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Solid-phase equilibria in the GeBi2Te4-Bi2Te3-Te system and thermodynamic properties of compounds of the GeTe·mBi2Te3 homologous series

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The GeBi2Te4-Bi2Te3-Te system was investigated by XRD and EMF measurements of the reversible concentration cell of the type

(-) GeTe (solid) │ glycerol +KCl │ Ge-Bi-Te (solid) (+)
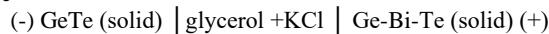
in the 300-450K temperature range. It was shown that, in the indicated temperature range, elementary tellurium forms tie lines with all telluride phases of the system. Equations for the temperature dependences of EMF in all phase regions have been obtained from the data of EMF measurements, from which the partial thermodynamic functions of GeTe in alloys have been calculated. The partial molar functions of germanium in alloys were determined by combining obtained data with the thermodynamic functions of GeTe. Standard Gibbs free energy and enthalpy of formation, as well as the standard entropy of the GeBi2Te4, GeBi4Te7, GeBi6Te10 compounds and solid solutions based on Bi2Te3 have been calculated using these data, solid-phase equilibrium diagram of the GeBi2Te4-Bi2Te3-Te system, and corresponding thermodynamic functions of Bi2Te3.

Keywords: germanium-bismuth tellurides, phase diagram, solid solutions, EMF method, thermodynamic properties.

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Introduction

Ternary compounds of the types $A^{IV}B^{V}_2Te_4$, $A^{IV}B^{V}_4Te_7$, and $A^{IV}B^{V}_6Te_{10}$ in the $A^{IV}Te-B^{V}_2Te_3$ systems (A^{IV}-Ge, Sn, Pb; B^{V}-Sb, Bi) with a layered tetradymite-like structure have long been in the focus of attention of researchers as thermoelectric materials with low thermal conductivity [1-6]. Moreover, Ge-B^{V}-Te alloys are widely used in optical storage devices and are considered the main class of materials with reversible phase transition between amorphous and crystalline states [7-10]. After the discovery of a new quantum state of matter - a topological insulator (TI) [11, 12], it was defined that these compounds exhibit the properties of three-dimensional TIs and are very upcoming for a variety of applications, including spintronics, quantum computers, medicine, security systems, etc. [13-21].

The search and development of methods for directed synthesis of new multi-component chalcogenide phases are based on data sets on phase equilibria and thermodynamic properties of the corresponding systems [17, 22]. Conducted in [17] analysis of the literature data on phase equilibria in the $A^{IV}Te-B^{V}_2Te_3$ systems showed that, despite growing interest in the above-mentioned ternary compounds, phase diagrams of these systems are far from perfection and need a throughout re-study using new approaches to obtain alloys close to equilibrium.

The GeTe-$B^{V}_2Te_3$ systems are interesting because, in addition to the compounds of the GeTe·$mB^{V}_2Te_3$ homologous series, characteristic for all $A^{IV}Te-B^{V}_2Te_3$ systems, compounds of the nGeTe·$B^{V}_2Te_3$ series are also formed [3, 17, 23-25]. However, only a few

representatives of the indicated homologous series are depicted on the relevant phase diagrams. For example, the first version of the GeTe-Bi_2Te_3 T-x diagram reflects the $Ge_3Bi_2Te_6$, $GeBi_2Te_4$, and $GeBi_4Te_7$ compounds with incongruent melting by peritectic reactions [26]. Later, careful X-ray studies of this system were carried out, and taking into account the data of [26], its compiled phase diagram was presented [3, 23]. In the enhanced version of the phase diagram, in addition to these three compounds, compositions of possible representatives of the above given homologous series were shown without indicating the nature and temperatures of their formation.

In [27, 28], we presented results of the detailed re-study of the GeTe-Bi_2Te_3 quasi-binary system and a new version of its phase diagram considerably different from those previously obtained in [3, 23, 26]. In addition to the $Ge_3Bi_2Te_6$, $GeBi_2Te_4$, and $GeBi_4Te_7$ compounds indicated in [26], this diagram reflects incongruently melting $Ge_4Bi_2Te_7$, $Ge_2Bi_2Te_5$, and $GeBi_6Te_{10}$ ternaries, as well as wide solid solutions areas based on both initial binary compounds.

In the literature, we have found only one work on the thermodynamic study of germanium-bismuth tellurides, carried out by the method of quantitative differential thermal analysis [29]. Taking this into account, we undertook a comprehensive study of phase equilibria and thermodynamic properties of the GeTe-Bi_2Te_3-Te system by the method of electromotive forces (EMF). Various modifications of this EMF method with liquid [30–36] and solid [36–41] electrolytes are successfully used to study chalcogenide systems.

