Interactions in the ternary reciprocal system
\( \text{Tl}_2\text{S} + \text{SnTe} \leftrightarrow \text{Tl}_2\text{Te} + \text{SnS} \)

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The phase diagram of the ternary reciprocal system \( \text{Tl}_2\text{S} + \text{SnTe} \leftrightarrow \text{Tl}_2\text{Te} + \text{SnS} \) was investigated using differential-thermal analysis, X-ray diffraction and microstructure analysis. The liquidus surface projection, the isothermal section at 520 K and phase diagrams of four vertical sections were constructed. The liquidus consists of seven primary crystallization fields. The extent of the continuous solid solution range based on the ternary phase \( \text{Tl}_4\text{SnTe}_3 \) was estimated.

Thermal analysis / X-ray diffraction/ Microstructure analysis/ Phase diagram / Isothermal section / Solid solution

Introduction

The \( \text{Tl}_2\text{XY}_3 \) (\( X = \text{Sn, Pb}; Y = \text{S, Se, Te} \)) compounds are characterized by low thermal conductivity and relatively high thermoelectric figures of merit \( \text{ZT} \) \(^1\). Therefore the \( \text{Tl}_4\text{SnS}_3(\text{Te}_3) \) compounds can be considered as perspective materials for thermoelectric devices. To increase the scope of their use, an investigation of the physico-chemical interaction in systems based on the compounds \( \text{Tl}_2\text{SnS}_3(\text{Te}_3) \) seemed promising. The two ternary compounds crystallize in isotypic tetragonal structures \(^2,3\), which indicates a high probability of formation of a solid solution.

Experimental

Binary thallium(I) and tin(II) sulfides and tellurides were prepared from stoichiometric amounts of high-purity initial elements (99.99 wt.%) in evacuated quartz ampoules. The \( \text{Tl}_2\text{SnS}_3, \text{Tl}_2\text{SnTe}_3 \) and \( \text{Tl}_2\text{SnS}_3 \) ternary compounds were obtained from stoichiometric amounts of binary \( \text{Tl}_2\text{S}, \text{SnS}, \text{SnTe} \). Multicomponent alloys were synthesized by the direct single-temperature method from binary and ternary sulfides and tellurides in quartz ampoules, which were evacuated to a residual pressure of 0.13 Pa. The highest synthesis temperature was 920 K. After thermal treatment at the highest temperature for 24-36 h the samples were slowly cooled (20-30 K per hour) down 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 including an \( x-y \) recorder PDA-1 and a chromel-alumel thermocouple (the linearity of heating and cooling was controlled by a RIF-101 programmer), with an accuracy of \( \pm 5 \) K. X-ray powder diffraction data was collected on a DRON-4 diffractometer (\( \text{Cu} \text{K}_\alpha \) radiation, Ni filter). The microstructure analysis was carried out with a metallographic microscope Lomo Metam R1. The simplex method of computer simulation of phase equilibria is described in \(^4\).

Results and discussion

The \( \text{Tl}_2\text{S} - \text{Tl}_2\text{Te} \) \(^5\) and \( \text{SnS} - \text{SnTe} \) \(^6\) systems are of the eutectic type; also in the \( \text{SnS} - \text{SnTe} \) system a eutectoid process takes place (based on the polymorphic transformation of \( \text{SnS} \) \(^6\). The quasi-binary systems \( \text{Tl}_2\text{S} - \text{SnS} \) \(^7\) and \( \text{Tl}_2\text{Te} - \text{SnTe} \) \(^8,9\) are characterized by the formation of one congruently melting ternary compound: \( \text{Tl}_4\text{SnTe}_3 \) (817 K), and two
incongruently melting compounds: Tl₄SnS₃ (626 K) and Tl₂Sn₂S₃ (679 K). A continuous series of solid solutions is formed between the binary thallium(I) telluride and Tl₄SnTe₃.

