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# Phase equilibria in the Tl–Tll–Te system and thermodynamic properties of the $Tl_5Te_{3-x}I_x$ solid solution

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# 1. Introduction

Complex chalcogenides and chalcogen-halides of heavy *p* metals are considered perspective functional materials. Many of them exhibit semiconductor, thermoelectric, photoelectric, and magnetic properties [1,2]. According to recent investigations, Tl<sub>6</sub>Sel<sub>4</sub> and Tl<sub>5</sub>Se<sub>2</sub>I are promising materials for efficient X-ray and  $\gamma$ -ray detection, outperforming the current state-of-the art material for room temperature operation, CdZnTe (CZT) [3,4]. Given the promising performance of thallium-based chalcogenides and chalcogenide-halide, these compounds continue to attract attention despite of toxicity of thallium derivatives.

The synthesis and growth of the single crystals from the melt requires the knowledge of the respective phase diagrams, which makes the investigation of phase equilibria very important in course of the material development. This is particularly true for quaternary phases, which frequently present wide homogeneity fields based on complex substitutional patterns. Typically, their functional properties can be tuned by varying the composition, which in turn calls for the development of a synthetic approach

### ABSTRACT

The Tl-TlI-Te ternary system was investigated by using the DTA and XRD analyses, microhardness and EMF measurements, leading to the construction of important polythermal and isothermal sections as well as the projection of the liquidus surface. Determined were the fields of primary crystallization and the types and coordinates of non- and monovariant equilibria. The system features the formation of continuous solid solutions ( $\delta$ -phase) between the Tl<sub>5</sub>Te<sub>3</sub> and Tl<sub>5</sub>Te<sub>2</sub>I compounds. The homogeneity area of the  $\delta$ -phase completely covers the Tl<sub>5</sub>Te<sub>2</sub>I-Tl<sub>5</sub>Te<sub>3</sub>-Tl<sub>2</sub>Te subsystem. The partial molar thermodynamic functions ( $\Delta \overline{\Delta}, \Delta \overline{H}, \Delta \overline{S}$ ) of thallium as well as the standard integral thermodynamic functions of the Tl<sub>5</sub>Te<sub>3-x</sub>I<sub>x</sub> solid solution (for various *x*) were calculated based on the results of the EMF measurements. © 2013 Elsevier B.V. All rights reserved.

toward the preparation of a required stoichiometry within a homogeneity range.

In our previous works, phase equilibria and thermodynamic properties of the systems Tl–TlCl–S [5], Tl–TlBr–S [6], Tl–TlL–S [7], Tl–TlCl–Se [8], Tl–TlBr–Se [9], Tl–TlCl–Te [10], and Tl–TlBr–Te [11] were investigated. A number of polythermal and isothermal sections as well as projections of liquidus surfaces were constructed. The homogeneity fields of the intermediate phases were fixed and their fundamental thermodynamic functions were calculated.

In this work, we report the results of the complete investigation of phase equilibria and thermodynamic properties of the Tl–Tll–Te system. The layout of this paper is as follows. We start with reviewing the literature data on this system and compounds in it, follow with the description of the experimental procedure, and then discuss our results on the phase equilibria, polythermal sections, liquidus surface, and thermodynamic properties of the  $Tl_5Te_{3-x}I_x$  solid solution.

# 1.1. Review of the literature data

The ternary system Tl–Te–I was investigated along various polythermal sections [12–15].

For the Tl–Te boundary system, 4 compounds have been reported; they are  $Tl_2Te$ ,  $Tl_5Te_3$ , TlTe, and  $Tl_2Te_3$ . The former two





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melt congruently at 698 and 726 K, respectively, whereas the latter two decompose upon melting at 573 and 511 K, respectively [16,17]. The quasi-binary system TII–Tl<sub>2</sub>Te is characterized by the formation of a ternary compound Tl<sub>5</sub>Te<sub>2</sub>I that melts by a synthectic reaction at 775 K [12]. The immiscibility area occupies the 20– 80 mol% TII concentration interval at a synthectic temperature. Eutectic is degenerated near TII and crystallizes at 713 K. Authors of [12] assume the presence of the peritectic equilibrium between Tl<sub>5</sub>Te<sub>2</sub>I and Tl<sub>2</sub>Te at ~730 K. The homogeneity region of Tl<sub>5</sub>Te<sub>2</sub>I at ~600 K is in the range ~65–745 mol% Tl<sub>2</sub>Te. The homogeneity areas of TII and Tl<sub>2</sub>Te were not determined in that work.

