# Thermodynamic investigation of the $Bi_2Se_3$–$Bi_2Te_3$ system by the EMF method

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**Abstract**

Binary and complex chalcogenides with a tetradimite-like layered structure are of great practical interest as topological insulators, thermoelectric, and optoelectronic materials. Their fundamental thermodynamic functions in combination with phase diagrams are important for the development and optimization of methods for the synthesis and growth of crystals.

The work presents the results of a thermodynamic study of the starting compounds and solid solutions of the $Bi_2Se_3$-$Bi_2Te_3$ system using the method of electromotive forces (EMF). Various modifications of this method are widely used to study binary and complex metal chalcogenides. Studies were carried out by EMF measurements of the concentration chains of the following type:

(−) Bi (solid) | ionic liquid + $Bi^{3+}$ | Bi in the alloy (solid) (+)

in the temperature range 300–450 K.

The pre-synthesized equilibrium $Bi_2Se_{3-x}Te_x$ alloys ($x$ = 0; 0.6; 1.2; 1.8; 2.0; 2.4; 3.0) with a 0.5 at% excess tellurium were used as right electrodes. Ionic liquid (morpholine formate) with the addition of $BiCl_3$ was used as the electrolyte.

The acquired experimental data were processed by the Microsoft Office Excel 2003 computer program using the least-squares method and linear equations of the type $E = a + bT$ were obtained. The obtained equations of the EMF temperature dependences were used to calculate the relative partial molar functions of bismuth in the alloys. The diagram of solid-phase equilibria of the Bi–Se–Te system was used to determine the equations of potential-forming reactions and the latter were used to calculate the standard thermodynamic functions of the formation and standard entropies of $Bi_2Se_3$, $Bi_2Te_3$ compounds and $Bi_2Se_{3-x}Te_x$ solid solutions of the above compositions. The thermodynamic functions of the formation of $Bi_2Se_{3-x}Te_x$ solid solutions from the initial binary compounds were also calculated. The results correlate well with the structural data that suggests some ordering in the arrangement of selenium and tellurium atoms in the b-phase crystal lattice of the $Bi_2SeTe_2$ composition: selenium atoms predominantly occupy the central layer of the five-layer, and tellurium atoms are located in the two outer layers.

**Keywords:** bismuth selenides, bismuth telluride, solid solutions, EMF method, thermodynamic properties.

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## 1. Introduction

The $Bi_2Se_3$, $Bi_2Te_3$ compounds, as well as solid solutions and composites based on them are of great interest as thermoelectric and optoelectronic materials [1–6]. Recent studies have shown that they are also topological insulators and are extremely promising for use in spintronics, quantum computers, and other high technology areas [7–12]. The introduction of magnetic elements into the crystal structure of these compounds led to the creation of a new class of innovative functional materials, i.e. magnetic topological insulators [13–16].

The thermodynamic functions of compounds and variable phases are their fundamental characteristics and, in combination with phase diagrams, form the basis for the synthesis and growth of crystals [17, 18]. Analysis of the reported data has shown that the thermodynamic properties of $Bi_2Se_3$ and $Bi_2Te_3$ have been studied in many works by various methods [19–23]. Experimental studies of the thermodynamic properties of the $Bi_2Se_3$–$Bi_2Te_3$ solid solutions were carried out by the electromotive force (EMF) method in the temperature range of 670–840 K [23]. An analysis showed that $Bi_2Te_3$+Te and $Bi_2Se_xTe_{3-x}$+Te alloys used as electrodes in the concentration cell contain a Te-based liquid solution in the indicated temperature range. According to the phase diagrams of the Bi-Te and Bi–Se–Te systems, the composition of this liquid phase varies with temperature, which should lead to a distortion of the EMF values, especially their temperature coefficient [24].

The aim of this work is the thermodynamic study of the initial compounds and solid solutions of the $Bi_2Se_3$–$Bi_2Te_3$ system by the EMF method.

Various modifications of the EMF method are widely used to study binary and complex metal chalcogenides [25–33]. In high-temperature studies, as a rule, eutectic melts of alkali metal salts are used as an electrolyte. In the study of solid metal chalcogenides, it is advisable to make measurements at temperatures below solidus. For this purpose, the most suitable electrolytes were glycerol solutions of alkali metal salts, first used in [34] in the study of amalgam systems. In our recent studies [35, 36], an ionic liquid was successfully tested as a liquid electrolyte.

## 2. Experimental

To study the thermodynamic properties of the $Bi_2Se_3$-$Bi_2Te_3$ system by the EMF method, the concentration cells of the following type

$$(-) \text{ Bi (solid)} \mid \text{ionic liquid} + Bi^{3+} \mid$$
$$\mid \text{Bi in the alloy (solid) (+)} \qquad (1)$$
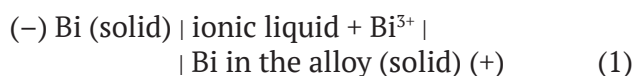
were assembled and their EMF in the temperature range 300–450 K were measured.

Elemental bismuth was used as the left electrode, and $Bi_2Se_{3-x}Te_x$ equilibrium alloys ($x$ = 0; 0.6; 1.2; 1.8; 2.0; 2.4; 3.0) with a 0.5 at% excess tellurium were used as the right electrodes.

The alloys of the right electrodes were synthesized by the melting of the previously synthesized and identified $Bi_2Se_3$, $Bi_2Te_3$ compounds, and excess tellurium in evacuated (~ $10^{-2}$ Pa) quartz ampoules at 1000 K, followed by annealing at 750 K (500 h) and 400 K (20 h). The phase composition of the obtained alloys was confirmed by XRD.

Ionic liquid (morpholine formate) with the addition of $BiCl_3$ was used as the electrolyte. Morpholine, formic acid, and anhydrous $BiCl_3$ purchased from Alfa Aesar were used to produce the ionic liquid. The ionic liquid was obtained using the procedure described in [37]. The assembly of electrochemical cells of type (1) and the method for measuring EMF are described in detail in [27, 36].

The first equilibrium EMF values were obtained after maintaining the electrochemical cell at ~350 K for 40–60 hours; the subsequent values were obtained every 3–4 hours after a specific temperature was established. The EMF values were considered equilibrium if they did not differ from each other by more than 0.2 mV when measured repeatedly at a given temperature, regardless of the direction of the temperature change.

