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Phase equilibriums and thermodynamic properties of the system Bi–Te–I

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ABSTRACT

The system Bi–Te–I was studied by methods of differential thermal analysis and the X-ray diffraction, and also by measurements of electromotive forces (EMF) of concentration chains of type

$$(-)\,\mathrm{Bi}\,(s)\,|\,\text{liquid electrolytic conductor},\ \mathrm{Bi}^{3+}\,|\,(\mathrm{Bi{-}Te{-}I})\,(s)\,(+)$$

in the temperatures range of 300–400 K. The series of polythermal sections and isothermal section of the phase diagram at 300 K, and a projection of the liquidus surface were constructed. Earlier indicated ternary compounds BiTeI, Bi_2TeI and $Bi_4TeI_{1.25}$ were confirmed, the position of phase areas and their relationships was established. Areas of primary crystallization fields, types and coordinates of the non- and mono-variant equilibriums were determined. The measurements of EMF have allowed calculation of partial molar functions ($\Delta\bar{G}$, $\Delta\bar{H}$, $\Delta\bar{S}$) of bismuth in alloys, standard thermodynamic functions of formation and standard entropies of the indicated ternary compounds.

1. Introduction

Chalcohalogenides of elements of arsenic subgroup relate to a number of promising semiconductor materials. Many of these compounds and phases on their basis have significant thermoelectric, photoelectric and ferroelectric properties [1–4].

The ternary system Bi–Te–I was studied in a series of works [5–13]. The greatest number of results [5–11] is devoted to the study of phase equilibria in the quasi-binary system Bi_2Te_3–BiI_3. The results of [5–7] are very similar. Those publications shows that the T-x diagram of this system relates to a dystectic type reaction with formation of one intermediate compound BiTeI with a melting temperature of 828 ± 5 K and it is characterized by a fine-bored area of homogeneity. The results of the works [8,10] made by the same authors concerning the melting temperature of BiTeI (743 K) and some elements of the phase diagram Bi_2Te_3–BiI_3 are a little bit different to the data [5–7].

BiTeI crystallizes with formation of hexagonal structure of type CdI_2 (space group $P\bar{3}ml$), the lattice parameters: $a = 4.31$ Å, $c = 6.83$ Å, $z = 1$, [1,5] and $a = 4.3392$ Å, $c = 6.854$ Å, $z = 1$ [8].

Isopleth sections BiI_3–Te and BiTeI–Te are also quasi-binary and relate to a simple eutectic type [11]. It is shown in [12] that the section Bi_2Te_3–I_2 is quasi-binary and shows existence of two congruently melting ternary compounds Bi_2Te_3–I_2 (693 K) and $Bi_2Te_3 \cdot 3I_2$ (653 K). Single crystals of these compounds were obtained by the Bridgman method [12].

The results of [11] and [12] are in contradiction, and as the two cross-sections with eutectic character are not quasi-binary.

In [14] existence of two new lowest telluroiodides of bismuth Bi_2TeI and $Bi_4TeI_{1.25}$ obtained by condensation from the gas phase is reported. A single crystals of Bi_2TeI obtained from a melt have a monoclinic structure with lattice parameters: $a = 7.586$ Å, $b = 4.380$ Å, $c = 17.74$ Å, $\beta = 98.20°$.

Taking into account the inconsistency of data on different isopleth sections available in the literature, and for the definition of existence areas of known bismuth telluroiodides in a T-x-y diagram we have launched the detailed study of phase equilibria in the system Bi–Te–I for all compositions areas. Moreover possible new ternary phases can be evidenced. In the previous reports some results on the subsystems Bi_2Te_3–BiTeI–Te [14] and BiI_3–BiTeI–Te [15] and BiI_3–TeI_4–Te [16] were presented. It was shown, that the first two subsystems relate to a type of systems with ternary eutectic equilibrium. In subsystem BiI_3–TeI_4–Te four field of primary crystallization (Te, BiI_3, TeI_4 and TeI) are shown. Some mono and invariant equilibria including these phases are present (peritectic as well as eutectic reactions). Below the solidus this subsystem consists of two three-phase areas BiI_3–TeI–Te and BiI_3–TeI–TeI_4.

In this work, the complete scheme of phase equilibria for the whole system Bi–Te–I is presented, and the fundamental thermodynamic functions of bismuth telluroiodides ΔG^0_{298} ΔH^0_{298}, S^0_{298}, were determined.