This compound forms a continuous solid solution with  $Tl_5Te_3$ [13]. The polythermal sections TII–TITe and TII–Tl\_2Te\_3 [14] are stable in subsolidus, i.e., consist of heterogeneous mixtures of primary compounds, but they are non-quasi-binary because of the peritectic decomposition of TITe and  $Tl_2Te_3$ . There are wide areas of immiscibility in the phase diagrams of both systems. The phase diagram of the quasi-binary system TII–Te is characterized by monotectic and eutectic equilibria [15]. The *T*–*x* diagrams of the boundary systems TI–TII [18] and TII–Te [15] are of the monotectic type. The binary compound TII constituting one of the corners of the ternary system TI–TII–Te melts congruently at 715 K and undergoes the TII<sub>I</sub>  $\Leftrightarrow$  TII<sub>II</sub> polymorph transformation at 451 K [18]. Also, the preparation, stability regions, and properties of Tl<sub>2</sub>Tel<sub>6</sub> were reported [19].

The following structural information is available from the literature regarding the binary and ternary compounds of the Tl–Te–I system (see Table 1). The low-temperature modification of Tll crystallizes in the orthorhombic symmetry and has a molecular-like crystal structure, whereas the high-temperature modification belongs to the CsCl structure type [20,21].

Tl<sub>2</sub>Te crystallizes in the monoclinic space group  $C_2/c$  with 44 formulas per unit cell and has an unusually complex structure composed of Tl<sup>1+</sup> and Te<sup>2–</sup> [17]. TlTe and Tl<sub>2</sub>Te<sub>3</sub> possess less complex crystal structures [22,23], however, they exhibit systems of homonuclear Tl–Tl or Te–Te bonds that make their structure somewhat similar to cluster halides of bismuth and tellurium [24,25]. Tl<sub>5</sub>Te<sub>3</sub> and Tl<sub>5</sub>Te<sub>2</sub>I belong to a structural family of compounds crystallizing in the In<sub>5</sub>Bi<sub>3</sub> structure type and its less symmetric analogs [26,27]. Crystal structures of other thallium selenahalides and tellurohalides of the 5:2:1 stoichiometry also belong to this structure family [8–11,28,29].

Finally, the crystal structure of  $Tl_2Tel_6$  features  $Te^{4+}$  cations in a distorted octahedral environment of iodine atoms [30]. Note that this compound does not belong to the ternary Tl–Tll–Te system studied in this work.

#### 2. Experimental

#### 2.1. Synthesis

Elemental thallium (Tl-99.999%, Alfa Aesar), tellurium (Te-99.999%, Alfa Aesar) and iodine (I-99% resublimed pearls, PA-ACS) were used as received. At the first step, they were used for the preparation of binary compounds  $Tl_2Te$ ,  $Tl_5Te_3$ , TITe,  $Tl_2Te_3$ , TII, and  $Tl_5Te_2I$ .

#### Table 1

Structural data for compounds of the TI-TII-Te system.

Congruently melting compounds Tl<sub>2</sub>Te and Tl<sub>5</sub>Te<sub>3</sub> were prepared from the stoic chiometric amounts of the corresponding elements by one-step melting in vacuumsealed (~10<sup>-2</sup> Pa) silica ampoules at 800 K, followed by cooling in a switched-off furnace. For incongruently melting TITe and Tl<sub>2</sub>Te<sub>3</sub> after fusing at 800 K the ampoules were slowly cooled to  $560 \pm 5$  K (TITe) or  $500 \pm 5$  K (Tl<sub>2</sub>Te<sub>3</sub>), annealed for 500 h, and then slowly cooled in a switched-off furnace.

Tll was synthesized from the elements following a specially designed procedure, which takes into account high volatility of iodine, describes in detail elsewhere [27].

Ternary compound  $Tl_5Te_2I$  was synthesized by melting appropriate amounts of the synthesized TII and  $Tl_2Te$  in a vacuum-sealed quartz ampoule. This compound decomposes by a synthectic reaction upon melting [12]. Accordingly, the ampoule after fusing at 800 K was cooled slowly to 730 K and held at this temperature for ~800 h.

Samples for the investigation of phase equilibria and thermodynamic properties were prepared from  $Tl_2Te$ ,  $Tl_5Te_3$ , TITe,  $Tl_2Te_3$ , TII, and  $Tl_5Te_2I$ . The total mass was 1 g. In most cases, after determining the solidus temperature, samples were annealed at 20–30 K below the solidus for 800–1000 h.

#### 2.2. Analysis

X-ray powder diffraction (XRD), differential thermal analysis (DTA), measurement of microhardness, and electromotive force were used to characterize the samples.

The XRD analysis was performed on a Bruker D8 ADVANCE diffractometer with the Cu K $\alpha_1$  radiation. The lattice parameters were refined using the Topas V3.0 software. XRD confirmed that the pre-synthesized binary and ternary compounds were phase-pure, and that the unit cell parameters perfectly matched the literature data for binary compounds. The powder XRD pattern for Tl<sub>5</sub>Te<sub>2</sub>I was indexed using Topas V3.0 software. It was confirmed that Tl<sub>5</sub>Te<sub>2</sub>I crystallizes in the tetragonal Tl<sub>5</sub>Te<sub>3</sub> structure type with the space group *I4/mcm* and the following unit cell parameters: *a* = 9.026(1), *c* = 13.324(3) Å, *z* = 4, which perfectly matches the literature data (see Table 1).

