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Thermodynamic Properties of the BiTe and Bi8Te9 Compounds

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Two-phase alloys $Bi_8Te_9+Bi_4Te_5$ and $BiTe+Bi_8Te_9$ were studied by the electromotive forces method (EMF) in the temperature range 300 - 450 K. From the EMF data, the relative partial molar functions of bismuth in the alloys were calculated. The potential-forming reactions responsible for these partial functions were compiled, the values of the standard thermodynamic functions of formation, and the standard entropies of Bi_8Te_9 and $BiTe$ compounds were calculated. A comparative analysis of the data for BiTe with the literature data was carried out; for Bi_8Te_9, the thermodynamic functions were obtained for the first time.

Keywords: bismuth tellurides, thermodynamic functions, EMF method, ionic liquid.

Introduction

The discovery of a new quantum state of matter - a topological insulator (TI) [1, 2] has sharply increased interest in layered compounds, in particular, bismuth tellurides and selenides. It was found that these compounds previously studied as thermoelectrics and optoelectronic materials [3-7] are also TI and are extremely promising materials for various applications, including spintronics, quantum computers, medicine, security systems, etc. [8-16].

Thermodynamic functions are fundamental characteristics of compounds and, together with phase diagrams, form the basis of their synthesis, crystal growth, doping, etc. [16-18].

Despite the increased interest in bismuth tellurides, their thermodynamic properties have been studied extremely insufficiently. Analysis of the available literature shows that modern handbooks and electronic databases contain thermodynamic data mainly for Bi_2Te_3 and to a lesser extent for BiTe [19-22].

In addition, various versions of the phase diagram of the Bi-Te system presented in the literature [23-25] differ significantly from each other and do not reflect all known bismuth tellurides. The compilation phase diagram [26] shows the compositions of all known bismuth tellurides without specifying their temperatures and melting character. In works [27, 28], carried out recently, the results of modeling and thermodynamic analysis of the phase diagram of the Bi-Te system, in particular, by the CALPHAD method, are presented. However, in these studies, compounds of the homologous series $nBi_2 \cdot mBi_2Te_3$ are not considered as individual compounds.

Taking into account the above, we have undertaken a comprehensive study of phase equilibria in the Bi-Te system and the thermodynamic properties of bismuth tellurides. In [29], a new refined phase diagram of this system in the composition range of ≤ 60 at% Te is presented, and the formation of some bismuth tellurides with incongruent melting was shown. The thermodynamic functions of Bi_2Te_3 and Bi_4Te_5 compounds obtained by the method of electromotive forces (EMF) are presented in [30].

In this work, we continued the thermodynamic study of the Bi-Te system and presented the results of the thermodynamic study of BiTe and Bi_8Te_9 compounds by using the EMF method.