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2. Experimental

The results of [14–16] primary determine the phase equilibria in the compositions field Bi_2Te_3–BiI_3–TeI_4–Te of the system Bi–Te–I. Therefore, we have prepared some alloys from the compositions areas Bi–Bi_2Te_3–BiI_3 and BiI_3–TeI_4–I_2. Firstly, the compounds Bi_2Te_3, BiTe, Bi_2Te, BiTeI, Bi_2TeI, $Bi_4TeI_{1.25}$, BiI_3, BiI, TeI_4 and TeI were synthesized by melting stoichiometric amount of the corresponding elements of a high pure grade in quartz ampoules under vacuum ($\approx 10^{-2}$ Pa). Bismuth tellurides were synthesized by heating at ≈900 K followed by a slow cooling rate. Taking into account the high pressure of iodine vapor, the synthesis of tellurium and bismuthiodides and telluroiodides have been made in a tilted furnace under temperature gradient conditions. The temperature of the top zone was 370 K, and the bottom at 20–30° higher than melting temperature of the corresponding compounds. After the interaction of the main part of iodine, the ampoule have been completely loaded in the lower zone, the content was carefully mixed, heated and then slowly (≈2–3°/min) cooled. Thus, the congruently melting compounds BiI_3, TeI_4 and BiTeI have been obtained as homogeneous phases. The incongruently melting phases BiTe, Bi_2Te, BiI, TeI, Bi_2TeI and $Bi_4TeI_{1.25}$ have been annealed at temperatures 20–30° below of the corresponding peritectics in the range 500–800 h in order to get a complete homogenization of the alloys. Every 200 h of annealing the alloys have been grinded to a fine powder and pressed to pellet. A completeness of the synthesis has been inspected by methods of differential thermal analysis and X-ray analysis with follow comparison to referred data [13,17].

The alloys from areas of compositions Bi–Bi_2Te_3–BiI_3 and BiI_3–TeI_4–I_2 have been synthesized also by solid state diffusion technique under vacuum from initial phases of given subsystems annealed firstly at mentioned conditions, and then at 400 K for 200 h.

The characterization has been made by using differential thermal analysis (with use of pyrometer NTR-72, chromel/alumel probes) and X-ray analysis (X-ray diffractometer DRON-2, Cu Kα-radiation), microhardness measurements (using a microhardnesmeter PMT-3, loading 20 g) and by measurements of electromotive forces (EMF). For the EMF measurements have been used chains of the follow type:

$$(-)\,\mathrm{Bi}\,(s)/\mathrm{glycerine} + \mathrm{KI} + \mathrm{BiI_3}/(\mathrm{Bi\text{–}Te\text{–}I})\,(s)\,(+) \qquad (1)$$

The similar concentration circuits are widely used in practice in thermodynamic study of ternary chalcogenides [18].

In such chains (1), the solid bismuth served as a left-hand electrode, and as right electrodes—the equilibrium alloys of the system Bi–Te–I. The choice of composition of the right electrode (1) is based on a general behaviour of the diagram described in [18].

Glycerin solution saturated by KI with addition of BiI_3 (0.1 mass.%) was used as an electrolytic conductor. Procedures of the preparation of electrolytic conductor and electrodes and assembly of an electrochemical cell were described in [18,19]. The assembled electrochemical cell was placed in a vertical tube-type furnace. The values of EMF of circuits of type (1) were measured in the temperature range 305–400 K by a compensation method using a digital voltmeter V7-34A. The temperatures were measured by a chromel/alumel thermocouple and by a mercury thermometer.

The first equilibrium values of EMF were measured in ∼30 h and following in each 4–5 h after achieve of a stationary value of temperature.

3. Results and discussion

The analysis of summarized experimental results and data of boundary binary systems Bi–Te, Bi–I and Te–I [18] and subsystem Bi_2Te_3–BiI_3–TeI_3–Te [14–16] has allowed us to find a general phase equilibria description in system Bi–Te–I (Figs. 1–6, Tables 1 and 2).

Fig. 1 shows the T-x phase diagram of the quasi-binary system BiI_3–Bi_2Te_3 constructed in [6,7] where our DTA data and results of a microhardness and an EMF for the selected compositions points are indicated. Thus, these data confirm the results of [6,7]. The phase BiTeI is well determined in the H_μ-x diagram with a microhardness value of ≈750 MPa (Fig. 1 b). The isothermal curve of E-x at 300 K consist of two horizontal straights with EMF values of 167 and 145 mV which step-wisely pass to each other at stoichiometric composition BiTeI that clearly fix a quality changing of phase composition of alloys.

The diagram of solid-phase equilibriums (Fig. 2) confirms the formation of ternary compounds BiTeI, Bi_2TeI and $Bi_4TeI_{1.25}$. Fig. 2 shows that the critical influence on distribution of phase areas in subsolidus. The phase BiI_3 is the more thermodynamically stable compound in the ternary. This compound is in interaction with tellurium, tellurium iodides (TeI_4 and TeI) and with all of the triple compounds. The whole Bi–Te–I system consists, in solid state, on 17 three-phase and 8 two-phase areas.