DTA was carried out with a Termoskan-2 device. The temperature was monitored by a Chromel–Alumel thermocouple. The ramp rate was 5 K min<sup>-1</sup>. Temperatures of thermal effects were taken mainly from the heating curves. The melting point of the ternary compound  $Tl_5Te_2l$  was found to be in agreement with the literature data [12,27].

Microhardness was measured with a PMT-3 tester, the typical loading being 20 g.  $\,$ 

For the electromotive force (EMF) measurements, the following concentration chains were assembled:

$$(-)Tl(solid)/glycerin + KI + TlI/[Tl - Te - I](solid)(+)$$

$$(1)$$

In the chains of type (1), metallic thallium was used as the left electrode, while equilibrium alloys of the system Tl–Te–I were exploited as the right electrode. A saturated glycerin solution of Kl with the addition of 0.1 mass% Tll was used as an electrolyte. The electrodes were prepared by pressing the powdered alloys in the form of pellets (0.5 g) in a molybdenum wire. The temperature was stabilized at 350 K for 40–50 h. EMF was measured by the compensation method in the temperature range of 300–400 K with the accuracy of  $\pm 0.1$  mV, using a high-resistance universal B7–34A digital voltmeter. The detailed description of the methods of assembling the electrochemical cell and carrying out the EMF measurements are given in [31,32].

#### 3. Results and discussion

To obtain complete a picture of phase equilibria in the system Tl–Tll–Te we have prepared and investigated a number of samples in the sections  $Tl_2Te$ –Tll,  $[Tl_2I]$ –Tl<sub>2</sub>Te, and  $Tl_5Te_2I$ –Te(Tl), and also several additional samples out of the given sections. The results are given in Figs. 1–8 and Tables 2–6.

Compound	Space group	Unit cell parameters	Ref.
TII	Cmcm (LT) Pm-3m (HT)	<i>a</i> = 4.57, <i>b</i> = 12.92, <i>c</i> = 5.24 Å <i>a</i> = 4.201 Å	[20,21]
Tl <sub>2</sub> Te	$C_2/c$	$a = 15.662, b = 8.987, c = 31.196$ Å, $\beta = 100.76^{\circ}$	[17]
Tl <sub>5</sub> Te <sub>3</sub>	I4/mcm	<i>a</i> = 8.929, <i>c</i> = 12.620 Å	[26]
TlTe	$P4_2/nmc$	a = 18.229, c = 6.157 Å	[22]
Tl <sub>2</sub> Te <sub>3</sub>	Сс	$a = 17.413, b = 6.552, c = 7.910$ Å, $\beta = 133.6^{\circ}$	[23]
Tl <sub>5</sub> Te <sub>2</sub> I	I4/mcm	<i>a</i> = 9.026; <i>c</i> = 13.324 Å	[27]
Tl <sub>2</sub> Tel <sub>6</sub> <sup>a</sup>	$P2_1/c$	<i>a</i> = 7.765, <i>b</i> = 8.174, <i>c</i> = 13.756 Å, $\beta$ = 124.2°	[30]
1121016	121/0	u = 7.705, v = 0.174, c = 15.750  A, p = 124.2	[30]

<sup>a</sup> Composition out of the TI-TITe-I system; see text.

#### 3.1. The polythermal section TlI–Tl<sub>2</sub>Te

The refined phase diagram of the system Tll–Tl<sub>2</sub>Te is shown in Fig. 1. The compound Tl<sub>5</sub>Te<sub>2</sub>I melts incongruently by a synthectic reaction at 775 K (Fig. 1, segment SS' on a bottom panel). The immiscibility field ranges from 20 to 75 mol% Tl<sub>2</sub>Te at the synthectic temperature. Tl<sub>5</sub>Te<sub>2</sub>I is in a peritectic equilibrium ( $p^*$ ) with Tl<sub>2</sub>Te (~99 mol% Tl<sub>2</sub>Te, 705 K) and an eutectic equilibrium ( $e_4$ ) with Tll (5 mol% Tl<sub>2</sub>Te, 710 K). There are wide areas of solid solution based on Tl<sub>5</sub>Te<sub>2</sub>I ( $\delta$ ) and Tl<sub>2</sub>Te ( $\alpha$ ). The homogeneity regions of  $\delta$  and  $\alpha$ -phases, defined using EMF and microhardness measurements, are 66.5–90% and ~97–100 mol% Tl<sub>2</sub>Te, respectively (Fig. 1).

XRD analysis confirms the phase diagram of the system  $Tl_2Te-TII$  (Fig. 2). Apparently, the samples in the 66.7–90 mol%  $Tl_2Te$  composition range keep the  $Tl_5Te_2I$  structure type, however, the shift of the peak positions point a the varying unit cell parameters. The sample containing 95 mol%  $Tl_2Te$  contains the lines of reflection of  $\alpha$ -phase and  $\delta$ -phase. This is in agreement with the data of EMF and microhardness.