This method is widely used to study binary and complex inorganic phases [31-40]. When studying solid chalcogenide phases, it is advisable to carry out the measurements at temperatures below the solidus. For this purpose, along with glycerol solutions of alkali metal salts [33-37], ionic liquids are also successfully used [30,
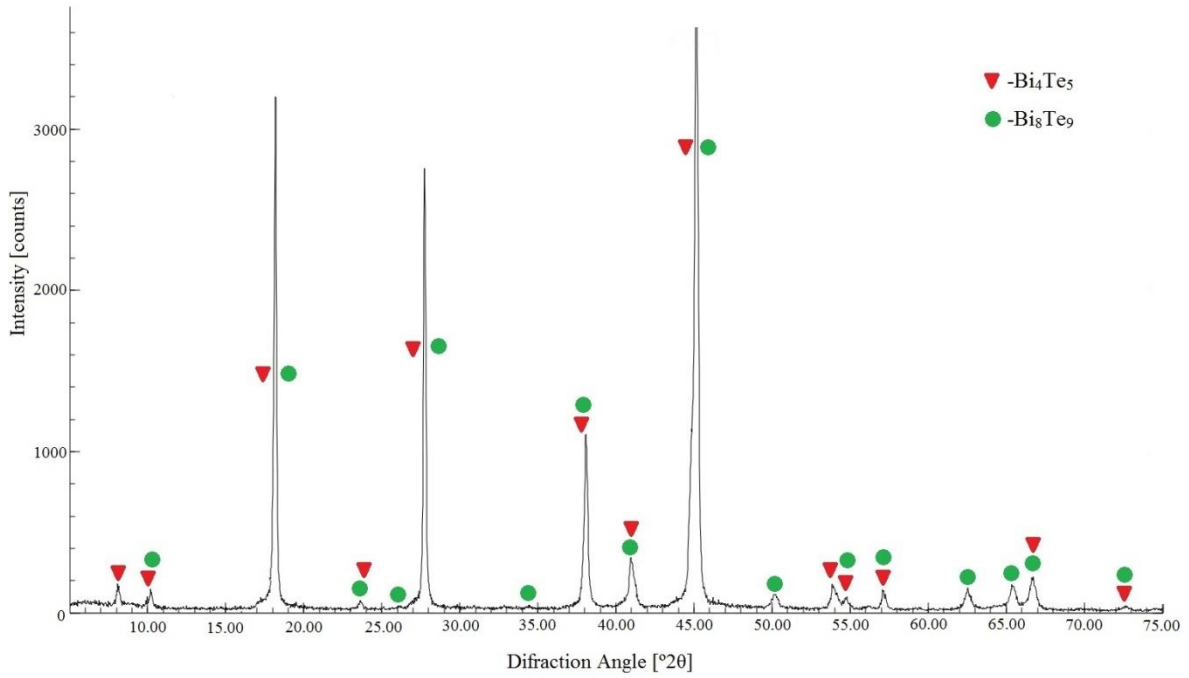
Fig.1. Powder X-ray powder diffraction pattern of an alloy with a composition of 54 at% Te.

41, 42], which we used in this work.

I. Experimental

To study the thermodynamic properties of the Bi-Te system by the EMF method, the concentration cells of the type:

(-) Bi (solid) │ ionic liquid + Bi^{3+} │ Bi-Te (solid) (+),   (1)

were assembled and their EMF was measured in the temperature range 300 - 450 K.

Elemental bismuth was used as the left electrode, and alloys from the two-phase regions Bi_8Te_9 + Bi_4Te_5 and $BiTe$ + Bi_8Te_9 were used as the right electrodes.

Alloys-right electrodes were synthesized by fusion of elementary bismuth and tellurium of high purity in vacuum ($\sim 10^{-2}$ Pa) quartz ampoules. After fusion at 900 K, the samples were quenched into cold water, followed by thermal annealing at 750 K (500 h) and 400 K (20 h). The phase composition of the obtained alloys was confirmed by XRD. As an example, Fig. 1 presents the powder X-ray powder diffraction pattern of an alloy with a composition of 54 at% Te. As can be seen, the diffraction pattern of this alloy consists of a set of reflection lines Bi_8Te_9 and Bi_4Te_5. This is in accordance with the refined phase diagram of the Bi-Te system [29].

An ionic liquid (morpholine formate) with the addition of $BiCl_3$ was used as the electrolyte. The ionic liquid was obtained following the procedure described in [43].

The assembly of electrochemical cells of type (1) and the method for EMF measurements are described in detail in [35, 36].

The first equilibrium EMF values were obtained after maintaining the electrochemical cell at ~ 350 K for 40 - 60 h., while the subsequent ones every 3 - 4 h. after a certain temperature. The EMF values were considered equilibrium, which did not differ from each other when repeatedly measured at a given temperature by more than 0.2 mV, regardless of the direction of the temperature change.

II. Results

As a result of the EHQ measurements, it was established that the EMF has a constant value in each of the phase areas of Bi_8Te_9 + Bi_4Te_5 and $BiTe$ + Bi_8Te_9 of the Bi-Te system, and linearly depends on the temperature (Fig. 2). This confirms the existence of pointed two-phase areas in the phase diagram and allows us to use this for the thermodynamic calculations.

The obtained experimental data were processed using the Microsoft Office Excel 2003 computer program using the least-squares method and linear equations of the type $E = a + bT$ were obtained. The linear equations obtained during the calculations are shown in Table 1 in the form recommended in [32, 33]

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

In equation (2), a and b are coefficients, n is the number of pairs of values of E and T; $\overline{T}$ - average temperature, K; Student's t-test, δ_E^2 and δ_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 ≤ 2.