The Tl₂SnTe₃ ternary compound, which melts congruently, exists on one of the sides of the Tl₂S+SnTe↔Tl₂Te+SnS system. Therefore, it may be that none of the Tl₂S–SnTe or Tl₂Te–SnS diagonals of the quadrangle will be stable and the stable sections could be formed by Tl₂SnTe₃ (Fig. 1). For this reason the quasibinary sections of the reciprocal Tl₂S+SnTe↔Tl₂Te+SnS system must be determined first.

The determination of the quasibinary sections was carried out by phase analysis of samples lying at the intersection of possible quasibinary sections [10]. Three points of intersection of possible quasibinary sections exist in the reciprocal system Tl₂S+SnTe↔Tl₂Te+SnSe (Fig. 1). For the determination of the quasibinary sections, alloys corresponding to points 1 and 3 were synthesized and investigated by XRD and microstructure analysis. Based on the results, quasibinary was established for the two sections (Tl₂S–Tl₄SnTe₃, SnSe–Tl₄SnTe₃). The Tl₂S–Tl₄SnTe₃ system belongs to the Rozeboom type V (Fig. 2). The system liquidus consists of two parts: the primary crystallization of solid solutions based on Tl₂S and Tl₄SnTe₃ crystals. The coordinates of the eutectic point are 82 mol.% Tl₂S, 605 K (eutectic process L↔Tl₂S+Tl₄SnTe₃). At the annealing temperature (520 K) the solid solution ranges of Tl₂S and Tl₄SnTe₃ do not exceed 10 and 65 mol.%, respectively. The formation of a wide region of solid solution based on the Tl₄SnTe₃ phase was confirmed by the change of the cell parameters according to Vegard’s law. Within the solid solution range the lattice parameters change from \( a = 8.819 \) Å, \( c = 13.013 \) Å for Tl₄SnTe₃ to \( a = 8.836 \) Å, \( c = 12.906 \) Å for the boundary solid solution (Fig. 3). The results of the microstructure analysis support the XRD data on the phase composition in the system Tl₂S–Tl₄SnTe₃.

![Fig. 1 Possible quasibinary sections in the reciprocal system Tl₂S+SnTe↔Tl₂Te+SnS.](image1)

![Fig. 2 Phase diagram of the Tl₂S–Tl₄SnTe₃ system: 1 – L, 2 – L+Tl₄SnTe₃, 3 – L+Tl₂S, 4 – [Tl₄SnTe₃], 5 – Tl₄SnTe₃+Tl₂S, 6 – [Tl₂S].](image2)

![Fig. 3 Lattice parameters of Tl₄SnTe₃ in the system Tl₂S–Tl₄SnTe₃.](image3)

![Fig. 4 Phase diagram of the SnS–Tl₄SnTe₃ system: 1 – L, 2 – L+ht-SnS, 3 – [ht-SnS], 4 – ht-SnS+lt-SnS, 5 – L+Tl₄SnTe₃, 6 – L+lt-SnS, 7 – [Tl₄SnTe₃], 8 – [lt-SnS], 9 – lt-SnS+Tl₄SnTe₃.](image4)
The phase diagram of the SnS–Tl₂S₄Te₃ system is presented in Fig. 4. The liquidus of the quasibinary system consists of three lines of primary crystallization, which cross in two invariant points with the following coordinates: 50 mol. % SnS, 706 K (eutectic process L↔It-SnS+Tl₂S₄Te₃) and 81 mol. % SnS, 866 K (metatectic process ht-SnS↔L+It-SnS). The solid solution ranges based on Tl₂SnTe₃ and It-SnS do not exceed 5 mol. % at 520 K. The Tl₂SnS₄–Tl₂SnTe₃ and Tl₂SnS₃–Tl₂SnTe₃ systems are non-quasibinary above the solidus, due to the incongruent melting of the Tl₂SnS₃ and Tl₂SnS₄ compounds.