In general, the phase diagram of the system  $Tl_2Te-Tll$  (Fig. 1) looks similar to one reported in the literature [12], but still some important differences are noticeable. Firstly, according to our data the homogeneity region of  $Tl_5Te_2l$  is wider than the one given in [12] and occupies ~66–90 mol%  $Tl_2Te$  concentration intervals. The solubility on the basis of  $Tl_2Te$  is no more than <5 mol%, but on the basis of both modifications of Tll is very small. This is specifically testified by the constancy of the phase transformation temperature (450 K) of Tll. We also verified the coordinates of eutectic and peritectic equilibria that slightly differ from those reported in the literature [12].



**Fig. 1.** Phase diagram (bottom), microhardnesses (middle), and EMF of the chains of type (1) at 300 K (top) for the system  $TII-TI_2Te$ .



Fig. 2. XRD patterns for different compositions of the Tll-Tl<sub>2</sub>Te system: 1-66.7 mol.% Tl<sub>2</sub>Te, 2-80 mol.% Tl<sub>2</sub>Te, 3-90 mol.% Tl<sub>2</sub>Te, 4-95 mol.% Tl<sub>2</sub>Te, 5-Tl<sub>2</sub>Te.

#### 3.2. The isothermal section of the ternary system Tl-TlI-Te at 300 K

An isothermal section of the phase diagram at 300 K demonstrates characteristics of solid-phase equilibria in the system Tl–Tll–Te (Fig. 3), including the wide homogeneity area of Tl<sub>5</sub>Te<sub>2</sub>I ( $\delta$ -phase). XRD analysis of the samples belonging to the subsystem Tl<sub>5</sub>Te<sub>2</sub>I–Tl<sub>5</sub>Te<sub>3</sub> confirms the formation of a continuous solid solution (Fig. 4). Apparently, the diffraction pattern for all samples are qualitatively the same, but the peaks are systematically shifted to higher angles with increasing of the Tl<sub>5</sub>Te<sub>3</sub> content. These results together with the data shown in Figs. 1 and 2 show that the homogeneity area of the  $\delta$ -phase covers a very large part of the subsystem Tl<sub>5</sub>Te<sub>2</sub>I–Tl<sub>5</sub>Te<sub>3</sub>–Tl<sub>2</sub>Te.

Existence of wide homogeneity areas of  $\alpha$ - and  $\delta$ -phases leads to the formation of two-phase areas  $\text{Tl}_I + \alpha$ ,  $\text{Tl}_I + \delta$ ,  $\alpha + \delta$ , and  $\text{TITe} + \delta$ . (The subscript index *I* refers to the low-temperature modification of thallium). Following three-phase areas exist in the system:  $\text{Tl}_1 + (\text{TII})_I + \delta$ ,  $\text{Tl}_I + \alpha + \delta$ ,  $(\text{TII})_I + \text{TITe} + \delta$ ,  $(\text{TII})_I + \text{TITe} + \text{Tl}_2\text{Te}_3$ , and  $(\text{TII})_I + \text{Tl}_2\text{Te}_3 + \text{Te}$ .

# 3.3. The liquidus surface of the system Tl-TlI-TeI

The liquidus surface (Fig. 5) consists of five fields corresponding to primary crystallization of the  $\delta$ -phase, (TII)<sub>II</sub>, Te, TITe, and Tl<sub>2</sub>Te<sub>3</sub>. The liquidus surfaces of thallium and  $\alpha$ -phase are degenerate. These fields are connected with different curves and points indicating non- and monovariant equilibria. Table 2 summarizes the types and coordinates of all non-variant equilibria, whereas monovariant equilibria are given in Table 3, temperature intervals of the latter can be obtained from Fig. 5.

The two largest primary crystallization regions belong to  $\delta$ -phase and (TII)<sub>II</sub>. Both of these phases primarily segregate by monotectic reactions in a wide composition area. The immiscibility areas which are formed by 3 liquid phases on the basis of Tl ( $L_1$ ), (TII)<sub>II</sub> ( $L_2$ ), tellurides and Te ( $L_3$ ) in different combinations ( $L_1 + L_2$ ,  $L_1 + L_3$ ,  $L_2 + L_3$ ,  $L_1 + L_2 + L_3$ ) cover a large part of the liquidus surface. An interesting feature of the system TI–TII–Te is the existence of triple aliquation (the triangle  $M_T M_T / M_T / M_T / M_T$ ) with non-variant syntectic equilibrium (#18 in Table 2). Coordinates of non-variant points, particularly immiscibility regions, were refined by constructing the above given polythermal sections of the phase diagram.