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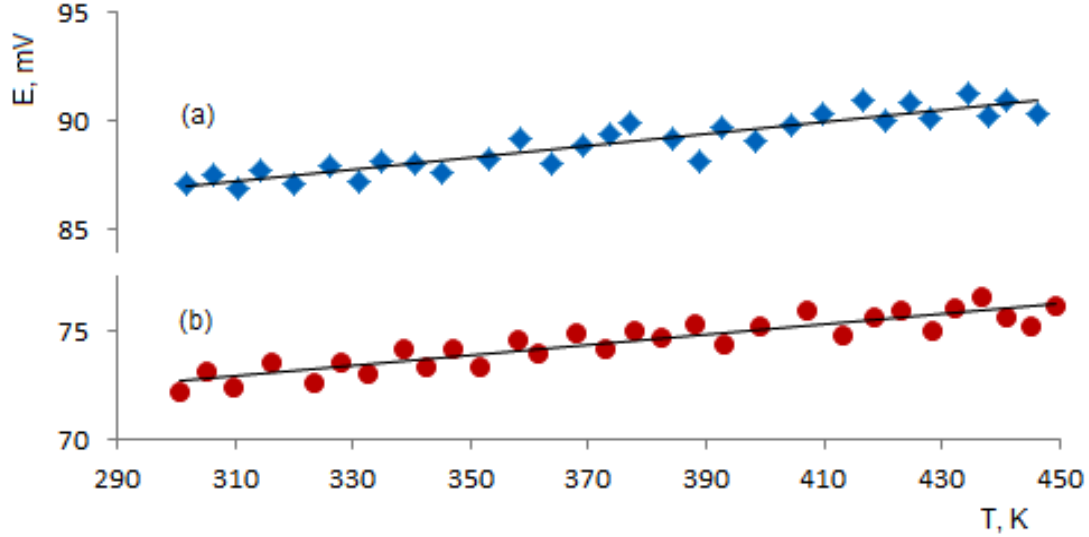
Fig. 2. Temperature dependence of the EMF of type (1) cells in the $Bi_8Te_9 + Bi_4Te_5$ (a) and $BiTe + Bi_8Te_9$ (b) two-phase regions.

Table 1

Relations between the EMF and the temperature for type (1) cells in alloys of the Bi-Te system in the 300–450 K temperature interval

№	Phase area	$E, mV = a + bT \pm t \cdot \delta_E(T)$
1	$Bi_8Te_9 + Bi_4Te_5$	$78.93 + 0.0268T \pm 2\left[\dfrac{0.23}{30} + 3.9 \cdot 10^{-6}(T - 376.17)^2\right]^{1/2}$
2	$BiTe + Bi_8Te_9$	$65.54 + 0.00238T \pm 2\left[\dfrac{0.23}{30} + 3.7 \cdot 10^{-6}(T - 376.38)^2\right]^{1/2}$

Table 2

Relative partial functions of bismuth in the alloys of the Bi-Se system at T = 298.15 K

Phase area	$-\overline{\Delta G}_{Bi}$	$-\overline{\Delta H}_{Bi}$	$\overline{\Delta S}_{Bi}$
	kJ/mol		J/(mol·K)
$Bi_2Te_3 + Te$	25.158 ± 0.069	22.85 ± 0.29	7.76 ± 0.76
$Bi_4Te_5 + Bi_2Te_3$	21.024 ± 0.067	18.97 ± 0.28	6.89 ± 0.74

From obtained equations (Table 1) by using the thermodynamic expressions:

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

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

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

the partial molar Gibbs free energy, enthalpy, and entropy of bismuth in the alloys were calculated (Table 2).