## 3. Results and discussion

The measurements showed that for each studied sample, the EMF value varied linearly with temperature (Fig. 1), and the EMF concentration dependence was a monotonic function. This confirms the phase diagram of the $Bi_2Se_3$–$Bi_2Te_3$ system, according to which, it is characterized by the formation of a continuous series of solid solutions [38].
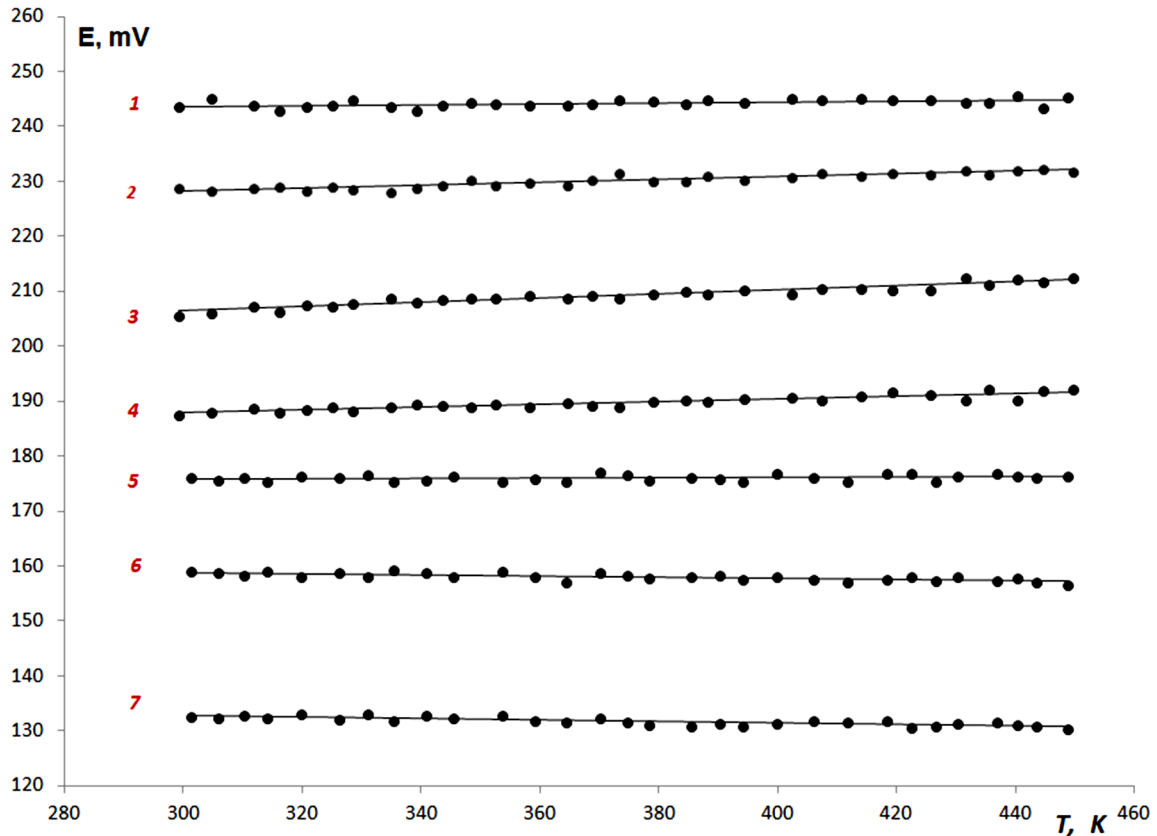
**Fig. 1.** Temperature dependencies of EMF for the alloys of the Bi$_2$Se$_3$–Bi$_2$Te$_3$ system. *1* – Bi$_2$Se$_3$; *2* – Bi$_2$Se$_{2.4}$Te$_{0.6}$; *3* – Bi$_2$Se$_{1.8}$Te$_{1.2}$; *4* – Bi$_2$Se$_{1.2}$Te$_{1.8}$; *5* – Bi$_2$SeTe$_2$; *6* – Bi$_2$Se$_{0.6}$Te$_{2.4}$; *7* – Bi$_2$Te$_3$

The acquired experimental data were processed by the Microsoft Office Excel 2003 computer program using the least-squares method and linear equations of the type $E = a + bT$ were obtained. The calculation steps for the Bi$_2$Se$_{2.4}$Te$_{0.6}$ sample are given in Table 1. The linear equations obtained during the calculations are shown in Table 2 in accordance with modern recommendations [26,27]:

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

In equation (2), $a$ and $b$ are coefficients, $n$ is the number of pairs of values of $E$ and $T$; $\overline{T}$ is the average temperature, K; $t$ is Student's t-test, $\delta_E^2$ and $\delta_b^2$ are dispersions of individual values of EMF and constant $b$. Given that the number of experimental points is $n = 30$, at a confidence level of 95 %, the Student test is $t \leqslant 2$ [26].

The obtained equations (Table 2) and known expressions [26]:

$$\overline{\Delta G}_{Bi} = -zFE \tag{3}$$

$$\overline{\Delta S}_{Bi} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb \tag{4}$$

$$\overline{\Delta H}_{Bi} = -zF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa \tag{5}$$

were used to calculate the partial molar Gibbs free energy, enthalpy, and entropy of bismuth in the alloys (Table 3).

As can be seen from Fig. 2, these partial molar functions continuously change with composition, which reflects the formation of a continuous series of solid solutions in the system.