#### 3.4. The non-quasi-binary polythermal sections

Phase diagrams of the non-quasi-binary systems  $Tl_5Te_2l$ -Te and  $[Tl_2l]$ -Tl\_2Te are given in Figs. 6 and 7, respectively. These sections



Fig. 3. The isothermal section of the phase diagram of the Tl-Tll-Te ternary system at 300 K.



Fig. 4. XRD patterns for different compositions of the  $Tl_5Te_2l-Tl_5Te_3$  system:  $1-Tl_5Te_2l$ , 2-30 mol.%  $Tl_5Te_3$ , 3-50 mol.%  $Tl_5Te_3$ , 4-70 mol.%  $Tl_5Te_3$ ,  $5-Tl_5Te_3$ .

intersect nearly all phase regions of the Tl–Tll–Te system and reflect the majority of non- and monovariant equilibria. A comparison of Figs. 6 and 7 with the data given in Figs. 3 and 5 and Tables 2 and 3 shows the self-consistence of the obtained results of phase equilibria.

# 3.4.1. The polythermal section $Tl_5Te_2I$ -Te

The polythermal section Tl<sub>5</sub>Te<sub>2</sub>I–Te (Fig. 6) illustrates the phase equilibria in the TII-Tl<sub>2</sub>Te-Te composition region. This section crosses the following phase areas in the subsolidus region:  $\delta$ ,  $\delta$  + (TII)<sub>II</sub>,  $\delta$  + TITe + (TII)<sub>I</sub>, Tl<sub>2</sub>Te<sub>3</sub> + TITe + (TII)<sub>I</sub>, and Tl<sub>2</sub>Te<sub>3</sub> + Te + (TII)<sub>I</sub>. These areas completely conform with the solid-phase diagram of the system (Fig. 3). The liquidus curve along the section Tl<sub>5</sub>Te<sub>2</sub>I–Te consists of 3 parts corresponding to the primary crystallization of Te,  $(TII)_{II}$  and  $\delta$ -phase. The immiscibility field ranges between ~65 and 100 mol% Tl<sub>5</sub>Te<sub>2</sub>I. From this two-phase field.  $\delta$ -phase primary crystallizes in the ~85–100 mol% Tl<sub>5</sub>Te<sub>2</sub>I composition range. Primary crystallization fields of (TII)<sup>11</sup> and Te occupy the 40-85 mol% and 0-40 mol% Tl<sub>5</sub>Te<sub>2</sub>I composition intervals, respectively. The outgoing horizontal lines  $U_1$ ,  $U_2$  and E conform to the four-phase transition and eutectic equilibria (Table 2), but the line existing at 450 K reflects the polymorphic transition (TII)<sub>II</sub>  $\Leftrightarrow$  (TlI)<sub>I</sub>.

#### 3.4.2. The polythermal section [Tl<sub>2</sub>I]–Tl<sub>2</sub>Te

This polythermal section is characterized by formation of a wide triple aliquation field  $L_1 + L_2 + L_3$  limited by the two-phase  $L_1 + L_2$  and  $L_2 + L_3$  areas (Fig. 7). There are four or even five thermal effects on the DTA curves belonging to the samples of this section. The horizontal lines at 575, 505 and 450 K conform to the melting



Fig. 5. Projection of the liquidus surface of the system. Primary crystallization fields are marked by numbers: 1-δ, 2-(TII)<sub>II</sub>, 3-Te, 4-TITe, 5-TI<sub>2</sub>Te<sub>3</sub>.



Fig. 6. The polythermal section Tl<sub>5</sub>Te<sub>2</sub>I-Te of the Tl-Tll-Te system.



Fig. 7. The polythermal section [Tl<sub>2</sub>I]-Tl<sub>2</sub>Te of the Tl-Tll-Te system.



Fig. 8. Dependence of the relative partial thermodynamic functions of thallium on the composition in the  $Tl_5Te_2I$ - $Tl_5Te_3$  system.

and polymorphic transition of thallium and polymorphic transition of TII, respectively. The thermal effects at 755 and 708 K reflect four-phase monotectic equilibria  $M_{\rm T}$  and  $M_1$  (Fig. 5, Table 2). In

the subsolidus region, this polythermal section crosses the following phase fields:  $Tl_I + \alpha$ ,  $Tl_I + \alpha + \delta$ ,  $Tl_I + \delta$ , and  $Tl_I + (TII)_I + \delta$ .

# 3.5. Thermodynamic properties of the solid solution $Tl_5Te_{3-x}l_x$

The results of the EMF measurements of the chains (1) are consistent with the solid-state phase diagram (Fig. 3).

It was found that EMF does not depend upon composition in the three-phase areas TII–TITe– $\delta$ , TII–TITe–Tl<sub>2</sub>Te<sub>3</sub>, and TII–Tl<sub>2</sub>Te<sub>3</sub>–Te. The EMF values change with drastically at each phase border. In the two latter fields, the values of EMF are equal to those reported for pure TITe and Tl<sub>2</sub>Te<sub>3</sub>, respectively [33]. This proves the reversibility of chains (1), as well as our results declaring the existence of small homogeneity areas of TITe and Tl<sub>2</sub>Te<sub>3</sub> in the system TI–TII–Te.