This work presents the data on solid-phase equilibria in the $GeBi_2Te_4$-Bi_2Te_3-Te system and the thermodynamic properties of the $GeBi_6Te_{10}$, $GeBi_4Te_7$, and $GeBi_2Te_4$ ternary compounds formed in it, as well as solid solutions based on Bi_2Te_3.

I.   Experimental part

1.1. Synthesis

Alloys of the $GeBi_2Te_4$-Bi_2Te_3-Te system were obtained by fusing pre-synthesized and identified binary compounds GeTe and Bi_2Te_3, as well as elemental tellurium in evacuated (~ 10^{-2} Pa) quartz ampoules. Elementary components Ge (CAS 7440-56-4), Bi (CAS 7440-69-9), and Te (CAS 13494-80-9) of high purity from Alfa Aesar were used in the synthesis.

When developing a technique for the preparation of alloys, we proceeded from the fact that bulk samples of layered tetradymite-like phases were obtained by the well-known fusion method, even after prolonged (up to 3000 h) thermal annealing, do not reach an equilibrium state [24, 42–44]. According to the authors of [30, 31], this is due to the fact that, in contrast to conventional bulk phases, van der Waals phases obtained by crystallization upon ordinary cooling of the melt practically do not undergo any changes during further heat treatment due to very weak diffusion between the layers. Therefore, taking into account the results of [30, 31], after alloying, the samples were quenched from the liquid state by throwing ampoules into ice water to obtain highly dispersed cast alloys. Then samples were

subjected to stepwise thermal annealing at 700 K (1000 h) and 400 K (100 h).

1.2. Research methods

For thermodynamic investigations, concentrations cells of the type

(-) GeTe (solid) │ glycerol +KCl │ Ge-Bi-Te (solid) (+)

were assembled, and their EMF was measured in the 300–450 K temperature interval.

At first, the character of solid-phase equilibria in the $GeBi_2Te_4$-Bi_2Te_3-Te composition area of the Ge-Bi-Te system was defined by powder X-ray diffraction (PXRD) analysis in order to select compositions of the electrode alloys.

The phase identification of powdered samples was performed using Bruker D8 diffractometer ($CuK_{\alpha1}$ radiation) at room temperature in the 2θ angle range of 6–75^0.

We have established that the diagram of solid-phase equilibria has the form given in Fig. 1, i.e. all telluride phases are in a conodal connection with elementary tellurium. Diffraction patterns of the powder of three samples, which are located on tie-lines $GeBi_6Te_{10}$-Te, $GeBi_4Te_7$-Te, and $GeBi_2Te_4$-Te confirm this. As can be seen, samples 1-3 consist of two-phase mixtures of the corresponding ternary compounds and elemental tellurium.
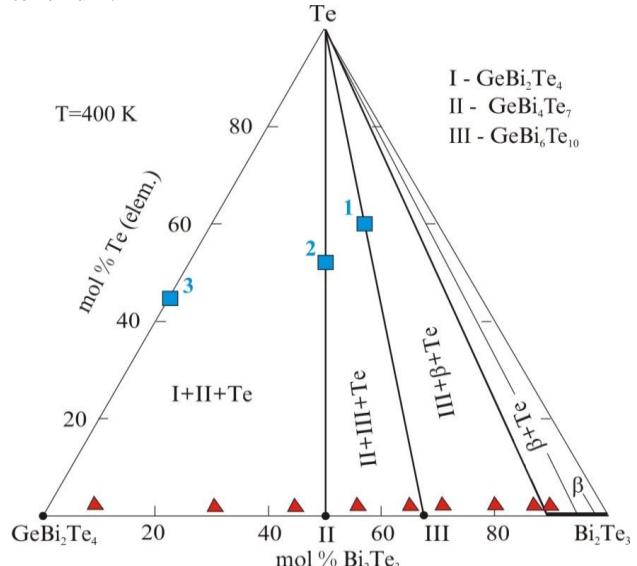

Fig.1. The solid-phase equilibria diagram of the $GeBi_2Te_4$-Bi_2Te_3-Te system at 400 K. Triangles – are alloys studied by the EMF method, and squares - by the XRD method.

Glycerol (CAS No. 56-81-5) solution of KCl (CAS No. 7447-40-7) was used as an electrolyte in electrochemical cells. The salt of the Ge^{2+} ion was not added to the electrolyte. Taking into account the results of [45], we assumed that due to the extremely low solubility of $GeCl_2$ in glycerol, the equilibrium concentration of Ge^{2+} ions can be provided by the electrochemical cell itself.

