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THERMODYNAMİC PROPERTİES OF THE Bi_2Te_3 AND Bi_4Te_5 COMPOUNDS

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Abstract: *The thermodynamic properties of the Bi-Te system were studied in the 55–65 at% Te compositions interval and temperatures 300–450 K by using the electromotive forces method. Relative partial molar functions of bismuth in the alloys were calculated. Based on the potential-forming reactions for Bi_2Te_3 and Bi_4Te_5 compounds, a mutually consistent set of standard thermodynamic functions and standard entropies is obtained. A comparative analysis of the data obtained for Bi_2Te_3 with literature is performed, for Bi_4Te_5 thermodynamic functions were obtained for the first time.*
Keywords: *bismuth tellurides, thermodynamic functions, EMF method, ionic liquid*
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Introduction

Bismuth tellurides, especially Bi_2Te_3, phases, and composites based on it have long been in the field of view of researchers as valuable thermoelectric materials [1-3]. After the discovery of a special quantum state of matter — a topological insulator (TI) [4], it was found that Bi2Te3 and many other layered compounds of tetradimite-like structures are TI which are rather promising for their varied applications [5-11]. In particular, the unique optical properties make them promising for the use in broadband optoelectronics as photodetectors [12-15].

The thermodynamic functions of compounds are their fundamental characteristics and, together with phase diagrams, form the basis for the synthesis and growth of crystals, as well as optimizing the development conditions for new materials based on them [10, 16-18].

Despite a growing interest in bismuth tellurides as the most innovative functional materials, no reliable picture of phase equilibria of this system in the Bi-Bi2Te3 composition interval has so far been established. Various versions of the T-x diagram given in [19–23] are contradictory. Even the results of recent studies [24, 25] do not agree on the character of the crystal structure and the homogeneity regions of the intermediate phases formed in it.

The thermodynamic properties of bismuth tellurides have also been studied extremely insufficiently. An analysis of the literature shows that modern handbooks and electronic databases contain thermodynamic data only for Bi_2Te_3 [26-29]. That's why we undertook a comprehensive study of phase equilibria in the Bi-Te system and the thermodynamic properties of bismuth tellurides. In [30], a new refined phase diagram of this system was presented in the composition range ≤60 at% Te, where the formation of a series of bismuth tellurides with incongruent melting is shown.

This work presents results of a thermodynamic study of the Bi_2Te_3 and Bi_4Te_5 compounds by using the electromotive force method (EMF).

Various modifications of the EMF method are widely used to study binary and complex metal chalcogenides [31–41]. 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 take measurements at temperatures below solidus. For this purpose, the most suitable electrolytes were glycerol solutions of alkali metal salts, first used in [41] in the study of amalgam systems. In our recent studies [42, 43], an ionic liquid (a mixture of morpholine and formic acid) was successfully used as a liquid electrolyte.

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 were measured in the temperature range 300-450 K.

Elemental bismuth was used as the left electrode, and alloys from the two-phase regions Bi_2Te_3+Te, Bi_4Te_5+Bi_2Te_3 were used as the right electrodes.

Alloys-right electrodes were synthesized by fusion of elementary bismuth and tellurium of high purity in vacuum (~ 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, in Fig. 1. presents the powder X-ray powder diffraction pattern of an alloy with a composition of 57 at% Te. As can be seen, the diffraction pattern of this alloy consists of a set of reflection lines Bi_2Te_3 and Bi_4Te_5 which is in accordance with the phase diagram of the Bi-Te system [21, 30].

An ionic liquid (morpholine formate) with the addition of $BiCl_3$ was used as electrolyte. To synthesis of the ionic liquid, the morpholine, formic acid, and anhydrous $BiCl_3$ purchased from Alfa Aesar were used. The ionic liquid was obtained following the procedure described in [44]:

The assembly of electrochemical cells of type (1) and the method for EMF measurements are described in detail in [33, 43].

