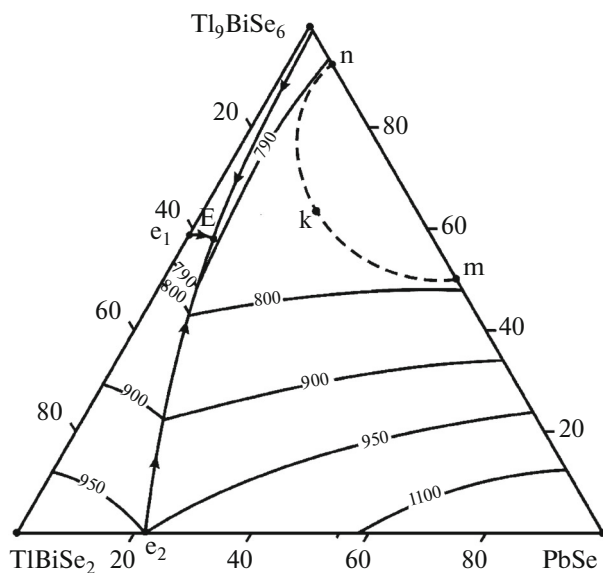


Fig. 5. Projection of the liquidus surface of the TlBiSe_2 - Tl_9BiSe_6 -PbSe quasi-ternary system.

cesses Tl_9BiSe_6 -E (process $L \leftrightarrow \alpha + \beta$, temperature range 784–754 K), e_1 -E (process $L \leftrightarrow \alpha + \gamma$, temperature range 760–754 K), and e_2 -E (process $L \leftrightarrow \beta + \gamma$, temperature range 950–754 K).

The lines of monovariant eutectic equilibria merge at the invariant eutectic point E; the coordinates of the ternary eutectic are (4 mol % PbSe, 62 mol % Tl_9BiSe_6 , 34 mol % TlBiSe_2 , 754 K).

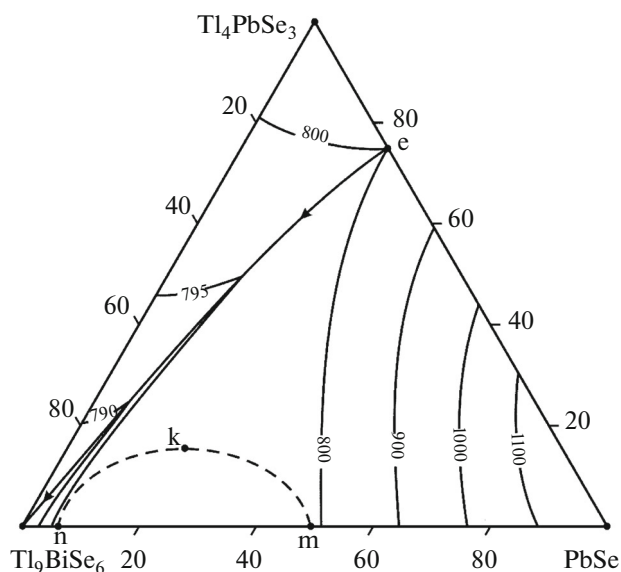


Fig. 4. Projection of the liquidus surface of the Tl_9BiSe_6 - Tl_4PbSe_3 -PbSe quasi-ternary system.

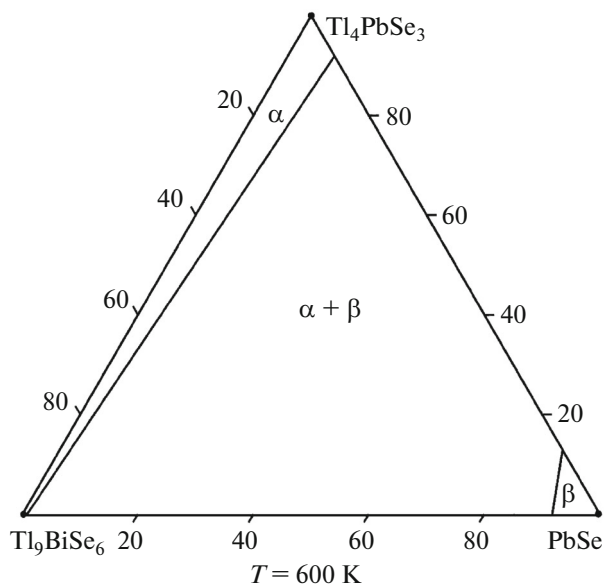


Fig. 6. Isothermal (600 K) section of the Tl_9BiSe_6 - Tl_4PbSe_3 -PbSe quasi-ternary system.

The monotectic equilibrium $L_1 \leftrightarrow L_2 + \beta$ occurs in the region bounded by the curve mkn (the coordinates of the point k are ~60 mol % Tl_9BiSe_6 , ~21 mol % TlBiSe_2 , ~19 mol % PbSe, ~790 K).

Based on the X-ray powder diffraction data, isothermal sections of systems I (Fig. 6) and II (Fig. 7) were constructed. In system I, boundary solid solutions form: α -solutions based on Tl_9BiSe_6 - Tl_4PbSe_3 compounds and β -solutions based on PbSe.

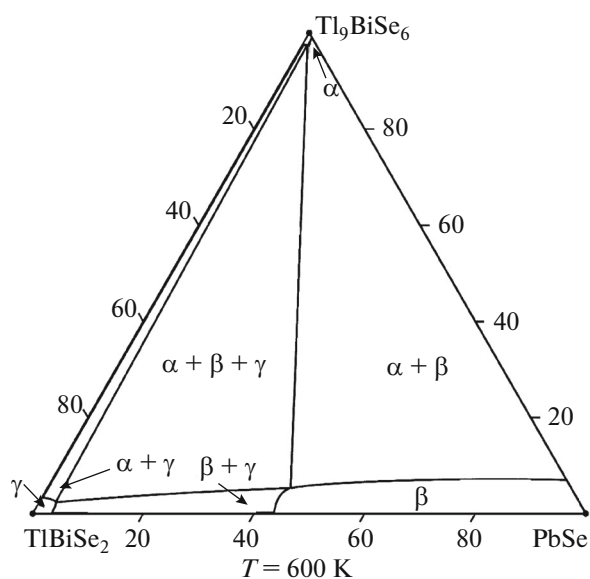


Fig. 7. Isothermal (600 K) section of the Tl_9BiSe_6 – TlBiSe_2 – PbSe quasi-ternary system.

The α -continuous series of solid solutions based on Tl_9BiSe_6 and Tl_4PbSe_3 can be considered a variable-composition phase, this system behaves as a pseudobinary system. This means that all the alloys behind the homogeneity region of the initial components in the solid state are two-phase.

In system II, solid solutions based on Tl_9BiSe_6 , TlBiSe_2 and PbSe form.

Because the TlBiSe_2 – PbSe system contains wide regions of solid solutions based on PbSe , the TlBiSe_2 – Tl_9BiSe_6 – PbSe ternary system contains a large two-phase region of $\alpha + \beta$ on the side of the quasibinary system Tl_9BiSe_6 – PbSe .

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