To calculate the integral thermodynamic functions of Bi$_2$Se$_x$Te$_{3-x}$ solid solutions, we constructed a diagram of the solid-phase equilibria of the Bi–Se–Te system in the Bi$_2$Se$_3$–Bi$_2$Te$_3$–Te–Se composition range (Fig. 3) using the data from [38, 39]. According to [38], alloys of the Bi–Se and Bi–Te boundary systems in the composition range < 40 at% Bi consist of the two-phase mixtures Bi$_2$Se$_3$+Se and Bi$_2$Te$_3$+Te accordingly. Another boundary Se–Te system

**Table 1.** Experimentally obtained data for temperature ($T_i$) and EMF ($E_i$) and data associated with the calculation steps for the $Bi_2Se_{2.4}Te_{0.6}$ sample

| $T_i$, K | $E_i$, мВ | $T_i - \bar{T}$ | $E_i(T_i - \bar{T})$ | $(T_i - \bar{T})^2$ | $\tilde{E}$ | $E_i - \tilde{E}$ | $(E_i - \tilde{E})^2$ |
|---|---|---|---|---|---|---|---|
| 299.3 | 228.63 | −74.26 | −16978.83 | 5515.04 | 228.13 | 0.50 | 0.25 |
| 304.8 | 228.12 | −68.76 | −15686.29 | 4728.40 | 228.27 | −0.15 | 0.02 |
| 311.7 | 228.71 | −61.86 | −14148.76 | 3827.07 | 228.45 | 0.26 | 0.07 |
| 316.2 | 228.95 | −57.36 | −13133.34 | 3290.55 | 228.57 | 0.38 | 0.14 |
| 320.6 | 228.23 | −52.96 | −12087.82 | 2805.11 | 228.69 | −0.46 | 0.21 |
| 325.1 | 229.02 | −48.46 | −11099.07 | 2348.69 | 228.81 | 0.21 | 0.05 |
| 328.6 | 228.56 | −44.96 | −10276.82 | 2021.70 | 228.90 | −0.34 | 0.11 |
| 334.8 | 228.11 | −38.76 | −8842.30 | 1502.60 | 229.06 | −0.95 | 0.90 |
| 339.2 | 228.86 | −34.36 | −7864.39 | 1180.84 | 229.18 | −0.32 | 0.10 |
| 343.5 | 229.17 | −30.06 | −6889.61 | 903.80 | 229.29 | −0.12 | 0.01 |
| 348.4 | 230.13 | −25.16 | −5790.84 | 633.19 | 229.42 | 0.71 | 0.51 |
| 352.5 | 229.14 | −21.06 | −4826.45 | 443.66 | 229.53 | −0.39 | 0.15 |
| 358.2 | 229.78 | −15.36 | −3530.19 | 236.03 | 229.68 | 0.10 | 0.01 |
| 364.7 | 229.22 | −8.86 | −2031.65 | 78.56 | 229.85 | −0.63 | 0.39 |
| 368.8 | 230.23 | −4.76 | −1096.66 | 22.69 | 229.96 | 0.27 | 0.07 |
| 373.4 | 231.42 | −0.16 | −37.80 | 0.03 | 230.08 | 1.34 | 1.80 |
| 379.1 | 230.08 | 5.54 | 1273.88 | 30.65 | 230.23 | −0.15 | 0.02 |
| 384.6 | 229.86 | 11.04 | 2536.89 | 121.81 | 230.37 | −0.51 | 0.26 |
| 388.2 | 230.98 | 14.64 | 3380.78 | 214.23 | 230.47 | 0.51 | 0.26 |
| 394.3 | 230.13 | 20.74 | 4772.13 | 430.01 | 230.63 | −0.50 | 0.25 |
| 402.4 | 230.82 | 28.84 | 6656.08 | 831.55 | 230.84 | −0.02 | 0.00 |
| 407.5 | 231.47 | 33.94 | 7855.32 | 1151.70 | 230.98 | 0.49 | 0.24 |
| 414.1 | 230.86 | 40.54 | 9358.29 | 1643.22 | 231.15 | −0.29 | 0.08 |
| 419.2 | 231.58 | 45.64 | 10568.54 | 2082.71 | 231.28 | 0.30 | 0.09 |
| 425.8 | 231.12 | 52.24 | 12072.94 | 2728.67 | 231.46 | −0.34 | 0.11 |
| 431.6 | 232.07 | 58.04 | 13468.57 | 3368.25 | 231.61 | 0.46 | 0.21 |
| 435.5 | 231.32 | 61.94 | 14327.19 | 3836.15 | 231.71 | −0.39 | 0.15 |
| 440.3 | 231.83 | 66.74 | 15471.56 | 4453.78 | 231.84 | −0.01 | 0.00 |
| 444.7 | 232.27 | 71.14 | 16522.91 | 5060.43 | 231.96 | 0.31 | 0.10 |
| 449.8 | 231.78 | 76.24 | 17670.13 | 5812.03 | 232.09 | −0.31 | 0.10 |
| $\bar{T} = 373.56$ | $\bar{E} = 230.08$ | | | | | | |

[39], as well as the $Bi_2Se_3$–$Bi_2Te_3$ [38] system, is characterized by the formation of a continuous series of solid solutions. Therefore, in the diagram of solid-phase equilibria in the $Bi_2Se_3$–$Bi_2Te_3$–Te–Se composition range, the α- and β-solid solutions are in the conode connection. Moreover, in the two-phase region α+β, the directions of the conodes will coincide with the ray lines from the bismuth angle of the concentration triangle.

On the other hand, according to the available data [40], the mixing heat of α-solid solutions of the Se–Te system with an accuracy of ±1 kJ is zero, i.e. these solid solutions are close to ideal. Therefore, the entropy and Gibbs free energy of mixing the α-phase can be calculated by the following relations:

$$\Delta S_{mix} = -RT[\ln x + (1-x)\ln(1-x)] \qquad (6)$$

$$\Delta G_{mix} = RT[\ln x + (1-x)\ln(1-x)] \qquad (7)$$

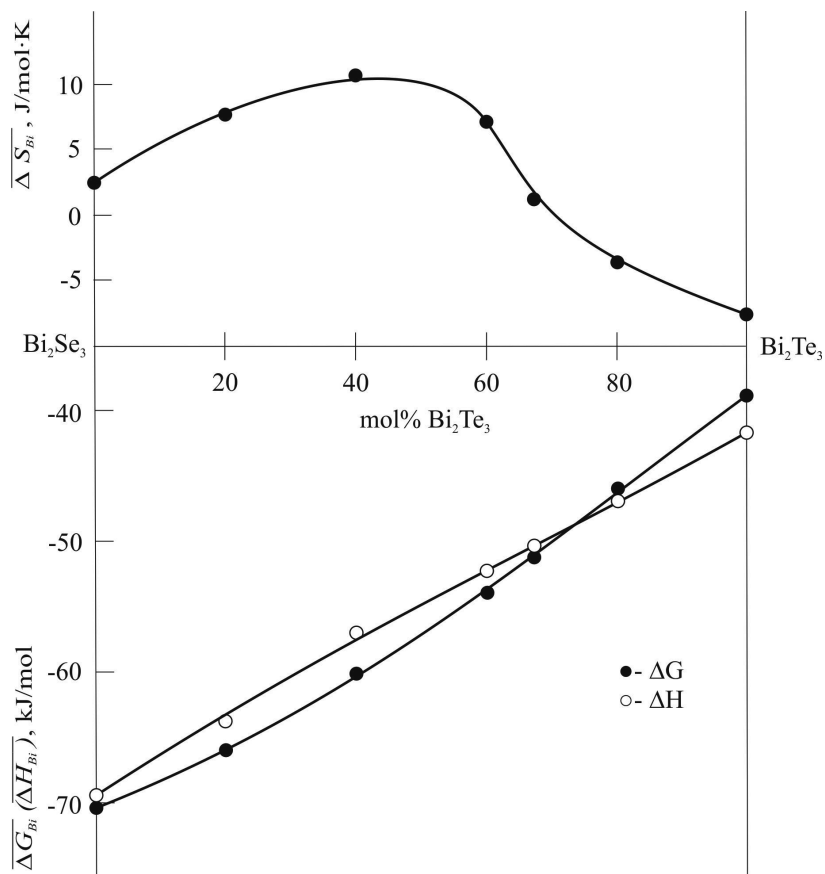Taking into account the ray nature of the conode in the two-phase region α+β (Fig. 3),

**Fig. 2.** Composition dependences of the partial molar functions of bismuth in the $Bi_2Se_3$–$Bi_2Te_3$ system at 298 K
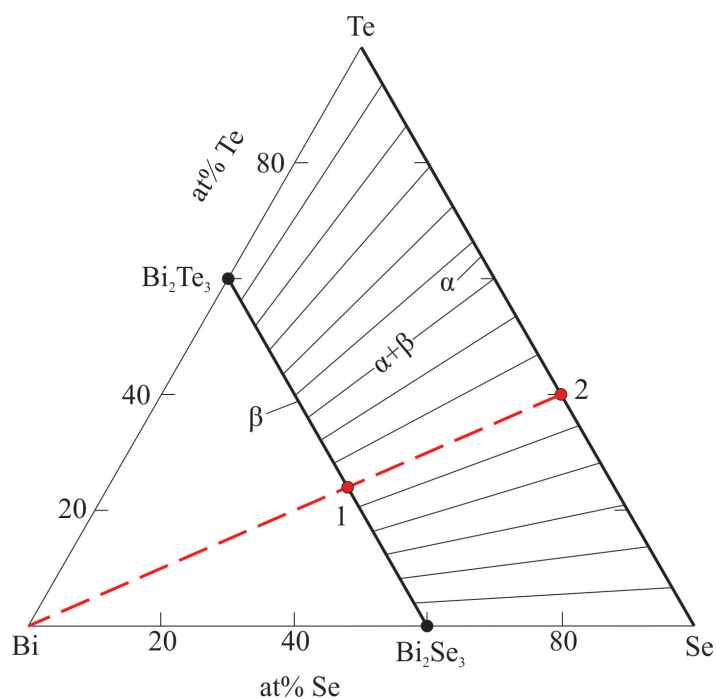


**Fig. 3.** Diagram of solid-phase equilibria of the Bi–Se–Te system in the $Bi_2Se_3$–$Bi_2Te_3$–Te-Se composition range

**Table 2.** Relations between the EMF and the temperature for type (1) cells for some samples of the $Bi_2Se_3$- $Bi_2Te_3$ system in the 300–450 K temperature interval

| Phase | $E$, mV $= a + bT \pm$ t·$d_E(T)$ |
|---|---|
| $Bi_2Se_3$ | $241.08 + 0.0082T \pm 2\left[\dfrac{0.33}{30} + 5.4\cdot10^{-6}(T-373.53)^2\right]^{1/2}$ |
| $Bi_2Se_{2.4}Te_{0.6}$ | $220.24 + 0.0263T \pm 2\left[\dfrac{0.22}{30} + 3.6\cdot10^{-6}(T-373.56)^2\right]^{1/2}$ |
| $Bi_2Se_{1.8}Te_{1.2}$ | $195.02 + 0.0379T \pm 2\left[\dfrac{0.27}{30} + 4.4\cdot10^{-6}(T-373.56)^2\right]^{1/2}$ |
| $Bi_2Se_{1.2}Te_{1.8}$ | $180.17 + 0.0256T \pm 2\left[\dfrac{0.22}{30} + 3.7\cdot10^{-6}(T-373.56)^2\right]^{1/2}$ |
| $Bi_2SeTe_2$ | $175.56 + 0.0018T \pm 2\left[\dfrac{0.2}{30} + 3.2\cdot10^{-6}(T-376.17)^2\right]^{1/2}$ |
| $Bi_2Se_{0.6}Te_{2.4}$ | $162.40 - 0,0117T \pm 2\left[\dfrac{0.21}{30} + 3.3\cdot10^{-6}(T-376.17)^2\right]^{1/2}$ |
| $Bi_2Te_3$ | $136.73 - 0.0133T \pm 2\left[\dfrac{0.21}{30} + 3.4\cdot10^{-6}(T-376.17)^2\right]^{1/2}$ |