The vertical section of the Tl₂SnS₃–Tl₂SnTe₃ system is presented in Fig. 5. The liquidus consists of two lines that belong to the fields of primary crystallization of Tl₂SnTe₃ and It-SnS, which participates in the peritectic process of formation of Tl₂SnS₃. The lines of primary crystallization intersect in the point with the coordinates 79 mol. % Tl₂SnS₃, 626 K. The fields of primary crystallization are separated by a three-phase field, L+It-SnS+Tl₂SnTe₃. At the annealing temperature (520 K) the solid solution ranges of Tl₂SnTe₃ and Tl₂SnS₃ do not exceed 50 and 5 mol. %, respectively. The formation of a wide region of solid solution based on the Tl₂SnTe₃ phase is confirmed by the change of the cell parameters according to Vegard’s law. The lattice parameters within the solid solution range change from a = 8.819 Å, c = 13.013 Å for Tl₂SnTe₃ to a = 8.864 Å, c = 12.933 Å for the boundary solid solution (Fig. 6).

The vertical section of the Tl₂SnS₃–Tl₂SnTe₃ system is presented in Fig. 7. The liquidus consists of two lines that belong to the fields of primary crystallization of Tl₂SnTe₃ and Tl₂S, which participates in the peritectic process of formation of the Tl₂SnS₃ phase. The lines of primary crystallization intersect in the point with the coordinates 83 mol. % Tl₂SnS₃, 600 K. The fields of primary crystallization are separated by the three-phase field L+Tl₂S+Tl₂SnTe₃. The Tl₂SnS₃–Tl₂SnTe₃ system is the connecting line of the quasiternary system Tl₂S–Tl₂SnTe₃–SnS. It divides the fields of completion of secondary crystallization. This explains the fact that the three-phase region L+Tl₂S+ht-Tl₂SnS₃ borders the single-phase region ht-Tl₂SnS₃. At 520 K the extents of the solid solution ranges based on Tl₂SnTe₃ and It-Tl₂SnS₃ are less than 20 and 10 mol. %, respectively.

The isothermal section of the Tl₂S+SnTe↔Tl₂Te+SnS system includes six single-phase solid solution ranges; four are located in the corners of a quadrangle and two are located between the binary sulfides (Fig. 8).

A projection of the liquidus surface of the reciprocal system Tl₂S+SnTe↔Tl₂Te+SnS (Fig. 9) onto the concentration quadrangle was constructed according to the results of the DTA investigation and a computer simulation of the phase equilibria in

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multicomponent systems by the simplex method. It consists of seven fields of primary crystallization: \( T_2 \) (\( T_1 \)-e1-e2-P1-p1-\( T_1 \)), the solid solution based on \( T_1 \)-Te and \( T_1 \)SnTe (\( T_2 \)-Te-TlSnTe-e4-E2-e5-P2-E1-P1-e2-e1-\( T_1 \)), ht-TlSnS (p1-P1-E1-e3-p1), \( T_1 \)SnS (p2-e3-E1-P2-p2), It-SnS (m1-p2-e5-E2-P3-m2-m1), ht-SnS (SnS-m1-m2-P3-e6-SnS), and SnTe (SnTe-e6-P3-E2-e4-SnTe). The fields of primary crystallization are divided by 14 monovariant eutectic, peritectic and metatectic lines. The types and temperatures of the processes in the reciprocal system \( T_1 \)S+SnTe↔\( T_1 \)Te+SnS are shown in Table 1.