Glycerol was completely dried and degassed by evacuation at ~ 450 K to release an electrolyte from moisture and oxygen.

Since concentration cells related to the germanium electrode became irreversible, germanium monotelluride

GeTe with a negligible (0.5 at%) tellurium excess was used as a left electrode.

Equilibrium alloys from different phase regions of the GeBi$_2$Te$_4$-Bi$_2$Te$_3$-Te subsystem with elemental tellurium excess (2 at%) were used as right electrodes (Fig.1).
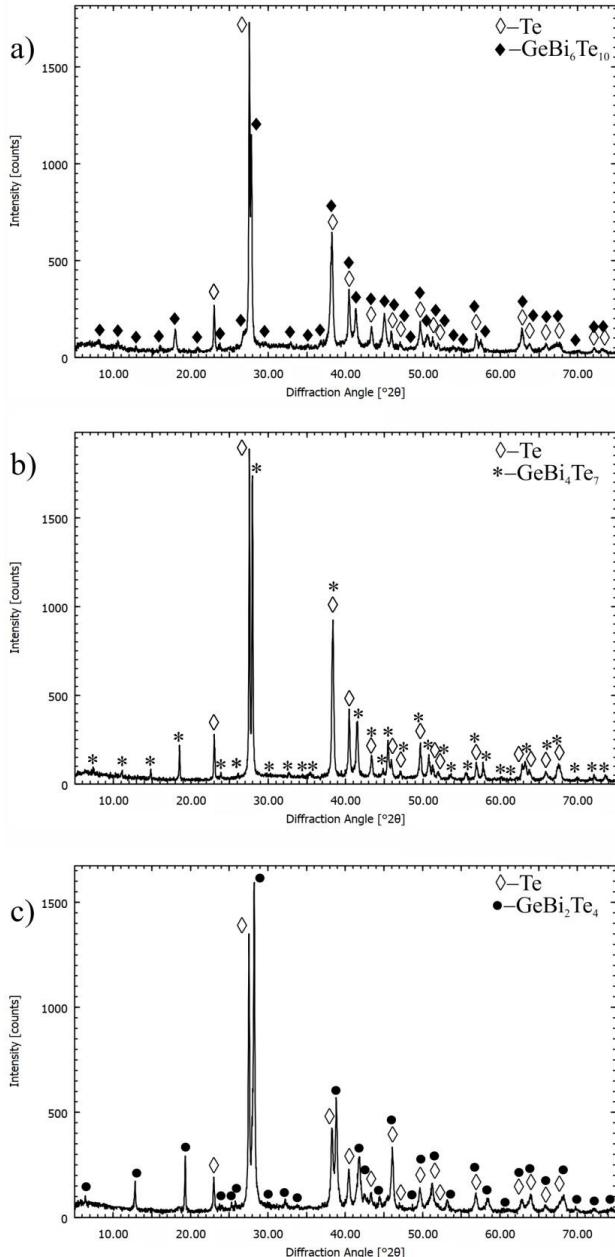
Fig.2. Powder diffraction patterns of alloys of the GeBi$_2$Te$_4$-Bi$_2$Te$_3$-Te system shown in Fig. 1: a) sample 1; b) sample 2; c) sample 3.

The methods used to prepare electrodes and assembling an electrochemical cell are described in detail [35, 36]. A Keithley 2100 6 ½ digital multimeter having 10^{14} Ω input resistance and ± 0.1 mV accuracy applied to measure the EMF. The chromel-alumel thermocouple and the mercury thermometer having ±0.5 K accuracy were used to measure the electrochemical cell temperature.

The first equilibrium EMF values were obtained after holding the electrochemical cell at ~350 K for ~40–

60 h, and the subsequent ones every 3–4 h after a certain temperature was established. There was no difference of more than 0.5 mV between the EMF values during the measurements repeated at a given temperature and they have been recorded as equilibrium values without taking into account the temperature change. The reversibility of the composed concentration cells was controlled by the fact that masses and phase compositions of electrodes were kept constant during measurements.