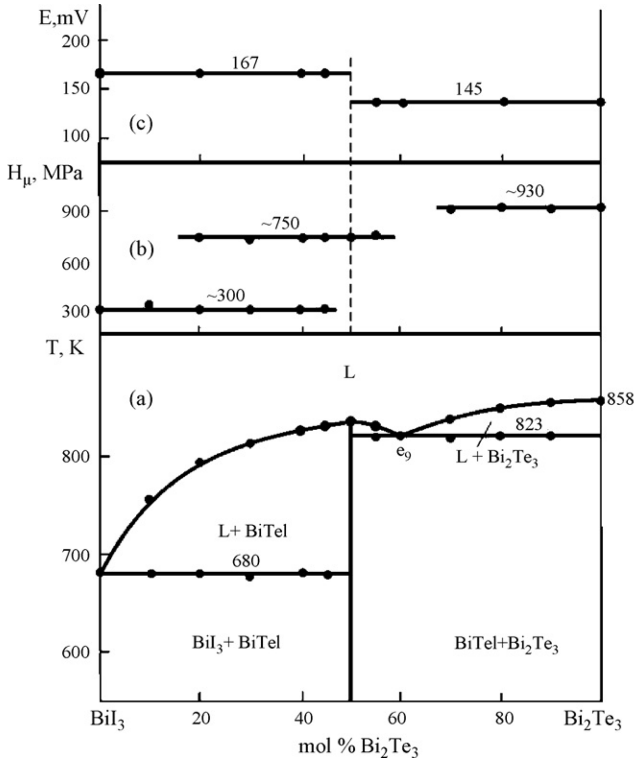

Fig. 1. Phase diagram (a), concentration relations of microhardnesses (b) and EMF of chains of type (1) at 300 K (c) of the systems BiI_3–Bi_2Te_3.

The qualitative vicinity of diffraction patterns of bismuth, its tellurides and telluroiodides rather complicates the determination of phase areas in the subsystem Bi–BiI_3–Bi_2Te_3 by X-ray diffraction. In the same time, the EMF method allows to differentiate these areas clearly. Fig. 2 shows the values of the EMF (mV) chains of the mode (1) in certain phase areas of the system Bi–Te–I at 300 K. The measurements are shown that under specified temperature in the range of each of three-phase areas the EMF has a strict constant value independent of general composition of alloys, but at transition from

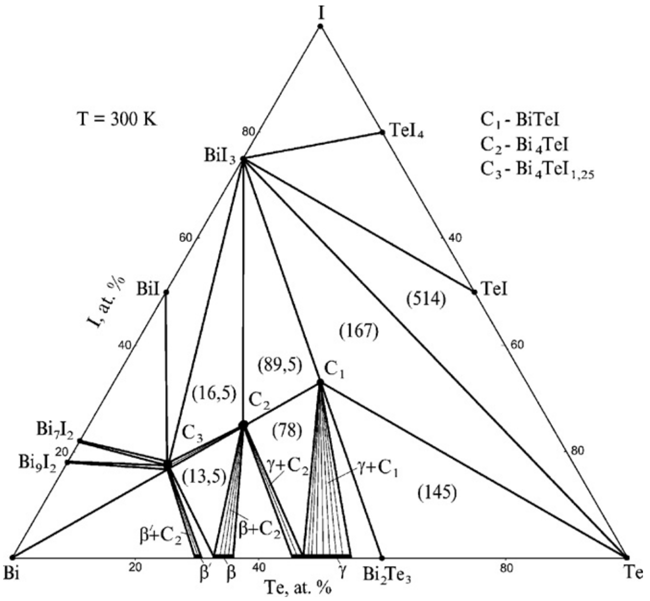

Fig. 2. Isothermal section at 300 K of the phase diagram of the system Bi–Te–I. The EMF values (mV) of concentration chains of type (1) in some phase areas are indicated in parenthesis.