**Table 3.** Partial molar functions of bismuth in the alloys of the $Bi_2Se_3$–$Bi_2Te_3$ system at $T$ = 298 K

| Phase | $-\Delta\overline{G}_{Bi}$, kJ/mol | $-\Delta\overline{H}_{Bi}$, kJ/mol | $\Delta\overline{S}_{Bi}$, J/(mol·K) |
|---|---|---|---|
| $Bi_2Se_3$ | 70.50 ± 0.08 | 69.78 ± 0.33 | 2.41 ± 0.87 |
| $Bi_2Se_{2.4}Te_{0.6}$ | 66.03±0.07 | 63.75±0.28 | 7.62±0.74 |
| $Bi_2Se_{1.8}Te_{1.2}$ | 59.73±0.07 | 56.45±0.30 | 10.98±0.81 |
| $Bi_2Se_{1.2}Te_{1.8}$ | 54.36±0.07 | 52.15±0.28 | 7.40±0.74 |
| $Bi_2SeTe_2$ | 50.97±0.06 | 50.82±0.26 | 0.52±0.69 |
| $Bi_2Se_{0.6}Te_{2.4}$ | 46.00±0.06 | 47.01±0.27 | -3.38±0.69 |
| $Bi_2Te_3$ | 38.86±0.06 | 41.50±0.26 | -7.71±0.70 |

the potential-forming reaction for any given composition of the β-phase should have the following form:

$$Bi + 1.5Se_{1-y}Te_y = 0.5Bi_2Se_{3-x}Te_x. \quad (8)$$
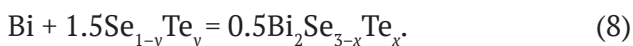
In our case $y$ = 0.2, 0.4, 0.6, 0.67, 0.8. For specific compositions, for example, $x = 0.6$, $y = 0.2$, this reaction has the following form:

$$Bi + 1.5Se_{0.8}Te_{0.2} = 0.5Bi_2Se_{2.4}Te_{0.6}. \quad (9)$$

According to reaction (9), for the β-phase of the $Bi_2Se_{2.4}Te_{0.6}$ composition, the standard thermodynamic functions of formation and the standard entropy can be calculated by the following relations:

$$\Delta_f G^0(Bi_2Se_{2.4}Te_{0.6}) = 2\Delta\overline{G}_{Bi} + 3\Delta G_{mix}(Se_{0.8}Te_{0.2}), \quad (10)$$

$$\Delta_f H^0(Bi_2Se_{2.4}Te_{0.6}) = 2\Delta\overline{H}_{Bi}, \quad (11)$$

$$\Delta_f S^0(Bi_2Se_{2.4}Te_{0.6}) = \\ = 2\Delta\overline{S}_{Bi} + 2S^0_{Bi} + 3\Delta S_{mix}(Se_{0.8}Te_{0.2}), \quad (12)$$

$$S^0(Bi_2Se_{2.4}Te_{0.6}) = 2\Delta\overline{S}_{Bi} + 2S^0_{Bi} + \\ + 3\Delta S_{mix}(Se_{0.8}Te_{0.2}) + 2.4S^0(Se) + 0.6S^0(Te). \quad (13)$$

The calculation results for the starting compounds and $Bi_2Se_{3-x}Te_x$ solid solutions are presented in Table 4.

As can be seen from Table 4, for the initial compounds, our data are coherent with the

**Table 4.** Standard integral thermodynamic functions of alloys of the $Bi_2Se_3$-$Bi_2Te_3$ system

| Phase | $-\Delta G^o$ (298 K), kJ/mol | $-\Delta H^o$ (298K), kJ/mol | $S^o$ (298K), J/(mol·K) | Ref. |
|---|---|---|---|---|
| | 141.0 ± 0.2 | 139.6 ± 0.7 | 245.1 ± 4.3 | This work |
| | 141.1±1.1 | 142.5±2.0 | | [41] |
| $Bi_2Se_3$ | 143.6±0.4 | 145.0±4.0 | | [23] |
| | 151.6±2.0 | 153.5±6.5 | | [42] |
| | | 140.2±3.0 | 240±8 | [19-22] |
| $Bi_2Se_{2.4}Te_{0.6}$ | 135.8±0.2 | 127.5±0.6 | 272.0±3.0 | This work |
| $Bi_2Se_{1.8}Te_{1.2}$ | 124.5±0.2 | 112.9±0.6 | 287.6±3.3 | This work |
| $Bi_2Se_{1.2}Te_{1.8}$ | 113.7±0.2 | 104.3±0.6 | 284.6±3.2 | This work |
| $Bi_2SeTe_2$ | 106.0±0.2 | 101.6±0.6 | 269.0±3.0 | This work |
| $Bi_2Se_{0.6}Te_{2.4}$ | 95.7±0.2 | 94.0±0.6 | 263.2±3.1 | This work |
| | 76.9±0.2 | 79.2±0.6 | 254.2±3.0 | This work |
| | 77.9±0.6 | 80.0±4.4 | | [43] |
| | 82.8 | 87.0 | | [42] |
| $Bi_2Te_3$ | 89.5±0.9 | 99.5±9.5 | | [23] |
| | 77.3±1.7 | 78.4±2.1 | 261.0±8.4 | [20. 22] |
| | 75.3±1.7 | 78.6±0.2 | 251.0±8.4 | [21] |

results of [41, 43] acquired by the EMF method and recommended in modern handbooks [19–22]. Results [42] for both compounds are somewhat overestimated. It should also be noted that the data of [23] for $Bi_2Se_3$ are in agreement with our data, while for $Bi_2Te_3$, they are somewhat overestimated.

By combining the standard thermodynamic functions of the formation of the β-phase of various compositions with the corresponding data for the initial binary compounds, we calculated the Gibbs free energy of the formation and the heat of the formation of β-solid solutions from binary compounds, i.e. thermodynamic mixing functions of $Bi_2Se_3–Bi_2Te_3$ (Table 5).

**Table 5.** Thermodynamic functions of mixing of $(Bi_2Se_3)_{1-y}$ $(Bi_2Te_3)_y$ solid solutions ($T$ = 298 K )

| $y$ | $-\Delta G^\circ_{mix}$, kC/mol | $-\Delta H^\circ_{mix}$, kC/mol |
|---|---|---|
| 0.2 | 7.6±0.4 | −3.1±1.2 |
| 0.4 | 9.1±0.4 | −2.6±1.2 |
| 0.6 | 11.2±0.4 | 0.9±1.2 |
| 0.667 | 8.8±0.4 | 2.3±1.2 |
| 0.8 | 6.3±0.4 | 1.7±1.2 |

It is obvious that the data given in Table 5, characterize the substitution of selenium atoms by tellurium atoms in the $Bi_2Se_{3-x}Te_x$ crystal lattice

per 3 mole chalcogen. Therefore, for 1 mole of the solution, these values should be divided by 3. Fig. 4 shows the dependences of the heat and Gibbs free energy of mixing on the composition obtained in this way. As can be seen, the enthalpy of mixing in absolute value does not exceed 1 kJ/mol. In this case, the sign of this function changes from positive to negative in the composition range > 0.6. A similar change in a sign is also observed for the partial entropy of bismuth (Fig. 2). This, as well as the fact that the deepest negative $\Delta G_{mix}$ values are observed for the β-phase with compositions $x$ = 0.6–0.7, indicates the structural ordering in solid solutions of these compositions. This correlates well with structural data [38] suggesting some ordering in the arrangement of selenium and tellurium atoms composition in the crystal lattice of the β- phase of the $Bi_2SeTe_2$: selenium atoms predominantly occupy the central layer of the five-layer and tellurium atoms are located in the two outer layers.