The analysis showed the linearity of the EMF dependences upon temperature for all alloys. Accordingly, the linear least-squares treatment of the data was performed and the results were expressed according to the literature [31,32] as

$$E = a + bT \pm t \left[ \frac{S_E^2}{n} + S_b^2 (T - \overline{T})^2 \right]^{1/2}$$
(2)

where *n* is the number of pairs of *E* and *T* values; *S<sub>E</sub>* and *S<sub>b</sub>* are the error variances of the EMF readings and *b* coefficient, respectively;  $\overline{T}$  is the average of the absolute temperature; *t* is the Student's test. At the confidence level of 95% and  $n \ge 20$ , the Student's test is  $t \le 2$  [32]. The composed equation of the mode (2) is presented in Table 4.

The partial molar functions of thallium ( $\Delta \overline{G}$ ,  $\Delta \overline{H}$ ,  $\Delta \overline{S}$ ) (Table 5) in the Tl<sub>5</sub>Te<sub>3-x</sub>l<sub>x</sub> solid solution were calculated by thermodynamic relations [31,32] using the data given in Table 4 as follows:

$$\Delta \overline{G}_{TI} = -zFE$$

$$\Delta \overline{S}_{TI} = zF \left(\frac{\partial E}{\partial T}\right)_{p} = zFb$$

$$\Delta \overline{H}_{TI} = -zF \left[E - T \left(\frac{\partial E}{\partial T}\right)_{p}\right] = -zFa$$
(3)

where z is the charge of the potential-forming cation  $TI^+$  and F is the Faraday constant.

The graphical dependences of the partial molar functions of thallium on the composition along the section  $Tl_5Te_2I-Tl_5Te_3$  are plotted in Fig. 8. The isotherms of  $\Delta \bar{G}_{TI}$ ,  $\Delta \bar{H}_{TI}$  and  $\Delta \bar{S}_{TI}$  are continuous and monotonous functions of the composition in the homogeneity range of the  $\delta$ -phase. The monotonous character of the concentration dependences of the partial thermodynamic functions of thallium in the homogeneity region of the  $\delta$ -phase indicates that formation of the solid solution is accompanied by minor structural and energetic changes. Besides, it confirms that  $\delta$ -phase belongs to the substitutional type of solid solutions.

According to Fig. 3 the partial molar values of thallium in the  $Tl_5Te_2I + TII + TITe$  phase area are the thermodynamic functions of the following potential-forming reaction [31,32]:

$$Tl(s) + 0.5Tll(s) + TlTe(s) = 0.5Tl5Te2I$$
 (4)

Then, the standard thermodynamic functions of formation of  $Tl_5Te_2l$  were calculated as:

$$\Delta Z^{0}(\text{Tl}_{5}\text{Te}_{2}I) = 2\Delta \overline{Z_{\text{TI}}} + 2\Delta Z^{0}(\text{TlTe}) + \Delta Z^{0}(\text{TlI})$$
(5)

where  $\Delta Z^0$  is the  $\Delta G^0_{298}$  and  $\Delta H^0_{298}$  values for the corresponding phase, whereas  $\Delta \overline{Z}_{T1}$  is  $\Delta \overline{H}_{T1}$  and  $\Delta \overline{G}_{T1}$ . The standard entropy of  $Tl_5Te_2l$  was calculated as:

$$S^{o}(Tl5Te2I) = 2\Delta \overline{Z_{Tl}} + 2S^{o}(Tl) + S^{o}(TlI) + 2S^{o}(TlTe)$$

$$(6)$$

Table 2	
Non-variant equilibria on the $T-x$	-v diagram of the system Tl-Tll-Te.