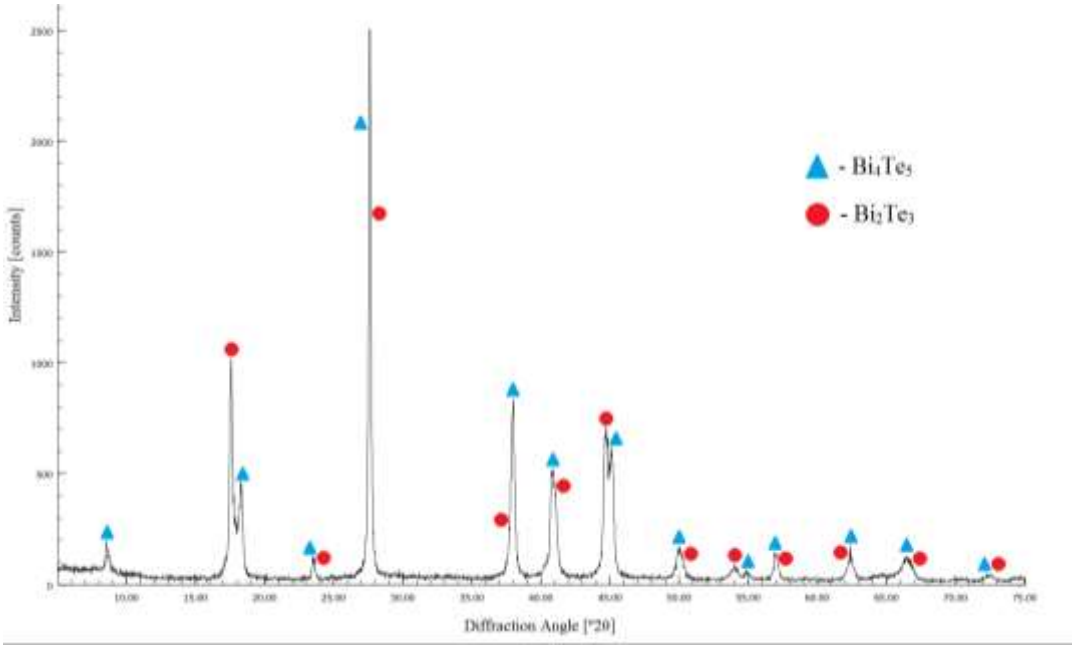

Fig. 1. Powder X-ray of a two-phase alloy Bi_4Te_5+Bi_2Te_3

The first equilibrium EMF values were obtained after maintaining the electrochemical cell at ~350 K for 40-60 h., while 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.

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_2Te_3+Te and Bi_4Te_5+Bi_2Te_3 of the Bi-Te system, and linearly depends on the temperature (Fig.2). This confirms the existence of two-phase areas in the phase diagram and allows us to use this for 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 E = a + bT type were obtained. The experimental data of Ti and Ei and steps of calculation for both regions are given in Table 1. The linear equations obtained during the calculations are shown in Table 2 in a form recommended by modern handbooks [32, 33]

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

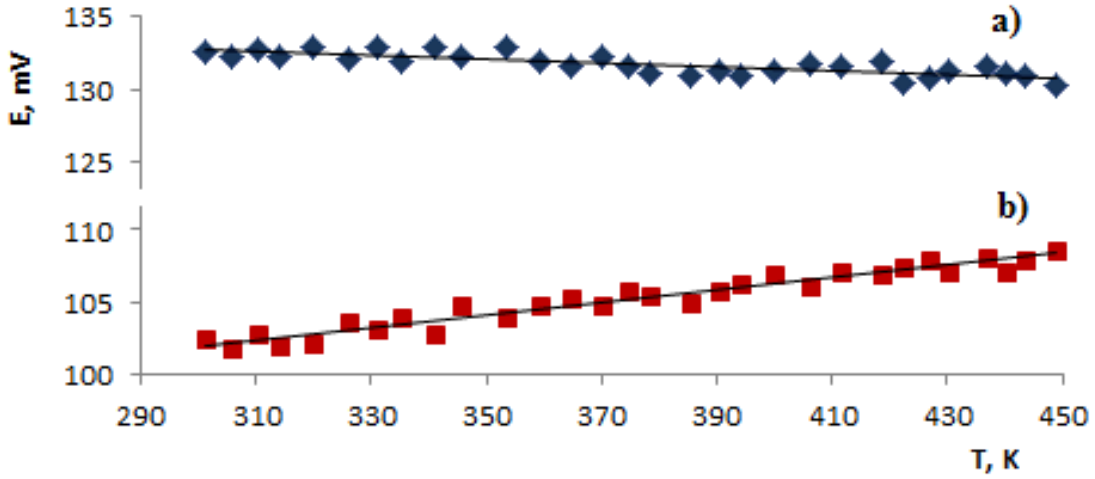

Fig. 2. Temperature dependence of the EMF type (1) cells in the Bi_2Te_3+Te (a) and Bi_4Te_5+ Bi_2Te_3 (b) two-phase regions

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.