The results of the EMF measurements of the concentration cells of type (1) have been in good consent with the solid-phase equilibria diagram of the system GeBi$_2$Te$_4$-Bi$_2$Te$_3$-Te (Fig.1). At a certain temperature, the EMF values in the two-phase area β+Te are continuous functions of composition, while in the β+GeBi$_6$Te$_{10}$+Te, GeBi$_6$Te$_{10}$+GeBi$_4$Te$_7$+Te and GeBi$_4$Te$_7$+GeBi$_2$Te$_4$+Te three-phase regions they have been constant regardless of the total composition of alloys and changed during transition from one phase to other ones. Along the GeBi$_2$Te$_4$-Bi$_2$Te$_3$ section, the concentration dependence of EMF has the form Fig. 3. An analysis of the obtained EMF data showed that, in addition to reproducibility, they agree with the necessary thermodynamic principle about the impossibility of reduction of numerical values of the EMF in the radial directions from the Ge vertex of the Ge-Bi-Te concentration triangle.
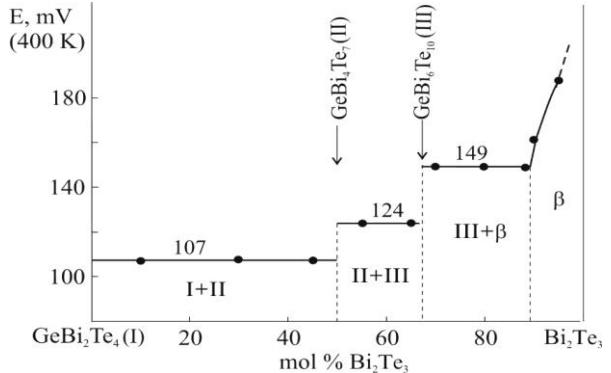

Fig.3. The concentration dependence of the EMF of the cells of type (1) along the GeBi$_2$Te$_4$-Bi$_2$Te$_3$ section at 400 K.

Fig. 4 illustrates the temperature dependencies of EMF for the studied phase areas. As it is seen, they are linear and it indicates the practical constancy of the compositions of the coexisting phases in the temperature range of EMF measurements, which allows to carry out thermodynamic calculations.

T_i(K) and E_i(mV) pairs of experimental data, as well as, their processing data for the β+GeBi$_6$Te$_{10}$+Te phase area are given in Table 1. Processing of these data using the least-squares method resulted in the following linear equations [35, 36]:

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

In equation (2), a and b are coefficients, n is the number of pairs of values E and T; $\overline{T}$ - average temperature in K, t is Student's test, δ_E^2 and δ_b^2 are the variances of individual EMF values and the constant b. With the number of experimental data points n = 30, and

the confidence level equal to 95%, the Student's test is $t \leq 2$.
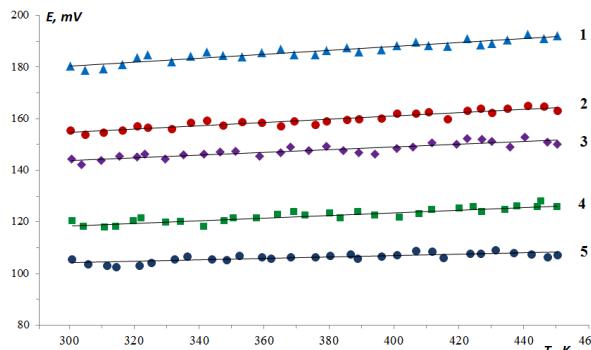
Fig.4. Temperature dependencies of EMF for alloys of the phase areas: 1- β (5mol% GeTe) + Te; 2- β (10mol% GeTe) + Te; 3- β + GeBi$_6$Te$_{10}$ + Te; 4- GeBi$_6$Te$_{10}$ + GeBi$_4$Te$_7$ + Te; 5- GeBi$_4$Te$_7$ + GeBi$_2$Te$_4$ + Te.

From the obtained equations (Table 2) by using the following thermodynamic relations

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

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

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

The partial molar Gibbs free energy, enthalpy, and entropy of GeTe in alloys were calculated (Table 3). These quantities are the difference of the corresponding partial molar functions of germanium for the left and right electrodes of the cells type (1):

Table 1

Experimentally obtained data for temperature (T_i) and EMF (E_i) of the β + GeBi$_6$Te$_{10}$ + Te phase region in the Ge-Bi-Te system.