The monovariant lines cross in three invariant peritectic and two invariant eutectic points:

- P1: \( L+T_1 \)S↔\( T_1 \)SnTe+ht-TlSnS; 60 mol.% 3\( T_1 \)S, 18 mol.% \( T_1 \)SnTe, 22 mol.% 3SnS, 600 K;
- P2: \( L+It-SnS\leftrightarrow T_1 \)SnS+\( T_1 \)SnTe; 31 mol.% 3\( T_1 \)S, 20 mol.% \( T_1 \)SnTe, 49 mol.% 3SnS, 621 K;
- P3: \( L+SnTe\leftrightarrow It-SnS+T_1 \)SnTe; 44 mol.% 3SnS, 20 mol.% \( T_1 \)SnTe, 36 mol.% 3SnTe, 816 K;
- E1: \( L+It-T_1 \)SnS+3\( T_1 \)SnS+3\( T_1 \)SnTe; 43 mol.% 3\( T_1 \)S, 17 mol.% \( T_1 \)SnTe, 40 mol.% 3SnS, 590 K;
- E2: \( L+lt-SnS\leftrightarrow SnTe+T_1 \)SnTe; 35 mol.% 3SnS, 36 mol.% \( T_1 \)SnTe, 29 mol.% 3SnTe, 700 K.

New complex compounds were not observed in the reciprocal system \( T_1 \)S+SnTe↔\( T_1 \)Te+SnS.

Conclusions

The physico-chemical interactions in the reciprocal system \( T_1 \)S+SnTe↔\( T_1 \)Te+SnS were for the first time investigated by differential thermal and microstructure analysis, X-ray powder diffraction and mathematical simulation of phase equilibria in multicomponent systems by the simplex method. The character of the monovariant processes and the temperatures and coordinates of the invariant processes were determined. The existence of solid solutions of the ternary compounds \( T_1 \)SnS\(_3\) and \( T_1 \)SnTe\(_3\) was established.

### Table 1 Type and temperature of the processes in the reciprocal system \( T_1 \)S+SnTe↔\( T_1 \)Te+SnS.

<table>
<thead>
<tr>
<th>Monovariant line</th>
<th>Process</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>e1-e2</td>
<td>L↔It-( T_1 )S+3( T_1 )Te+3( T_1 )SnTe</td>
<td>628-605</td>
</tr>
<tr>
<td>e2-P1</td>
<td>L↔It-( T_1 )S+3( T_1 )SnTe</td>
<td>605-600</td>
</tr>
<tr>
<td>p1-P1</td>
<td>L+It-( T_1 )S↔ht-( T_1 )SnS(_3)</td>
<td>626-600</td>
</tr>
<tr>
<td>P1-E1</td>
<td>L+It-( T_1 )S↔ht-( T_1 )SnS(_3)+3( T_1 )SnTe</td>
<td>600-590</td>
</tr>
<tr>
<td>e3-E1</td>
<td>L↔ht-( T_1 )SnS(_3)+3( T_1 )SnS</td>
<td>613-590</td>
</tr>
<tr>
<td>e5-P2</td>
<td>L↔lt-SnS↔It-( T_1 )SnTe</td>
<td>706-621</td>
</tr>
<tr>
<td>p2-P2</td>
<td>L+lt-SnS↔It-( T_1 )SnS(_3)</td>
<td>679-621</td>
</tr>
<tr>
<td>P2-E1</td>
<td>L+lt-SnS↔It-( T_1 )SnS(_3)+3( T_1 )SnTe</td>
<td>621-590</td>
</tr>
<tr>
<td>m2-m1</td>
<td>ht-SnS↔lt-( T_1 )S</td>
<td>866-864</td>
</tr>
<tr>
<td>m2-P3</td>
<td>ht-SnS↔lt-( T_1 )S</td>
<td>866-816</td>
</tr>
<tr>
<td>e6-P3</td>
<td>L↔ht-SnS+SnS+( T_1 )S</td>
<td>973-816</td>
</tr>
<tr>
<td>e5-E2</td>
<td>L↔It-SnS+3( T_1 )SnTe</td>
<td>706-700</td>
</tr>
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<td>e4-E2</td>
<td>L↔It-SnS+3( T_1 )SnTe</td>
<td>773-700</td>
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<tr>
<td>P3-E2</td>
<td>L+ht-SnS↔lt-SnS+( T_1 )Te</td>
<td>739-730</td>
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References