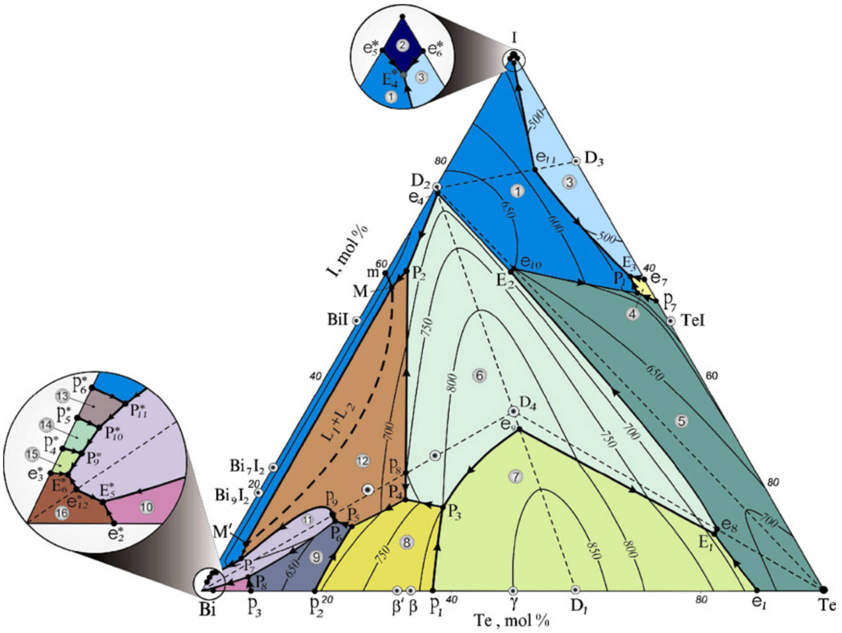

Fig. 3. Projection of liquidus surface of the system BiI–Te–I. Areas of primary crystallization of phases: 1-BiI_3; 2-I_2; 3-TeI_4; 4-TeI; 5-Te; 6-BiTeI; 7-Bi_2Te_3; 8-γ; 9-β; 10-β′; 11-$Bi_4TeI_{1.25}$; 12-Bi_2TeI; 13-BiI; 14-Bi_7I_2; 15-Bi_9I_2; 16-Bi. Dot lines—quasi-binary sections and area of immiscibility.

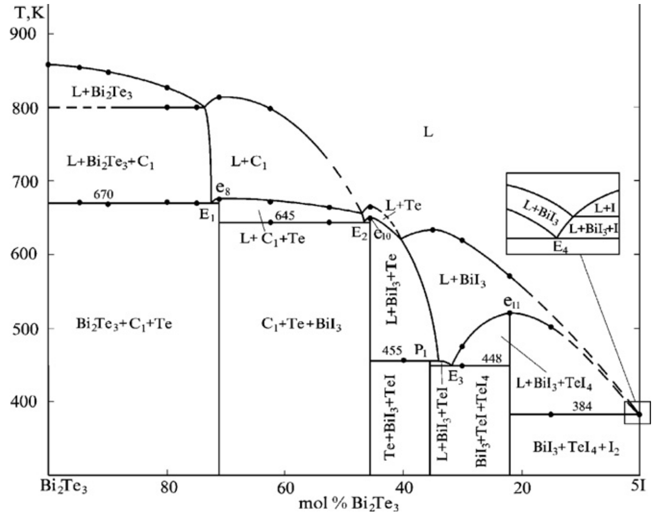

Fig. 4. Polythermal section Bi_2Te_3–I_2.

one three-phase area to another a jump is observed. For example, the jumps of the EMF at transition from BiI_3–$Bi_4TeI_{1.25}$–Bi_2TeI to BiI_3–Bi_2TeI–BiTeI gives 73 mV (error of the measurement does not exceed ±0.2 mV).

Liquidus surface (Fig. 3) consists of 16 areas of the primary crystallization fields; five of them (areas of the primary crystallization of Bi, I_2, BiI, Bi_7I_2 and Bi_9I_2) are degenerated. These areas are connected by different curves and points indicating the mono- and invariant eutectic and peritectic equilibria (Tables 1 and 2). In Table 1, it is also presented invariant equilibria of border binary systems and quasi-binary sections of the ternary system Bi–Te–I.

The quasi-binary sections divide the system Bi–Te–I on five independent subsystems: BiI_3–TeI_4–I (I), BiI_3–TeI_4–Te (II), BiI_3–BiTeI–Te (III), Bi_2Te_3–BiTeI–Te (IV) and Bi–Bi_2Te_3–BiI_3 (V).

The liquidus of the subsystem (I) consist on surfaces of the primary crystallization fields of BiI_3, TeI_4 and I_2. The last area and the corresponding eutectic point E_4 are degenerated on the melting temperature.

The subsystems (III) and (IV) are also related to the invariant eutectic reactions E_1 and E_2 type.

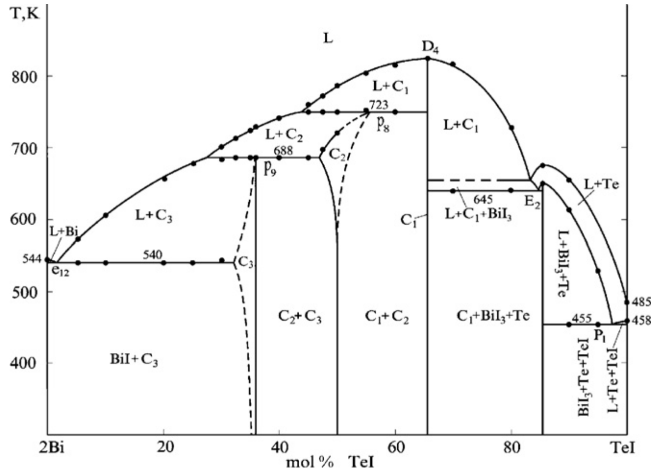

Fig. 5. Polythermal section Bi–TeI.