A comparison of the data in Tables 4 and 5 with the results of [23] shows their general agreement. A more detailed analysis of data [23] is difficult since, in the temperature range of EMF measurements (670–840 K), a change in the liquid composition of the electrode of $Bi_2Te_3$+Te (L) and $Bi_2Se_xTe_{3-x}$+Te (L)
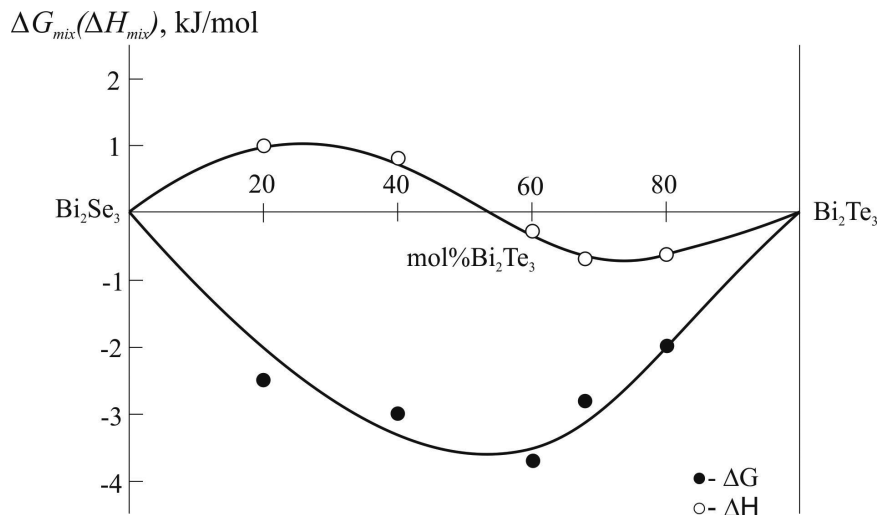
**Fig. 4.** Concentration dependences of the thermodynamic mixing functions of $Bi_2Se_3$ and $Bi_2Te_3$ during the formation of $Bi_2Se_{3-x}Te_x$ solid solutions per 1 mol of chalcogen

alloys along the liquidus is inevitable. It means that the EMF temperature coefficient reflects not only the partial entropy of bismuth but also the change in the melt composition [24].

## 4. Conclusions

The $Bi_2Se_3$–$Bi_2Te_3$ system was studied by analysing the EMF measurements of the concentration cells relative to the bismuth electrode in the temperature range 300–450 K. The obtained experimental data was used to calculate the partial thermodynamic functions of bismuth in the alloys. The diagram of solid-phase equilibria of the Bi–Se–Te system in the $Bi_2Se_3$–$Bi_2Te_3$–Te–Se composition range was used to determine the potential-forming reactions and the latter were used to calculate the standard thermodynamic functions of the formation and standard entropies of the $Bi_2Se_3$, $Bi_2Te_3$, and $Bi_2Se_xTe_{3-x}$ solid solutions. The thermodynamic functions of mixing binary compounds during the formation of these solid solutions were calculated by combining these data. The analysis of these functions allowed us to make the conclusion about the ordered arrangement of selenium and tellurium atoms in the crystal lattice of solid solutions with $Bi_2Te_2Se$ composition.

## Acknowledgements

## Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

## References

1. Rowe D. M. *Thermoelectrics Handbook: Macro to Nano*. Boca Raton, FL, USA: CRC Press, Taylor & Francis Group; 2006. 1008 p.

2. Shevelkov A. V. Chemical aspects of the design of thermoelectric materials. *Russ. Chem. Rev.* 2008;77(1): 1–19. DOI: https://doi.org/10.1070/RC2008v077n01ABEH003746

3. Adam A. M., Lilov E., Ibrahim E. M. M., Petkov P., Panina L. V., Darwish M. A. Correlation of structural and optical properties in as-prepared and annealed $Bi_2Se_3$ thin films. *Journal of Materials Processing Technology*. 2019;264: 76–83. DOI: https://doi.org/10.1016/j.jmatprotec.2018.09.005

4. Wang Q., Wu X., Wu L., Xiang Y. Broadband nonlinear optical response in $Bi_2Se_3$–$Bi_2Te_3$ heterostructure and its application in all-optical switching. *AIP Advances 9*. 2019; 025022. DOI: https://doi.org/10.1063/1.5082725

5. Hosokawa Y., Wada K., Tanaka M., Tomita K., Takashiri M. Thermal annealing effect on structural and thermoelectric properties of hexagonal $Bi_2Te_3$ nanoplate thin films by drop-casting technique.