T_i, K	E_i, mV	$T_i - \overline{T}$	$E_i(T_i - \overline{T})$	$(T_i - \overline{T})^2$	$\widetilde{E}$	$E_i - \widetilde{E}$	$(E_i - \widetilde{E})^2$
300.8	144.35	-75.28	-10866.19	5666.58	143.90	0.45	0.20
303.8	142.18	-72.28	-10276.30	5223.92	144.06	-1.88	3.54
309.9	143.91	-66.18	-9523.48	4379.35	144.38	-0.47	0.22
315.4	145.44	-60.68	-8824.81	3681.66	144.66	0.78	0.60
320.9	145.27	-55.18	-8015.51	3044.46	144.95	0.32	0.10
323.2	146.33	-52.88	-7737.44	2795.94	145.07	1.26	1.59
329.5	144.41	-46.58	-6726.14	2169.39	145.40	-0.99	0.97
335.3	145.95	-40.78	-5951.35	1662.74	145.70	0.25	0.06
341.5	146.27	-34.58	-5057.53	1195.55	146.02	0.25	0.06
346.4	147.14	-29.68	-4366.62	880.70	146.27	0.87	0.75
351.2	147.33	-24.88	-3665.08	618.85	146.52	0.81	0.65
358.7	145.42	-17.38	-2526.91	301.95	146.91	-1.49	2.23
365.2	146.86	-10.88	-1597.35	118.30	147.25	-0.39	0.15
368.2	148.93	-7.88	-1173.07	62.04	147.41	1.52	2.32
373.8	147.64	-2.28	-336.13	5.18	147.70	-0.06	0.00
379.3	149.28	3.22	481.18	10.39	147.98	1.30	1.68
384.5	147.63	8.42	1243.54	70.95	148.25	-0.62	0.39
389.2	146.92	13.12	1928.08	172.22	148.50	-1.58	2.49
394.1	146.24	18.02	2635.73	324.84	148.75	-2.51	6.31
400.8	148.54	24.72	3672.40	611.24	149.10	-0.56	0.31
405.9	149.15	29.82	4448.15	889.43	149.36	-0.21	0.05
411.7	150.62	35.62	5365.59	1269.02	149.67	0.95	0.91
419.3	150.16	43.22	6490.42	1868.26	150.06	0.10	0.01
422.5	152.33	46.42	7071.67	2155.13	150.23	2.10	4.42
427.2	151.91	51.12	7766.15	2613.60	150.47	1.44	2.07
430.2	151.26	54.12	8186.70	2929.34	150.63	0.63	0.40
435.9	149.05	59.82	8916.67	3578.83	150.92	-1.87	3.51
440.3	152.93	64.22	9821.67	4124.64	151.15	1.78	3.16
447.3	150.82	71.22	10741.90	5072.76	151.52	-0.70	0.48
450.3	150.19	74.22	11147.60	5509.10	151.67	-1.48	2.20
$\overline{T}$ =376.08	$\overline{E}$=147.82						

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$$\Delta \overline{G}_{GeTe}(\text{in alloy}) = \Delta \overline{G}_{Ge} \ (\text{in alloy}) - \Delta \overline{G}_{Ge}(\text{in GeTe})$$

therefore

$$\Delta \overline{G}_{Ge} \ (\text{in alloy}) = \Delta \overline{G}_{GeTe} \ (\text{in alloy}) + \Delta \overline{G}_{Ge}(\text{in GeTe}) \qquad (6)$$

Hence, the calculation of the partial thermodynamic functions of germanium in alloys can be carried out by summation of the data of Table 3 with the corresponding partial molar functions of Ge in GeTe. In our calculations, we used the data from [46]:

$\Delta \overline{G}_{Ge} = $ -52.87±0.09 кJ·mol^{-1}

$\Delta \overline{H}_{Ge} = $ 49.50±0.38 кJ·mol^{-1}

$\Delta \overline{S}_{Ge} = $ 11.3±1.0 J·mol^{-1}·K^{-1}

Obtained results are given in Table 4.

Calculation of the standard thermodynamic functions of the formation of β-solid solutions was carried out by graphical integration of the Gibbs-Duhem equation

$$\Delta_f Z^0(\beta - phase) = (1-x)\int_0^x \frac{\Delta \overline{Z}_{GeTe}}{(1-x)^2} dx + (1-x)\Delta_f Z^0(Bi_2Te_3) + x\Delta_f Z^0(GeTe) \qquad (7)$$

along the GeTe-Bi$_2$Te$_3$ section according to the well-known method [38]. In equation (7), x – is the mole fraction of GeTe. $\Delta \overline{Z}_{GeTe}$ - are the partial molar functions of GeTe in the β-phase (Table 3).

Table 2

Temperature dependencies of the EMF for the cells of type (1) in some phase regions of the Ge-Bi-Te system in the 300–450 K temperature interval.

Phase area	E = a + bT ±2S$_E$ (T)
β(5 mol% GeTe) + Te	$157.89 + 0.0752 \, T \pm 2 \left[\frac{1.5}{30} + 2.4 \cdot 10^{-5}(T - 376.5)^2\right]^{1/2}$
β(10 mol% GeTe) + Te	$135.47 + 0.0641 \, T \pm 2 \left[\frac{1.1}{30} + 1.7 \cdot 10^{-5}(T - 376.5)^2\right]^{1/2}$
β + GeBi$_6$Te$_{10}$ + Te	$128.28 + 0.0520 \, T \pm 2 \left[\frac{1.4}{30} + 2.2 \cdot 10^{-5}(T - 376.1)^2\right]^{1/2}$
GeBi$_6$Te$_{10}$ + GeBi$_4$Te$_7$ + Te	$103.20 + 0.0511 \, T \pm 2 \left[\frac{1.3}{30} + 2.0 \cdot 10^{-5}(T - 376.4)^2\right]^{1/2}$
GeBi$_4$Te$_7$ + GeBi$_2$Te$_4$ + Te	$95.79 + 0.0281 \, T \pm 2 \left[\frac{1.0}{30} + 1.7 \cdot 10^{-5}(T - 376.7)^2\right]^{1/2}$

Table 3.