Table 1. Experimentally obtained data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the Bi_2Te_3+Te phase region of the Bi-Te system

T_i, K	E_i, mV	$T_i - \overline{T}$	$E_i(T_i - \overline{T})$	$(T_i - \overline{T})^2$	$\tilde{E}$	$E_i - \tilde{E}$	$(E_i - \tilde{E})^2$
301.3	132.63	-74.87	-9930.01	5605.52	132.72	-0.09	0.01
305.8	132.18	-70.37	-9301.51	4951.94	132.66	-0.48	0.23
310.1	132.81	-66.07	-8774.76	4365.24	132.60	0.21	0.04
314	132.22	-62.17	-8220.12	3865.11	132.55	-0.33	0.11
319.9	132.95	-56.27	-7481.10	3166.31	132.47	0.48	0.23
326.2	132.13	-49.97	-6602.54	2497.00	132.39	-0.26	0.07

331.1	132.95	-45.07	-5992.06	2031.30	132.32	0.63	0.39
335.3	131.87	-40.87	-5389.53	1670.36	132.27	-0.40	0.16
340.8	132.92	-35.37	-4701.38	1251.04	132.19	0.73	0.53
345.4	132.21	-30.77	-4068.10	946.79	132.13	0.08	0.01
353.6	132.82	-22.57	-2997.75	509.40	132.02	0.80	0.63
359.2	131.89	-16.97	-2238.17	287.98	131.95	-0.06	0.00
364.5	131.54	-11.67	-1535.07	136.19	131.88	-0.34	0.11
370.2	132.21	-5.97	-789.29	35.64	131.80	0.41	0.17
374.7	131.52	-1.47	-193.33	2.16	131.74	-0.22	0.05
378.3	131.11	2.13	279.26	4.54	131.69	-0.58	0.34
385.5	130.86	9.33	1220.92	87.05	131.60	-0.74	0.55
390.2	131.25	14.03	1841.44	196.84	131.54	-0.29	0.08
394.1	130.84	17.93	2345.96	321.48	131.48	-0.64	0.42
399.8	131.25	23.63	3101.44	558.38	131.41	-0.16	0.03
406	131.74	29.83	3929.80	889.83	131.33	0.41	0.17
411.7	131.58	35.53	4675.04	1262.38	131.25	0.33	0.11
418.4	131.92	42.23	5570.98	1783.37	131.16	0.76	0.58
422.5	130.48	46.33	6045.14	2146.47	131.11	-0.63	0.39
426.7	130.71	50.53	6604.78	2553.28	131.05	-0.34	0.12
430.2	131.27	54.03	7092.52	2919.24	131.00	0.27	0.07
436.9	131.52	60.73	7987.21	3688.13	130.91	0.61	0.37
440.3	131.08	64.13	8406.16	4112.66	130.87	0.21	0.04
443.6	130.93	67.43	8828.61	4546.80	130.83	0.10	0.01
448.8	130.31	72.63	9464.42	5275.12	130.76	-0.45	0.20
$\overline{T}$ =376.17	$\overline{E}$ =131.7233						

Table 2. Experimentally obtained data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the Bi_4Te_5+ Bi_2Te_3 phase region of the Bi-Te system

T_i, K	E_i, мВ	$T_i - \overline{T}$	$E_i(T_i - \overline{T})$	$(T_i - \overline{T})^2$	$\tilde{\tilde{E}}$	$E_i - \tilde{\tilde{E}}$	$(E_i - \tilde{\tilde{E}})^2$
301.3	102.44	-74.87	-7669.68	5605.52	102.04	0.40	0.16
305.8	101.81	-70.37	-7164.37	4951.94	102.23	-0.42	0.18
310.1	102.75	-66.07	-6788.69	4365.24	102.42	0.33	0.11
314	101.91	-62.17	-6335.74	3865.11	102.58	-0.67	0.45
319.9	102.19	-56.27	-5750.23	3166.31	102.83	-0.64	0.42
326.2	103.62	-49.97	-5177.89	2497.00	103.10	0.52	0.27
331.1	103.14	-45.07	-4648.52	2031.30	103.31	-0.17	0.03
335.3	103.86	-40.87	-4244.76	1670.36	103.49	0.37	0.13
340.8	102.85	-35.37	-3637.80	1251.04	103.73	-0.88	0.77
345.4	104.74	-30.77	-3222.85	946.79	103.92	0.82	0.66