*Japanese Journal of Applied Physics*. 2017;57(2S2): 02CC02. DOI: https://doi.org/10.7567/jjap.57.02cc02

6. Adam A. M., Elshafaie A., Abd El-Moez A. M., Petkov P., Ibrahim E. M. M. Thermoelectric properties of Te doped bulk Bi$_2$Se$_3$ system. *Materials Research Express*. 2018;5(3): 035514. DOI: https://doi.org/10.1088/2053-1591/aab5e8

7. Flammini R., Colonna S., Hogan C., Mahatha S., Papagno M., Barla A., Sheverdyaeva P., Moras P., Aliev Z., Babanly M. B, Chulkov E. V., Carbone C., Ronci F. Evidence of β-antimonene at the Sb/Bi$_2$Se$_3$ interface. *Nanotechnology*. 2018;29(6): 065704. DOI: https://doi.org/10.1088/1361-6528/aaa2c4

8. Hogan C., Holtgrewe K., Ronci F., Colonna S., Sanna S., Moras P., Sheverdyaeva P. M., Mahatha S., Papagno M., Aliev Z. S., Babanly M. B., Chulkov E. V., Carbone C., Flammini R. Temperature driven phase transition at the antimonene/Bi$_2$Se$_3$ van der Waals heterostructure. *ACS Nano*. 2019;13(9): 10481–10489. DOI: https://doi.org/10.1021/acsnano.9b04377

9. Otrokov M. M., Ernst A., Mohseni K., Fulara H., Roy S., Castro G. R., Rubio-Zuazo J., Ryabishchenkova A. G., Kokh K. A., Tereshchenko O. E., Aliev Z. S., Babanly M. B., Chulkov E. V., Meyerheim H. L., Parkin S. S. P. Geometric and electronic structure of the Cs-doped Bi$_2$Se$_3$(0001) surface. *Phys. Rev. B*. 2017;95(20): 205429. DOI: https://doi.org/10.1103/physrevb.95.205429

10. Lamuta C., Cupolillo A., Politano A., Aliev Z. S., Babanly M. B., Chulkov E. V., Pagnotta L. Indentation fracture toughness of a single-crystal Bi$_2$Te$_3$ topological insulator. *Nano Research*. 2016;9(4): 1032–1042. DOI: https://doi.org/10.1007/s12274-016-0995-z

11. Viti L., Coquillat D., Politano A., Kokh K. A., Aliev Z. S., Babanly M. B., Tereshchenko O. E., Knap W., Chulkov E. V., Vitiello M. S. Plasma-wave terahertz detection mediated by topological insulators surface states. *Nano Letters*. 2016;16(1): 80–87. DOI: https://doi.org/10.1021/acs.nanolett.5b02901

12. Babanly M. B., Chulkov E. V., Aliev Z. S., Shevel'kov A. V., Amiraslanov I. R. Phase diagrams in materials science of topological insulators based on metal chalcogenides. *Russ. J. Inorg. Chem*. 2017;62(13): 1703–1729. DOI: https://doi.org/10.1134/S0036023617130034

13. Otrokov M. M., Klimovskikh I. I., Bentmann H., et al. Prediction and observation of the antiferromagnetic topological insulator. *Nature*. 2019;576(7787): 416–422. DOI: https://doi.org/10.1038/s41586-019-1840-9

14. Shanna Z., Gang S., Peng Z., Dechao M., Genhao L., Xiaofang Z., Yalin L., Yongqing L., Lan C., Kehui W. Growth and transport properties of topological insulator Bi$_2$Se$_3$ thin film on a ferromagnetic insulating substrate. *Chinese Physics B*. 2017;27(7). DOI: https://doi.org/10.1088/1674-1056/27/7/076801

15. Walsh L. A., Smyth C. M., Barton A. T., Qingxiao W., Zifan C., Ruoyu Y., Jiyoung K., Moon J. K., Wallace R. M., Hinkle C. L. Interface chemistry of contact metals and ferromagnets on the topological insulator Bi$_2$Se$_3$. *J. Phys. Chem. C*. 2017;121(42): 23551–23563. DOI: https://doi.org/10.1021/acs.jpcc.7b08480

16. Liguo Z., Dapeng Z., Yunyi Z., Yonghao Y., Gaoyuan J., Menghan L., Ding Z., Ke H., Xucun M., Qikun X. Ferromagnetism in vanadium-doped Bi$_2$Se$_3$ topological insulator films. *APL Materials*. 2017;5(7): 076106. DOI: https://doi.org/10.1063/1.4990548

17. Voronin G. F., Gerasimov Ya. I. The role of chemical thermodynamics in the development of semiconductor materials science In: *Thermodynamics and Semiconductor Materials*. Moscow: MIET Publ., 1980. p. 3–10. Available at: https://search.rsl.ru/ru/record/01001069961 (In Russ.)

18. Babanly M. B., Mashadiyeva L. F., Babanly D. M., Imamaliyeva S. Z., Taghiyev D. B., Yusibov Y. A. Some issues of complex investigation of the phase equilibria and thermodynamic properties of the ternary chalcogenid systems by the EMF method. *Russian J. Iniorg.Chem*. 2019;64(13): 1649–1671. DOI: https://doi.org/10.1134/S0036023619130035

19. Barin I. *Thermochemical data of pure substances*. Third Edition. Weinheim: Wiley-VCH; 1995. DOI: https://doi.org/10.1002/9783527619825

20. Kubaschewski O., Alcock C. B., Spenser P. J. *Materials Thermochemistry*. New York: Pergamon Press; 1993. 350 p.

*21. Baza dannykh termicheskikh konstant veshchestv. Elektronnaya versiya pod. red. V. S. Yungmana. 2006* [Database of thermal constants of substances. Electronic version under. ed. V. S. Yungman. 2006]. Available at: http://www.chem.msu.su/cgi-bin/tkv.pl?show=welcom.html

22. Gerasimov Ya. I., Krestovnikov A. N, Gorbov S. I. *Khimicheskaya termodinamika v tsvetnoi metallurgii. Spravochnik. t. 6* [Chemical thermodynamics in nonferrous metallurgy. Directory. vol. 6] Moscow: Metallurgiya Publ.; 1974. 312 p. (In Russ.)

23. Sidorko V. R., Goncharuk L. V., Antonenko R. V. Thermodynamic properties of bismuth sesquiselenide and sesquitelluride and their solid solutions. *Powder Metallurgy and Metal Ceramics*. 2008;47: 234–241. DOI: https://doi.org/10.1007/s11106-008-9009-3

24. Voronin G. F. *Partsial'nye termodinamicheskie funktsii geterogennykh smesei i ikh primenenie v termodinamike splavov* [Partial thermodynamic functions of heterogeneous mixtures and their application in the thermodynamics of alloys]. In: Modern problems of physical chemistry, vol. 9. Moscow: MSU Publ., 1976. pp. 29–48. (In Russ.)