The areas of homogeneity of the compounds Bi_8Te_9 and BiTe are very small [29], so these partial molar values are the thermodynamic characteristics of the following potential-forming reactions (the substances in the crystalline state) [32, 33]:

$$Bi + 2.25\,Bi_4Te_5 = 1.25\,Bi_8Te_9 \tag{6}$$
$$Bi + Bi_8Te_9 = 9BiTe \tag{7}$$
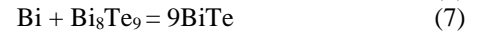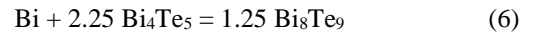
From relations (6) and (7) by using the equations:

$$\Delta_f Z^0(Bi_8Te_9) = 0.8\Delta\overline{Z}_{Bi} + 1.8\Delta Z^0(Bi_4Te_5), \tag{8}$$

$$\Delta_f Z^0(BiTe) = \frac{1}{9}\Delta\overline{Z}_{Bi} + \frac{1}{9}\Delta_f Z^0(Bi_8Te_9), \tag{9}$$

$$S^0(Bi_8Te_9) = 0.8\Delta\overline{S}_{Bi} + 0.8S^0(Bi) + 1.8S^0(Bi_4Te_5), \tag{10}$$

$$S^0(BiTe) = \frac{1}{9}\Delta\overline{S}_{Bi} + \frac{1}{9}S^0(Bi) + \frac{1}{9}S^0(Bi_8Te_9), \tag{11}$$

the standard thermodynamic functions of the formation of Bi_8Te_9 and BiTe were calculated. In the relations (8) and (9) $Z \equiv G$ or H. For the calculations, we used the thermodynamic data [30] for Bi_4Te_5 (Table 3) as well as

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Table 3

Standard integral thermodynamic functions of the bismuth tellurides

Compound	$-\Delta_f G^o$ (298K)	$-\Delta_f H^o$ (298K)	S^o (298K)
	kJ·mol^{-1}		J·mol^{-1}·K^{-1}
Bi_8Te_9	268.2 ± 1.5	286.8 ± 2.3	897.0 ± 12.0
BiTe	34.2 ± 0.2	34.0 ± 0.3	106.7 ± 1.3
	25.6 [44]*	68.6 [44]*	-
		34.4[21]	110.9 ± 12.6 [21]
Bi_4Te_5 [30]	147.8 ± 0.8	149.2 ± 1.1	469.7 ± 6.2
Bi_2Te_3 [30]	76.9 ± 0.2	79.2 ± 0.5	254.2 ± 3.0

data for 766 K.

the standard entropy of elementary bismuth (56.7 ± 0.5 J·mol^{-1}·K^{-1}) [19]. The obtained values are summarized in Table 3. In all cases, the estimated standard uncertainties were calculated by accumulating the errors. In Table 3, in addition to the results of the present work, the result of previous work [30] and literature data for BiTe are also presented.

As can be seen from Table 3, the standard enthalpy of formation and entropy of BiTe determined by us is in good agreement with the data [21] and differ significantly from the results of [44] obtained by high temperatures EMF measurements. The thermodynamic functions of Bi_8Te_9 were determined by us for the first time. A comparative analysis of our and published data for Bi_2Te_3 compound was performed in [30].

Conclusion

The thermodynamic properties of the alloys of the Bi_8Te_9 and BiTe compounds were studied by EMF measurements of the concentration cells relative to the bismuth electrode in the 300 – 450 K temperatures interval. Relative partial molar functions of bismuth in the alloys, standard thermodynamic formation functions, and standard entropies of above-stated compounds were calculated. The results obtained for BiTe supplement and refine the literature data, while the thermodynamic functions for Bi_8Te_9 are determined for the first time.

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Термодинамічні властивості сполук BiTe та Bi$_8$Te$_9$

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Двофазні сплави Bi$_8$Te$_9$ + Bi$_4$Te$_5$ та BiTe + Bi$_8$Te$_9$ досліджували методом електрорушійних сил (ЕРС) в інтервалі температур 300 - 450 К. За даними ЕРС розраховували відносні часткові молярні функції бісмуту в сплавах. Було складено реакції, що утворюють потенціал, відповідальні за ці часткові функції, розраховані значення стандартних термодинамічних функцій утворення та стандартні ентропії сполук Bi$_8$Te$_9$ та BiTe. Проведено порівняльний аналіз даних для BiTe з літературними даними; для Bi$_8$Te$_9$ термодинамічні функції були отримані вперше.

Ключові слова: телуриди бісмуту, термодинамічні функції, метод ЕРС, іонна рідина.