No.	Points in Fig. 5	Equilibria	Composition, at.%		Т, К
			Tl	Te	
1	$D_1$	$L \leftrightarrow Tl_2Te(\alpha)$	66.7	33.3	698
2	$D_2$	$L \leftrightarrow \mathrm{Tl}_{5}\mathrm{Te}_{3}(\delta)$	62.5	37.5	723
3	<i>e</i> <sub>1</sub>	$L \leftrightarrow \alpha + \delta$	65.5	34.5	695
4	<i>e</i> <sub>2</sub>	$L \leftrightarrow Tl_2Te_3 + Te$	30.0	70.0	497
5	<i>e</i> <sub>3</sub>	$L \leftrightarrow (\text{TII})_{\text{II}} + \text{Te}$	12.5	75.0	707
6	<i>e</i> <sub>4</sub>	$L \leftrightarrow (\text{TII})_{\text{II}} + \delta$	50.8	1.7	710
7	Ε	$L \leftrightarrow (\text{TlI})_{\text{II}} + \text{Tl}_2\text{Te}_3 + \text{Te}$	30.0	68.0	491
8	$p_1$	$L + \delta \leftrightarrow \text{TlTe}$	43.0	57.0	573
9	$p_2$	$L + TITe \leftrightarrow Tl_2Te_3$	35.0	65.0	511
10	$U_1$	$L + \delta \leftrightarrow (TII)_{II} + TITe$	41.0	57.5	568
11	$U_2$	$L + TITe \leftrightarrow (TII)_{II} + TI_2Te_3$	29.0	70.0	505
12	$m_1(m_1)$	$L_3 \leftrightarrow L_1 + Tl_2Te$	69.5(97.0)	30.5(3.0)	680
13	$m_2(m_2)$	$L_2 \leftrightarrow L_1 + (\text{TlI})_{\text{II}}$	51.0(98.0)	_	714
14	$m_3(m_3)$	$L_2 \leftrightarrow L_3 + (\text{TlI})_{\text{II}}$	48.0(15.0)	4.0(70.0)	712
15	S(S')	$L_2 + L_3 \leftrightarrow \text{Tl}_5\text{Te}_2\text{I}(\delta)$	54.5(63.5)	9.0(27.5)	775
16	$M_1(M_1')$	$L_2 \leftrightarrow L_1 + (\text{TII})_{\text{II}} + \delta$	51.5(97.0)	1.5(1.0)	708
17	$M_2(M_2)$	$L_2 \leftrightarrow L_3 + (\text{TII})_{\text{II}} + \delta$	51.0(53.0)	8.0(40.0)	695
18	$M_{\mathrm{T}}(M_{\mathrm{T}},M_{\mathrm{T}})$	$L_2 + L_3 \leftrightarrow L_1 + \delta$	57.0(69.0; 94.0)	5.0(27.0;3.0)	755

Indexes 1 and 11 in the formulas are low- and high-temperature modifications.

 Table 3

 Monovariant equilibria on *T*-*x*-*y* diagram of the system TI-TII-Te.

No.	Curves in Fig. 5	Equilibria	Temperature intervals
1	$SM_{\rm T}; SM_{\rm T}$	$L_2 + L_3 \leftrightarrow \delta$	775–755
2	$SM_2$ ; $S'M_2'$	$L_2 + L_3 \leftrightarrow \delta$	775–695
3	$M_{\rm T}M_1; M_{\rm T}''M_1'$	$L_2 \leftrightarrow L_1 + \delta$	755–708
4	$M_{T}'m_{1}; M_{T}''m_{1}'$	$L_3 \leftrightarrow L_1 + \delta$	755-680
5	$m_2M_1; m_2 M_1'$	$L_2 \leftrightarrow L_1 + (\text{TII})_{\text{II}}$	714–708
6	$m_3M_2; m_3' M_2'$	$L_2 \leftrightarrow L_3 + (TII)_{II}$	712-695
7	$e_4 \cdot M_1$ ;	$L_2 \leftrightarrow (\text{TII})_{\text{II}} + \delta$	710–708
8	$e_4 \cdot M_2$	$L_2 \leftrightarrow (TII)_{II} + \delta$	710–695
9	$M_2 U_1$	$L_3 \leftrightarrow (\text{TII})_{II} + \delta$	695-568
10	$p_1U_1$	$L_3 + \delta \leftrightarrow TlTe$	573-568
11	$U_1U_2$	$L_3 \leftrightarrow (\text{TlI})_{II} + \text{TlTe}$	568-505
12	$p_2U_2$	$L_3$ + TITe $\leftrightarrow$ Tl <sub>2</sub> Te <sub>3</sub>	511-505
13	$U_2E$	$L_3 \leftrightarrow (\text{TlI})_{II} + \text{Tl}_2\text{Te}_3$	505-491
14	e <sub>2</sub> E	$L_3 \leftrightarrow Tl_2Te_3 + Te$	497-491
15	e₃E	$L_3 \leftrightarrow (\text{TlI})_{\text{II}} + \text{Te}$	707-491

#### Table 4

Temperature dependencies of the EMF for the chains of type (1) for various phase areas in the  $Tl_5Te_3-Tl_5Te_2l$  system (*T* = 300–400 K).