Relative partial molar functions of GeTe in the alloys of the Ge-Bi-Te system at 298 K.

| Phase area	$-\Delta \overline{G}_{GeTe}$	$-\Delta \overline{H}_{GeTe}$	$-\Delta \overline{S}_{GeTe}$,
	kJ/mol		J/mol· K
β(5 mol % GeTe) + Te	34.79 ± 0.09	30.47 ± 0.36	14.49 ± 0.95
β(10 mol % GeTe) + Te	29.83 ± 0.07	26.14 ± 0.30	12.38 ± 0.80
β + GeBi$_6$Te$_{10}$ + Te	27.74 ± 0.08	24.75 ± 0.34	10.03 ± 0.91
GeBi$_6$Te$_{10}$ + GeBi$_4$Te$_7$ + Te	22.85 ± 0.08	19.91 ± 0.32	9.86 ± 0.85
GeBi$_4$Te$_7$ + GeBi$_2$Te$_4$ + Te	20.10 ± 0.07	18.48 ± 0.30	5.43 ± 0.78

Table 4.

Relative partial molar functions of germanium in the alloys of the Ge-Bi-Te system at 298 K.

Phase area	$-\Delta \overline{G}_{Ge}$	$-\Delta \overline{H}_{Ge}$	$-\Delta \overline{S}_{Ge}$,
	kJ/mol		J/mol· K
β (5 mol % GeTe) + Te	87.66 ± 0.18	79.97 ± 0.76	25.8 ± 1.96
β (10 mol % GeTe) + Te	82.70 ± 0.16	75.64 ± 0.70	23.7 ± 1.90
β + GeBi$_6$Te$_{10}$ + Te	80.61 ± 0.17	74.25 ± 0.74	21.3 ± 1.94
GeBi$_6$Te$_{10}$ + GeBi$_4$Te$_7$ + Te	75.72 ± 0.17	69.41 ± 0.72	21.2 ± 1.92
GeBi$_4$Te$_7$ + GeBi$_2$Te$_4$ + Te	72.97 ± 0.16	67.98 ± 0.70	16.7 ± 1.90

$\Delta_f Z^0(Bi_2Te_3)$ - are the standard thermodynamic functions of the formation of Bi_2Te_3.

Considering stability of compositions of the coexisting phases in the mentioned three-phase regions, the standard integral thermodynamic functions of the $GeBi_6Te_{10}$, $GeBi_4Te_7$, and $GeBi_2Te_4$ were calculated by the method of potential-forming reactions [35-38]. According to the solid-phase equilibria diagram (Fig. 1), the values of the partial molar functions of germanium in the $\beta+GeBi_6Te_{10}+Te$, $GeBi_6Te_{10}+GeBi_4Te_7+Te$, and $GeBi_4Te_7+GeBi_2Te_4+Te$ regions are thermodynamic functions of the following virtual-cell reactions (all

substances are in the crystalline state)

$$Ge + 5\, Ge_{0.1}Bi_{1.8}Te_{2.9} + Te = 1.5\, GeBi_6Te_{10} \qquad (8)$$

$$Ge + 2GeBi_6Te_{10} + Te = 3\, GeBi_4Te_7 \qquad (9)$$

$$Ge + GeBi_4Te_7 + Te = 2\, GeBi_2Te_4 \qquad (10)$$
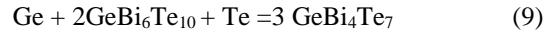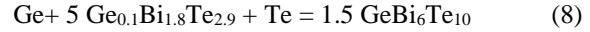
According to the equations of these reactions, the standard thermodynamic functions of formation of the $GeBi_6Te_{10}$, $GeBi_4Te_7$, and $GeBi_2Te_4$ ternaries can be calculated using

$$\Delta_f Z^0(GeBi_6Te_{10}) = \frac{2}{3}\overline{\Delta Z}_{Ge} + \frac{2}{5}\Delta_f Z^0(Ge_{0.1}Bi_{1.8}Te_{2.9}) \qquad (11)$$

$$\Delta_f Z^0(GeBi_4Te_7) = \frac{1}{3}\overline{\Delta Z}_{Ge} + \frac{2}{3}\Delta_f Z^0(GeBi_6Te_{10}) \qquad (12)$$

$$\Delta_f Z^0(GeBi_2Te_4) = 0.5\overline{\Delta Z}_{Ge} + 0.5\Delta_f Z^0(GeBi_4Te_7) \qquad (13)$$