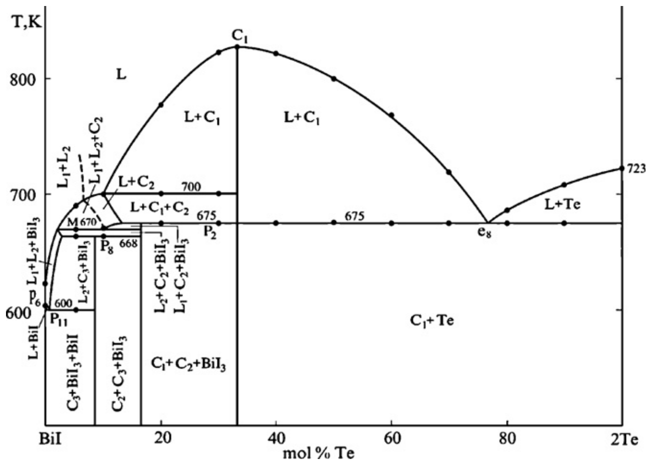

Fig. 6. Polythermal section BiI–Te.

Table 1
Nonvariant equilibriums in Bi–Te–I system.

No.	Point in Fig. 3	Equilibrium	Composition, at.%		*T*, K
			Bi	Te	
1	D1	$L_{D1} \Leftrightarrow Bi_2Te_3$	–	60	858
2	D_2	$L_{D2} \Leftrightarrow BiI_3$	75	–	680
3	D_3	$L_{D3} \Leftrightarrow TeI_4$	80	20	553
4	D_4	$L_{D4} \Leftrightarrow BiTeI$	33.3	33.3	828
5	e1	$L \Leftrightarrow Bi_2Te_3 + Te$	–	90	686
6	$e_2{}^*$	$L \Leftrightarrow BI + \beta'$	–	–	539
7	e3	$L \Leftrightarrow Bi + Bi_9I_2$	–	–	542
8	$e_4{}^*$	$L \Leftrightarrow BiTeI + BiI_3$	–	–	678
9	$e_5{}^*$	$L \Leftrightarrow BiI_3 + I_2$	–	–	386
10	$e_6{}^*$	$L \Leftrightarrow TeI_4 + I_2$	–	–	386
11	e_7	$L \Leftrightarrow TeI_4 + TeI$	58	42	451
12	e_8	$L \Leftrightarrow BiTeI + Te$	11.5	77	675
13	e_9	$L \Leftrightarrow BiTeI + Bi_2Te_3$	30	36	823
14	e_{10}	$L \Leftrightarrow BiI_3 + Te$	60	20	650
15	e_{11}	$L \Leftrightarrow BiI_3 + TeI_4$	78.5	14	523
16	$e_{12}{}^*$	$L \Leftrightarrow Bi + Bi_4TeI_{1.25}$	–	–	540
17	E_1	$L \Leftrightarrow Bi_2Te_3 + BiTeI + Te$	10.5	77	670
18	E_2	$L \Leftrightarrow BiTeI + Te + BiI_3$	59	20	645
19	E_3	$L \Leftrightarrow BiI_3 + TeI + TeI_4$	58.5	39.5	448
20	$E_4{}^*$	$L \Leftrightarrow BiI_3 + TeI_4 + I_2$	–	–	383
21	$E_5{}^*$	$L \Leftrightarrow Bi + \beta' + Bi_4TeI_{1.25}$	–	–	535
22	$E_6{}^*$	$L \Leftrightarrow Bi + Bi_9I_2 + Bi_4TeI_{1.25}$	–	–	538
23	p_1	$L + Bi_2Te_3 \Leftrightarrow \gamma$	–	37	821
24	p_2	$L - \gamma \Leftrightarrow \beta$	–	18	693
25	p_3	$L + \beta \Leftrightarrow \beta'$	–	8	585
26	$p_4{}^*$	$L + Bi_7I_2 \Leftrightarrow Bi_9I_2$	–	–	568
27	$p_5{}^*$	$L + BiI \Leftrightarrow Bi_7L$	–	–	573
28	$p_6{}^*$	$L + BiI_3 \Leftrightarrow B1I$	–	–	603
29	p_7	$L + Te \Leftrightarrow TeI$	54	46	458
30	p_8	$L + BiTeI \Leftrightarrow Bi_9TeI$	22	22	750
31	p_9	$L + Bi_2TeI \Leftrightarrow Bi_4TeI_{1.25}$	15	13	688
32	P1	$L + Te \Leftrightarrow TeI - BiI_3$	55.5	42	455
33	P_2	$L + BiTeI \Leftrightarrow BiI_3 + Bi_2TeI$	60	3	675
34	P_3	$L + Bi_2Te_3 \Leftrightarrow \gamma + BiTeI$	15.5	31	800
35	P_4	$L - BiTeI \Leftrightarrow \gamma - Bi_2TeI$	17	24	730
36	P_5	$L + \gamma \Leftrightarrow \beta + Bi_2TeI$	12	18	683
37	P_6	$L + Bi_2TeI \Leftrightarrow \beta + Bi_4TeI_{1.25}$	13	15	670
38	P_7	$L + Bi_2TeI \Leftrightarrow Bi_4TeI_{1.25} + BiI_3$	6	3	665
39	P_8	$L + \beta \Leftrightarrow \beta' + Bi_4TeI_{1.25}$	3	6	570
40	$P_9{}^*$	$L - Bi_7I_2 \Leftrightarrow BiTeI_{1.25} + Bi_9I_2$	–	–	560
41	$P_{10}{}^*$	$L - BiI \Leftrightarrow BiTeI_{1.25} + Bi_7I_2$	–	–	570
42	$P_{11}{}^*$	$L + BiI_3 \Leftrightarrow Bi_4TeI_{1.25} + Bi_7I_2$	–	–	600
43	m(m′)	$L \Leftrightarrow L_2 + BiI_3$	59(5)	–	623
44	M(M′)	$L \Leftrightarrow L_2 + BiI_3 + Bi_2TeI$	56.5 (9)	2(3)	670