Phase area	$E, \mathbf{mV} = a + bT \pm t \left[ \frac{S_E^2}{n} + S_b^2 (T - \overline{T})^2 \right]^{1/2}$
Tl₅Te₂I + TII + TITe	$464.3 - 0.062T \pm 2 \left[\frac{1.5}{26} + 3.9 \cdot 10^{-5} (T - 361.5)^2\right]^{1/2}$
$Tl_5Te_{2.2}I_{0.8}$	$453.5 - 0.044T \pm 2 \left[ \frac{2.0}{26} + 5.1 \cdot 10^{-5} (T - 363.1)^2 \right]^{1/2}$
$Tl_5Te_{2.4}I_{0.6}$	$446.2 - 0.030T \pm 2 \left[ \frac{1.7}{26} + 4.5 \cdot 10^{-5} (T - 363.6)^2 \right]^{1/2}$
$Tl_5Te_{2.6}I_{0.4}$	$442.8 - 0.043T \pm 2 \left[ \frac{2.6}{26} + 7.1 \cdot 10^{-5} (T - 368.2)^2 \right]^{1/2}$
$Tl_5Te_{2.8}I_{0.2}$	$440.7 - 0.0667 \pm 2 \left[ \frac{2.3}{26} + 6.2 \cdot 10^{-5} (T - 364.1)^2 \right]^{1/2}$
$Tl_5Te_3$	$440.1 - 0.0867 \pm 2 \left[ \frac{13}{23} + 4.4 \cdot 10^{-5} (T - 362.7)^2 \right]^{1/2}$

Besides our own  $\Delta \overline{Z}_{TI}$  data, we used the standard thermodynamic functions of formation of TITe [33] and TII [34] and the standard entropy of thallium ( $S_{298}^0 = 64.2 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ) [34] for the calculations.

The integral thermodynamic functions of the solid solutions  $Tl_5Te_3-Tl_5Te_2l$  were calculated by integration of the Gibbs–Duhem equation [31]. Results are given in Table 6. Standard deviations were calculated by accumulation of the errors.

Table 5	
Relative partial thermodynamic functions of thallium in the solid solution Tl <sub>5</sub> Te <sub>3</sub> .	${x}I_{x}$
at 298 K.	

Phase	$-\Delta \bar{G}_{Tl} (kJ mol^{-1})$	$-\Delta \bar{H}_{\mathrm{Tl}}$ (kJ mol <sup>-1</sup> )	$-\Delta \bar{S}_{Tl} (J K^{-1} mol^{-1})$
Tl <sub>5</sub> Te <sub>2</sub> I	43.02 ± 0.08	$44.80 \pm 0.44$	-5.98 ± 1.21
Tl <sub>5</sub> Te <sub>2.2</sub> I <sub>0.8</sub>	42.49 ± 0.09	43.76 ± 0.50	$-4.25 \pm 1.38$
Tl <sub>5</sub> Te <sub>2.4</sub> I <sub>0.6</sub>	42.19 ± 0.09	43.05 ± 0.47	$-2.89 \pm 1.29$
Tl <sub>5</sub> Te <sub>2.6</sub> I <sub>0.4</sub>	41.49 ± 0.09	42.72 ± 0.58	$-4.15 \pm 1.63$
Tl <sub>5</sub> Te <sub>2.8</sub> I <sub>0.2</sub>	40.62 ± 0.09	42.52 ± 0.55	$-6.37 \pm 1.52$
Tl <sub>5</sub> Te <sub>3</sub>	39.99 ± 0.09	$42.46 \pm 0.46$	$-8.30 \pm 1.28$

Table 6						
Standard integral	thermodynamic i	functions of	the solid	solution	$Tl_5Te_{3-x}I_x$	at 298 K.

Phase	$-\Delta G_{298}^0 (\mathrm{kJ} \ \mathrm{mol}^{-1})$	$-\Delta H_{298}^0$ (kJ mol <sup>-1</sup> )	$S_{298}^0$ (J K <sup>-1</sup> mol <sup>-1</sup> )
Tl₅Te <sub>2</sub> I	300.4 ± 1.3	301.1 ± 2.3	475.8 ± 6.6
Tl <sub>5</sub> Te <sub>2.2</sub> I <sub>0.8</sub>	288.0 ± 1.5	287.8 ± 2.4	477.0 ± 7.0
Tl <sub>5</sub> Te <sub>2.4</sub> I <sub>0.6</sub>	274.1 ± 1.6	271.6 ± 2.5	483.1 ± 7.4
Tl <sub>5</sub> Te <sub>2.6</sub> I <sub>0.4</sub>	257.3 ± 1.6	253.9 ± 2.5	484.3 ± 7.8
Tl <sub>5</sub> Te <sub>2.8</sub> I <sub>0.2</sub>	236.9 ± 1.7	235.5 ± 2.6	475.9 ± 8.2
Tl <sub>5</sub> Te <sub>3</sub>	213.5 ± 1.7	216.6 ± 2.4	459.1 ± 8.1

# 4. Conclusions

Application of various experimental methods, including DTA, XRD, as well as measurement of microhardness and EMF enabled us to construct a self-consistent phase diagram of the system Tl–TlI–Te containing only one ternary compound  $Tl_5Te_2I$ , which forms solid solution ( $\delta$ -phase) with a wide homogeneity range. Several polythermal and isothermal sections and the projection of the liquidus surface were constructed. The fields of primary crystallization as well as types and coordinates of non- and monovariant equilibria were determined. From the electromotive force measurements, the partial molar functions of  $Tl_5Te_2I$  and the solid solution  $Tl_5Te_3-Tl_5Te_2I$  were calculated.

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