$(Z \equiv G, H)$, while the standard entropies, from the relations

$$S^0(GeBi_6Te_{10}) = \frac{2}{3}\overline{\Delta S}_{Ge} + \frac{2}{3}S^0(Ge) + \frac{2}{3}S^0(Te) + \frac{2}{5}S^0(Ge_{0.1}Bi_{1.8}Te_{2.9}) \qquad (14)$$

$$S^0(GeBi_4Te_7) = \frac{1}{3}\overline{\Delta S}_{Ge} + \frac{1}{3}S^0(Ge) + \frac{1}{3}S^0(Te) + \frac{2}{3}S^0(GeBi_6Te_{10}) \qquad (15)$$

$$S^0(GeBi_2Te_4) = 0.5\overline{\Delta S}_{Ge} + 0.5S^0(Ge) + 0.5S^0(Te) + 0.5S^0(GeBi_4Te_7) \qquad (16)$$

In calculations using relations (11) - (16), along with own experimental data (Table 4), we used the standard entropy of Ge (31.13 ± 0.30 J mol^{-1} K^{-1}), Te (49.50 ± 0.21 J · mol^{-1} · K^{-1}) [47] and also thermodynamic data for Bi_2Te_3 (Table 5), obtained by the EMF method [31] and well consistent with the data recommended in well-known reference books [47-49].

When calculating the partial molar thermodynamic functions of germanium (Table 4) and the integral

thermodynamic functions of germanium-bismuth tellurides (Table 5), errors have been found by the uncertainty propagation method.

Table 5 also shows the values of the enthalpy of formation of the $GeBi_4Te_7$, and $GeBi_2Te_4$ compounds obtained by the quantitative DTA method [29]. These values are 20-25% lower compared to our data. It should be noted that they are also significantly lower than the sum of the heats of formation of GeTe and Bi_2Te_3 per

Table 5.

Standard integral thermodynamic functions of binary and ternary phases of the Ge-Bi-Te system

Phase	$-\Delta_f G°$(298 K)	$-\Delta_f H°$(298 K)	$S°$(298 K)
	kJ/mol		J/mol·K
GeTe [46]	52.9 ± 0.1	49.5 ± 0.4	91.1 ± 1.4
Bi_2Te_3 [31]	76.9 ± 0.2	79.2 ± 0.5	254.2 ± 3.0
β ($Ge_{0.05}Bi_{1.9}Te_{2.9}$)	77.5 ± 0.2	79.2 ± 0.6	246.8 ± 3.0
β ($Ge_{0.1}Bi_{1.8}Te_{2.8}$)	77.9 ± 0.2	79.0 ± 0.6	239.3 ± 3.0
$GeBi_6Te_{10}$	313.4 ± 0.8	312.8 ± 2.5	865.6 ± 11.7
$GeBi_4Te_7$	234.2 ± 0.6	231.7 ± 1.9	611.0 ± 8.7
	-	191 ± 14 [29]	-
$GeBi_2Te_4$	153.6 ± 0.4	149.8 ± 1.3	354.2 ± 5.6
	-	114 ± 8 [29]	-

formula units of GeBi$_4$Te$_7$, and GeBi$_2$Te$_4$. In our opinion, the relatively low values of the standard heats of formation of these compounds [29] can be associated with nonequilibrium of the samples. Unfortunately, in [29], there are no specific data on the synthesis conditions and identification of the studied GeBi$_4$Te$_7$, and GeBi$_2$Te$_4$ samples, the preparation of which is a single-phase form, as shown above, is associated with certain difficulties.

Conclusion

This work presents a new set of experimental data on solid-phase equilibria in the GeBi$_2$Te$_4$-Bi$_2$Te$_3$-Te composition area of the Ge-Bi-Te system, obtained by the PXRD and EMF methods. From the EMF measurements of the cells relative to the germanium monotelluride electrode in the 300–450 K temperature range, the relative partial molar functions of GeTe in the different concentration regions were calculated. By combining these functions with the partial molar functions of germanium in GeTe, the corresponding partial functions of germanium in the alloys were calculated. Based on the solid-phase equilibria diagram of the GeBi$_2$Te$_4$-Bi$_2$Te$_3$-Te subsystem, the virtual-cell reactions for the GeBi$_6$Te$_{10}$, GeBi$_4$Te$_7$, and GeBi$_2$Te$_4$ compounds were determined, with which the standard thermodynamic functions of formation and the standard entropies of the above-mentioned ternary compounds were calculated. The integral thermodynamic functions

of β-solid solutions were calculated by integrating the Gibbs-Duhem equation.