25. Wagner K. *Termodinamika splavov* [Thermodynamics of alloys]. Moscow: Metallurgizdat Publ.; 1957. 179 p. (In Russ.)

26. Morachevsky A. G., Voronin G. F., Geyderich V. A., Kutsenok I. B. *Elektrokhimicheskie metody issledovaniya v termodinamike metallicheskikh sistem ITsK* [Electrochemical methods of investigation in

thermodynamics of metal systems]. Moscow: Akademkniga Publ.; 2003. 334 p. (In Russ.)

27. Babanly M. B., Yusibov Y. A. *Elektrokhimicheskie metody v termodinamike neorganicheskikh sistem* [Electrochemical methods in thermodynamics of inorganic systems]. Baku: BSU Publ.; 2011. 306 p.

28. Vassiliev V., Gong W. Electrochemical cells with the liquid electrolyte in the study of semiconductor, metallic and oxide systems. In: *Electrochemical cells – new advances in fundamental researches and applications*. Shao Y. Rijeka (ed.) IntechOpen; 2012. pp. 71–102. DOI: https://doi.org/10.5772/39007

29. Babanly D. M., Veliyeva G. M., Imamaliyeva S. Z., Babanly M. B. Thermodynamic functions of arsenic selenides. *Russ. J. Phys. Chem. A.* 2017;91(7): 170–1173. DOI: https://doi.org/10.1134/s0036024417070044

30. Aliev Z. S., Musayeva S. S., Jafarli F. Y., Amiraslanov I. R., Shevelkov A. V., Babanly M. B. The phase equilibria in the Bi–S–I ternary system and thermodynamic properties of the BiSI and Bi$_{19}$S$_{27}$I$_3$ ternary compounds. *Journal of Alloys and Compounds.* 2014;610: 522–528. DOI: https://doi.org/10.1016/j.jallcom.2014.05.015

31. Jafarov Y. I., Ismaylova S. A., Aliev Z. S., Imamaliyeva S. Z., Yusibov Y. A., Babanly M. B. Experimental study of the phase diagram and thermodynamic properties of the Tl–Sb–S system. *Calphad.* 2016;55: 231–237. DOI: https://doi.org/10.1016/j.calphad.2016.09.007

32. Imamaliyeva S. Z., Babanly D. M., Gasanly T. M., Tagiev D. B., Babanly M. B. Thermodynamic properties of Tl$_9$GdTe$_6$ and TlGdTe$_2$. *Russian Journal of Physical Chemistry A.* 2018;92(11): 2111–2117. DOI: https://doi.org/10.1134/s0036024418110158

33. Moroz M. V., Prokhorenko M. V., Prokhorenko S. V., Yatskov M. V., Reshetnyak O. V. Thermodynamic properties of AgIn$_2$Te$_3$I and AgIn$_2$Te$_3$Br, determined by the EMF method. *Russian Journal of Physical Chemistry A.* 2018;92(1): 19–23. DOI: https://doi.org/10.1134/s0036024418010168

34. Kozin L. F., Nigmetova R. Sh. *Termodinamicheskie svoistva zhidkikh splavov olovo-rtut'* [Thermodynamic properties of liquid tin-mercury alloys]. *Russian J. Inorgan.Chem.* 1963;8(11): 2556–2562. (In Russ.)

35. Aliev Z. S., Musayeva S. S. Imamaliyeva S. Z., Babanlə M. B. Thermodynamic study of antimony chalcoiodides by EMF method with an ionic liquid. *J. Therm. Anal. Calorim.* 2018;133(2): 1115–1120. DOI: https://doi.org/10.1007/s10973-017-6812-4

36. Imamaliyeva S. Z., Musayeva S. S., Babanly D. M., Jafarov Y. I., Tagiyev D. B., Babanly M. B. Determination of the thermodynamic functions of bismuth chalcoiodides by EMF method with morpholinium formate as electrolyte. *Thermochimica Acta.* 2019;679: 178319.DOI: https://doi.org/10.1016/j.tca.2019.178319

37. Brigouleix C., Anouti M., Jacquemin J., Caillon-Caravanier M., Galiano H., Lemordant D. Physico-chemical characterization of morpholinium cation based protic ionic liquids used as electrolytes. *J. Phys. Chem. B.* 2010;114(5): 1757–1766. DOI: https://doi.org/10.1021/jp906917v

38. Abrikosov N. Kh., Bankina V. F., Poretskaya L. V., et al. *Poluprovodnikovye khal'kogenidy i splavy na ikh osnove* [Semiconductor chalcogenides and alloys based on them]. Moscow: Nauka Publ.; 1975. 220 p. (In Russ.)

39. Chizhevskaya S. N. Shelimova L. E. Se–Te phase diagram and structures of amorphous and crystalline Se$_{1-x}$Te$_x$ alloys: critical review. *Russ. J. Inorg. Chem.* 1997;42(5): 827-837.

40. Ghosh G., Lukas H. L., Delaey L. A thermodynamic assessment of the Se-Te system. *Calphad.* 1988;12(3): 295–299. DOI: https://doi.org/10.1016/0364-5916(88)90010-7

41. Vasilev V. P., Somov A. P., Nikol'skaya A. V., Gerasimov Ya. I. *Issledovanie termodinamicheskikh svoistv selenida vismuta metodom EDS* [Investigation of the thermodynamic properties of bismuth selenide by the EMF method]. *Zh. Fiz. khimii.,* 1968;42(3): 675–677. (In Russ.)

42. Melekh B. T. and Semenkovich S. A. *Termodinamicheskie svoistva tellurida i selenida trekhvalentnogo vismuta* [Thermodynamic properties of telluride and selenide of trivalent bismuth]. *Izv. AN SSSR. Neorgan. Mater.* 1968;4(8): 1346–1348. (In Russ.)

43. Gerasimov Ya. I. and Nikol'skaya A. V. *Termodinamicheskie svoistva tellurida vismuta (Bi$_2$Te$_3$) i tellurida sur'my (Sb$_2$Te$_3$)* [Thermodynamic properties of bismuth telluride (Bi$_2$Te$_3$) and stibium telluride (Sb$_2$Te$_3$). In: Metallurgy and Physics of Semiconductors. Moscow: 1961. p. 30–33. (In Russ.)

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