The subsystem (II) is characterized by a peritectic (P_1) and by eutectic (E_3) reactions. Under the solidus three-phase areas exist: BiI_3–TeI–Te and BiI_3–TeI_4–TeI. The initial crystallization of TeI from melt takes place in very narrow composition range.

The subsystem (V) is characterized by more complicate reaction scheme. It is characterized by formation of two ternary compounds (Bi_2TeI and $Bi_4TeI_{1.25}$) decomposing by peritectic reactions corresponding to the invariant points p_8 and p_9 in the section TeI–Bi, and to points P_2, P_4 and P_{11} from which last three points degenerated at Bi corner of the concentration triangle. Eutectics E_5 and E_6 are also degenerated.

The area of immiscibility mm' of the boundary binary system Bi–I to penetrated into a ternary system and forms a wide area of mixing of two liquid phases (surface $mMkM'm'$). The curve of peritectic issued from point P_2 go through this area and result the isotherm (MM') associated to monotectic equilibrium.

On Figs. 4–6 it is presented some isopleth sections showing the processes of the equilibrium crystallization in the system.

The section Bi_2Te_3–I_2 (Fig. 4) is presented as a non quasi-binary contrarily to data [11]. This section traverses four (I–IV) of the five independent subsystems and indicates practically all processes of the crystallization occurred there.

Table 2
Monovariant equilibriums in system Bi–Te–I.

Curves in Fig. 3	Equilibrium	Temperature ranges, K
e_1E_1	$L \Leftrightarrow Bi_2Te_3 + Te$	680–670
e_8E_1; e_8E_2	$L \Leftrightarrow BiTeI + Te$	675–670; 675–645
e_9E1; e_9P_3	$L \Leftrightarrow BiTeI + Bi_2Te_3$	823–670; 823–800
$e_{10}E_2$; $e_{10}P_1$	$L \Leftrightarrow Bilj + Te$	650–645; 650–455
enE_3; enE_4	$L \Leftrightarrow BiI_3 + TeI_4$	523–448; 523–383
$e_5{}^*E_4{}^*$	$L \Leftrightarrow BiI_3 + I_2$	386–383
$e_6{}^*E_4{}^*$	$L \Leftrightarrow TeI_4 + I$	386–383
p_7P_1	$L + Te \Leftrightarrow TeI$	458–455
e_7E_3	$L \Leftrightarrow TeI_4 - TeI$	451–448
P_0E_3	$L \Leftrightarrow BiI_3 + TeI$	455–448
e_4E_2; e_4P_2	$L \Leftrightarrow BiI_3 + BiTeI$	678–645; 678–675
P_2M ($M'P_7$)	$L_1(L_2) - BiI_3 \Leftrightarrow Bi_2TeI$	675–665
p_8P_2; p_8P_4	$L + BiTeI \Leftrightarrow Bi_2TeI$	750–675; 750–730
p_1P_3	$L - Bi_2Te_3 \Leftrightarrow \gamma$	821–800
P_3P_4	$L + BiTeI \Leftrightarrow \gamma$	800–730
P_4P_5	$L + \gamma \Leftrightarrow Bi_2TeI$	730–683
p_2P_5	$L + \gamma \Leftrightarrow \beta$	693–683
P_5P_6	$L + \beta \Leftrightarrow Bi_2TeI$	683–670
p_9P_6; p_9P_7	$L + Bi_2TeI \Leftrightarrow Bi_4TeI_{1.25}$	688–670; 688–665
p_3P_8	$L + \beta \Leftrightarrow \beta'$	585–570
P_6P_8	$L + \beta \Leftrightarrow Bi_4TeI_{1.25}$	670–570
$P_8E_5{}^*$	$L + \beta' \Leftrightarrow Bi_4TeI_{1.25}$	665–535
$e_2{}^*E_5{}^*$	$L \Leftrightarrow Bi + \beta'$	539–535
$e_{12}{}^*$ $E_5{}^*$; $e_{12}{}^*$ $E_6{}^*$	$L \Leftrightarrow Bi - Bi_4TeI_{1.25}$	540–535; 539–535
e3$^*E_6{}^*$	$L \Leftrightarrow Bi - Bi_9I_2$	542–538
$P_4{}^*E_9{}^*$	$L - Bi_7I_2 \Leftrightarrow Bi_9I_2$	568–560
$P_9{}^*E_6{}^*$	$L \Leftrightarrow Bi_9I_2 + Bi_4TeI_{125}$	560–538
$p_5{}^*P_{10}{}^*$	$L + BiI \Leftrightarrow Bi_7I_2$	573–570
$P_{10}{}^*P_9{}^*$	$L + Bi_7I_2 \Leftrightarrow Bi_4TeI_{1.25}$	570–560
$p_6{}^*P_{11}{}^*$	$L + BiI_3 \Leftrightarrow BiI$	603–600
$P_{11}{}^*P_{10}{}^*$	$L + BiIoBi_4TeI_{1.25}$	600–570
$P_7P_{11}{}^*$	$L - BiI \Leftrightarrow Bi_4Te_{1.25}$	665–600