353.6	103.97	-22.57	-2346.60	509.40	104.28	-0.31	0.09
359.2	104.81	-16.97	-1778.63	287.98	104.51	0.30	0.09
364.5	105.25	-11.67	-1228.27	136.19	104.74	0.51	0.26
370.2	104.76	-5.97	-625.42	35.64	104.99	-0.23	0.05
374.7	105.72	-1.47	-155.41	2.16	105.18	0.54	0.29
378.3	105.46	2.13	224.63	4.54	105.33	0.13	0.02
385.5	104.93	9.33	979.00	87.05	105.64	-0.71	0.50
390.2	105.75	14.03	1483.67	196.84	105.84	-0.09	0.01
394.1	106.24	17.93	1904.88	321.48	106.01	0.23	0.05
399.8	106.91	23.63	2526.28	558.38	106.25	0.66	0.43
406	106.05	29.83	3163.47	889.83	106.52	-0.47	0.22
411.7	107.02	35.53	3802.42	1262.38	106.76	0.26	0.07
418.4	106.93	42.23	4515.65	1783.37	107.05	-0.12	0.01
422.5	107.38	46.33	4974.92	2146.47	107.22	0.16	0.03
426.7	107.91	50.53	5452.69	2553.28	107.40	0.51	0.26
430.2	107.05	54.03	5783.91	2919.24	107.55	-0.50	0.25
436.9	108.16	60.73	6568.56	3688.13	107.84	0.32	0.10
440.3	107.08	64.13	6867.04	4112.66	107.98	-0.90	0.81
443.6	107.95	67.43	7279.07	4546.80	108.12	-0.17	0.03
448.8	108.57	72.63	7885.44	5275.12	108.35	0.22	0.05
$\overline{T}$ =376.17	$\overline{E}$ =105.24						

Table 3. Relations between the EMF and the temperature for type (1) cells in some phase regions of the Bi-Te system in the 300–450 K temperature interval

№	Phase area	E, mV=a+bT± t· δ_E(T)
1	Bi_2Te_3 + Te	$136.73 - 0.0133\mathrm{T} \pm 2\left[\frac{0.21}{30} + 3.4\cdot10^{-6}(\mathrm{T}-376.17)^2\right]^{1/2}$
2	Bi_4Te_5 +Bi_2Te_3	$89.16 + 0.0428T \pm 2\left[\frac{0.23}{30} + 3.7\cdot10^{-6}(T-376.17)^2\right]^{1/2}$

From obtained equations (Table 3) by using the thermodynamic expressions

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

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

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

the partial molar Gibbs free energy, enthalpy, and entropy of bismuth in the alloys were calculated (Table 4).

Table 4. 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	38,429±0,064	39,58±0,27	-3,85±0,71
Bi_4Te_5 +Bi_2Te_3	29,497±0,067	25,81±0,28	12,38±0,74

The areas of homogeneity of the compounds Bi_2Te_3 and Bi_4Te_5 are very small [21, 30], so these partial molar values are the thermodynamic characteristics of the following potential-forming reactions (the substances in the crystalline state) [32, 33]

$$Bi+1.5Te=0.5Bi_2Te_3 \quad (6)$$

$$Bi+2.5Bi_2Te_3=1.5Bi_4Te_5 \quad (7)$$

From relations (6) and (7) by using relations

$$\Delta_f Z^0(Bi_2Te_3) = 2\Delta\overline{Z}_{Bi} \quad (8)$$

$$\Delta_f Z^0(Bi_4Te_5) = \frac{2}{3}\Delta\overline{Z}_{Bi} + \frac{5}{3}\Delta\overline{Z}_{Bi_2Te_3} \quad (9)$$

$$S^0(Bi_2Te_3) = 2\Delta\overline{S}_{Bi} + 2S^0(Bi) + 3S^0(Te) \quad (10)$$

$$S^0(Bi_4Te_5) = \frac{2}{3}\Delta\overline{S}_{Bi} + \frac{2}{3}S^0(Bi) + \frac{5}{3}S^0(Bi_2Te_3) \quad (11)$$

the standard thermodynamic functions of the formation of Bi_2Te_3 and Bi_4Te_5 were calculated. In relations (8) and (9) Z ≡ G or H. For the thermodynamic calculations, we used the literature data [29] on the standard entropies of elementary bismuth (56.7 ± 0.5 $J\cdot mol^{-1}\cdot K^{-1}$) and tellurium (49.5±0.2 $J\cdot mol^{-1}\cdot K^{-1}$). The obtained values are summarized in Table 5. In all cases, the estimated standard uncertainties were calculated by accumulating the errors. In Table 5, in addition to our experimental results, literature data are also presented.