The liquidus consists of curves of the primary crystallization field of Bi_2Te_3, BiTeI, Te, BiI_3 and I_2. The liquidus of tellurium occupies wide area of compositions, and the liquidus of the I_2 is degenerated. It is well indicated on this section that the thermal effects are representative of mono-variant processes of the phases crystallization (isotherm ≈800 K, curves e_8E_1, e_8E_2, $e_{10}P_1$, P_1E_3, $e_{11}E_3$, etc.), and of an invariant peritectic as well as an eutectic equilibriums P_1, E_1, E_2, E_3, E_4 (horizontal lines at 455, 670, 645, 448 and 384 K) (Fig. 3, Tables 1 and 2).

The section BiI–Te (Fig. 5) is a partial quasi-binary. In the area of the compositions BiTeI–Te this section is characterized by an eutectic type reaction (e_8) and in the area of the compositions BiI–BiTeI the section BiI–Te cross the three-phase areas and is characterized by the peritectics (P_8, P_{11}) monotectic (M) equilibria.

The section Bi–TeI (Fig. 6) is also partial quasi-binary, it is practically quasi-binary in the area of the compositions Bi–BiTeI. The T-x diagram (Fig. 6) shows clearly marked isotherm at 723 and 688 K according to peritectic reactions (p_8, p_9) of formation of the intermediate phases based on the ternary compositions Bi_2TeI and $Bi_4TeI_{1.25}$.

The stability of equilibria this section in composition area Bi–BiTeI is proved using X-ray diffraction, micro-structural, microhardness analysis and EMF.

In the composition area BiTeI–TeI this section goes through the subsystems (II) and (III) and reflected the invariants (E_2, P_1) and the monovariant equilibria.

Thermodynamic properties of telluroiodides of bismuth. The results of the EMF measurements of chains of type (1) also have allowed calculating thermodynamic properties of telluroiodides of bismuth (Tables 4 and 5).

For analysis, we had used values of the EMF for three-phase areas BiI_3–I–Te, BiI_3–I–II and BiI_3–II–III which are responsible in potential-forming reactions with involving of the ternary compounds [18,19].

Table 3
Temperature dependences of EMF of chains type (1) in some phase areas of the system Bi–Te–I ($T = 305–400$ K).

Phase area on Fig. 2	$E = a + bT \pm t\left[\frac{S_E^2}{n} + S_b^2(T-\overline{T})^2\right]^{1/2}$
$BiI_3 + BiTeI + Te$	$E = 168.1 - 0.004 \pm 2\left[\frac{1.84}{26} + 1.4\times10^{-4}(-342.4)^2\right]^{1/2}$
$BiI_3 + Bi_2TeI + BiTeI$	$E = 97.06 - 0.025 \pm 2\left[\frac{7.26}{26} + 6.7\times10^{-4}(-346.6)^2\right]^{1/2}$
$BiI_3 + Bi_4TeI_{1.25} + Bi_2TeI$	$E = 12.4 + 0.020 \pm 2\left[\frac{2.68}{26} + 3\times10^{-4}(-354.5)^2\right]^{1/2}$

Table 4
Relative partial thermodynamic functions of bismuth in alloys of the system Bi–Te–I at 298 K.

Phase area from Fig. 2	$-\Delta\bar{G}_{Bi}$	$-\Delta\bar{H}_{Bi}$	$\Delta\bar{S}_{Bi}$
	kJ/mol		J/mol K
$BiI_3 + BiTeI + Te$	48.31 ± 0.11	48.66 ± 0.78	−1.2 ± 2.3
$BiI_3 + Bi_2TeI + BiTeI$	25.94 ± 0.26	28.1 ± 1.7	−7.2 ± 5.0
$BiI_3 + Bi_4TeI_{1.25} + Bi_2TeI$	5.32 ± 0.20	3.6 ± 1.2	5.9 ± 3.3

The analysis of the temperature dependences of the EMF of the alloys in the indicated heterogeneous areas has shown that they are practically linear. It is confirmed by these data that the compositions of coexisted phases in the given heterogeneous areas in the studied temperature range are constant, and it gives a base for estimations of the partial entropy and enthalpy from values of the temperature coefficients of the EMF [18,19]. The EMF results had been analyzed by an approximation of the linear temperature function using the method of least squares [20]. Thus, according to recommendations [21], it is expressed as linear equation:

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

where n—number of pairs of values E and T; S_E and S_b—dispersion of individual measurements of the EMF and the factor b, accordingly; $\overline{T}$ —average absolute temperature; t—Student's criteria. *Remark*: the Student's criteria is less than 2 ($t \le 2$) at the confidence level of 95% and at the number of runs more than 20 ($n \ge 20$).

The composed equations of the mode (2) are presented in Table 3. The partial molar functions of bismuth in the indicated three-phase areas (Table 2) had been calculated from these equations using the known thermodynamic relations (Table 4).

According to [18,19] and Fig. 2, these partial molar values are related to the follow potential-formation reactions:

$$Bi + 0.5BiI_3 + 1.5Te = 1.5BiTeI \qquad (3)$$

$$Bi + BiTeI = Bi_2TeI \qquad (4)$$

$$Bi + 0.522Bi_2TeI + 0.043BiI_3 = 0.522Bi_4TeI_{1.25} \qquad (5)$$

According to equations of the reactions (3)–(4), the standard thermodynamic functions of telluroiodides of bismuth are calculated in relations (6)–(8):

$$\Delta Z^0_{BiTeI} = 0.667\overline{\Delta Z}_{Bi} + 0.333\,\Delta Z^0_{BiI_3} \qquad (6)$$

$$\Delta Z^0_{Bi_2TeI} = \overline{\Delta Z}_{Bi} + \Delta Z^0_{BiTeI} \qquad (7)$$

$$\Delta Z^0_{Bi_4TeI_{1.25}} = 1.917\overline{\Delta Z}_{Bi} + \Delta Z^0_{Bi_2TeI} + 0.083\,\Delta Z^0_{BiI_3} \qquad (8)$$

(ΔZ^0- ΔG^0_{298} and ΔH^0_{298} —values for the corresponding compound, $\overline{\Delta Z}_{Bi} - \overline{\Delta G}_{Bi}$, $\overline{\Delta H}_{Bi}$). The standard entropies of telluroiodides of bismuth are calculated using relations (9)–(11):

$$S^0_{BiTeI} = 0.667(\overline{\Delta S}_{Bi} + S^0_{Bi}) + 0.333S^0_{BiI_3} + S^0_{Te} \qquad (9)$$

$$S^0_{Bi_2TeI} = \overline{\Delta S}_{Bi} + S^0_{Bi} + S^0_{BiTeI} \qquad (10)$$

$$S^0_{Bi_4TeI_{1,25}} = 1.917(\overline{\Delta S}_{Bi} + S^0_{Bi}) + S^0_{Bi_2TeI} + 0.083S^0_{BiI_3} \qquad (11)$$

The corresponding thermodynamic data of BiI_3 (Table 5), Te ($S^0 = 49.5 \pm 0.3$ J/(K mol)) and Bi ($S^0 = 56.9 \pm 0.5$ J/(K mol)) [22,23] had been used for calculations in relations (6)–(11).

The results of calculations are presented in Table 5. The accuracy has been determined by a method of errors accumulation. In Table 5, it is also shown some data of the work [3] obtained by an indirect way from the measurements of the saturated vapor pressure of BiTeI which agree with our data in the range of errors.

Table 5
Standard integral thermodynamic functions of telluroiodides and triiodide of bismuth.

Compound	$-\Delta G^0_{298}$ kJ/mol	$-\Delta H^0_{298}$	S^0_{298} J/mol K
BiI_3 [23]	148.8 ± 8.0	150.6 ± 6.0	224.7 ± 6.3
BiTeI	81.8 ± 2.7	82.6 ± 2.5 77 ± 9 [3]	161.6 ± 3.6 176 ± 11 [3]
Bi_2TeI	107.7 ± 3.0	110.7 ± 4.2	211.3 ± 9.1
$Bi_4TeI_{1.25}$	130.1 ± 4.0	130.0 ± 6.8	350.1 ± 16.6

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