Table 5. Standard integral thermodynamic functions of bismuth tellurides

Compound	$-\Delta_f G^o$ (298K)	$-\Delta_f H^o$ (298K)	S^o (298K)	Source, method
	$kJ\cdot mol^{-1}$		$J\cdot mol^{-1}\cdot K^{-1}$	
Bi_4Te_5	147.8±0.8	149.2±1.1	375.2±5.1	Present work, EMF
Bi_2Te_3	76.9±0.2	79.2±0.5	254.2±3.0	Present work, EMF
	77.9±0.6	80.0±4.4		[45], EMF
	89.5±0.9	99.5±9.5		[46], EMF
	82.8	87.0		[47] , EMF
		78.5±0.2		[48], calorim.
		84.1±3.2		[49], calorim.
		80.5±5.0		[50], tenzim.
	77.1	77.4	260.9	[26], recomend.
	77.3±1.7	78.2±0.5	260.8	[27], recomend.
		78.7±2.1	261.1±8.4	[28], recomend.
	75.3±1.7	78.6±0.2	251.0±8.4	[29], recomend.

As can be seen from the Table 5, the standard enthalpy of of Bi_2Te_3 formation determined by us is in good agreement with the data [45, 48-50] obtained by the methods of

EMF, calorimetry, and tensimetry. Very close $\Delta_f H^0$ values are recommended in handbooks [26-29]. The data obtained by high-temperature EMF measurements [46, 47] are somewhat overestimated. The value of the standard Gibbs energy of formation obtained by us also agrees with the data of [45] and the values recommended in [26-29]. The thermodynamic functions of Bi_4Te_5 were determined by us for the first time.

Conclusion

The thermodynamic properties of the alloys of the Bi-Te system were studied by EMF measurements of the concentration cells relative to the bismuth electrode in the 55-65 at% Te compositions and temperatures in 300-450 K intervals. Relative partial molar functions of bismuth in the alloys, standard thermodynamic formation functions, and standard entropies of Bi_2Te_3 and Bi_4Te_5 compounds were calculated. Results obtained for Bi_2Te_3 supplement and refine the literature data, while the thermodynamic functions for Bi_4Te_5 are determined for the first time.

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Bi_2Te_3 VƏ Bi_4Te_5 BİRLƏŞMƏLƏRİNİN TERMODİNAMİK XASSƏLƏRİ

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Bi-Te sisteminin termodinamik xassələri ilə 55-65 at% Te tərkib və 300-450 K temperatur intervalında tədqiq edilmişdir. Xəlitələrdə bismutun nisbi parsial molyar funksiyaları hesablanmışdır. Potensialəmələgətirici reaksiyalar əsasında Bi_2Te_3 və Bi_4Te_5 birləşmələrinin standart əmələgəlmə termodinamik funksiyalarının və standart entropiyalarının qarşılıqlı tənzimlənmiş qiymətləri kompleksləri alınmışdır. Bi_2Te_3 üçün termodinamik xassələri alınmış nəticələr ədəbiyyatla müqayisəli təhlil edilmiş, Bi_4Te_5 üçün isə termodinamik funksiyalar ilk dəfə təyin olunmuşdur.
Açar sözlər: *termodinamik funksiyalar, Bi-Te sistemi, elektrik hərəkət qüvvəsi üsulu*

ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА Bi_2Te_3 И Bi_4Te_5 СОЕДИНЕНИЙ

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Методом электродвижущих сил изучены термодинамические свойства системы Bi-Te в интервале составов 55-65 ат% Te и температур 300-450 К. Рассчитаны относительные парциальные молярные функции висмута в сплавах. На основании потенциалобразующих реакций получены взаимосогласованные комплексы значений стандартных термодинамических функций образования и стандартных энтропий для соединений Bi_2Te_3 и Bi_4Te_5. Проведен сравнительный анализ полученных для Bi_2Te_3 данных с литературными, для Bi_4Te_5 термодинамические функции определены впервые.
Ключевые слова: *теллуриды висмута, термодинамические функции, метод ЭДС, ионная жидкость*