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[1] G. K. Ahluwalia, Applications of Chalcogenides: S, Se, and Te (Springer International Publishing, Switzerland, 2016).

[2] A. V. Shevelkov, Russ. Chem. Rev., 77(1), 1 (2008); https://doi.org/10.1070/RC2008v077n01ABEH003746.

[3] L. E. Shelimova, O. G. Karpinskii, P. P. Konstantinov. Inorg. Mater., 40(5), 451 (2004); https://doi.org/10.1023/b:inma.0000027590.43038.a8.

[4] P. C. Wei, C. X. Cai, C. R. Hsing, Sci. Rep., 9(1), 8616 (2019); https://doi.org/10.1038/s41598-019-45071-9.

[5] O. Tatsuro, K. Hiroki; I. Hiroki, K. Yoshiki, K. Kouichi, K. Atsuko, J. Electron. Mater., 45(3), 1478 (2016); https://doi.org/10.1007/s11664-015-4083-z.

[6] J. Zhang, Y. Yan, H. Xie, T. Zhu, C. Zhang, J. Qiu, X. Tang, Ceram. Int., 45(13), 16039 (2019); https://doi.org/10.1016/j.ceramint.2019.05.119.

[7] R. Lan. Thermophysical Properties and Measuring Technique of Ge-Sb-Te Alloys for Phase Change Memory (Springer Singapore, 2020).

[8] Y. Meng, T. Cao, Y. Long, J. Appl. Phys., 128, 140904 (2020); https://doi.org/10.1063/5.0023925.

[9] J. Tominaga, MRS Bulletin, 43(05), 347 (2018); https://doi.org/10.1557/mrs.2018.94.

[10] P. Guo 1, A. M. Sarangan, I. Agha, Appl. Sci., 9(3), 530 (2019); https://doi.org/10.3390/app9030530.

[11] J. E. Moore, Nature, 464(7286), 194 (2010); https://doi.org/10.1038/nature08916.

[12] C. L. Kane, J. E. Moore, Phys World, 24(2), 32 (2011); https://doi.org/10.1088/20587058/24/02/36.

[13] S. V. Eremeev, G. Landolt, T. V. Menshchikova, B. Slomski, Y. M. Oroteev, Z. S. Aliev, M. B. Babanly, J. Henk, A. Ernst, L. Patthey, A. Eich, A. A. Khajetoorians, J. Hagemeister, O. Pietzsch, J. Wiebe, R. Wiesendanger, P. M. Echenique, S. S. Tsirkin, I. R. Amiraslanov, J. H. Dil, E. V. Chulkov, Nat. Commun., 3, 635 (2012); https://doi.org/10.1038/ncomms1638.

[14] J. Kim, S-H. Jhi, J. Appl. Phys., 117, 195701 (2015); https://doi.org/10.1063/1.4921294.

[15] Y-C. Zou, Z-G. Chen, E. Zhang, F. Kong, Y. Lu, L. Wang, J. Drennan, Z. Wang, F. Xiu, K. Cho, J. Zou, Nano Res., 11(2), 696 (2018); https://doi.org/10.1007/s12274-017-1679-z.

[16] D. Pacile, S. V. Eremeev, M. Caputo, M. Pisarra, O. De Luca, I. Grimaldi, J. Fujii, Z. S. Aliev, M. B. Babanly, I. Vobornik, R. G. Agostino, A. Goldoni, E. V. Chulkov, M. Papagno, pss RRL, 12(12), 1800341-8 (2018); https://doi.org/10.1002/pssr.201800341.

[17] M. B. Babanly, E. V. Chulkov, Z. S. Aliev, A. V. Shevelkov, I. R. Amiraslanov, Russ. J. Inorg. Chem., 62(13), 1703 (2017); https://doi.org/10.1134/S0036023617130034.

[18] M. Nurmamat, K. Okamoto, S. Zhu, T. V. Menshchikova, I. P. Rusinov, V. O. Korostelev, K. Miyamoto, T. Okuda, T. Miyashita, X. Wang, Y. Ishida, K. Sumida, E. F. Schwier, M. Ye, Z. S. Aliev, M. B. Babanly, I. R. Amiraslanov, E. V. Chulkov, K. A. Kokh, O. Tereshchenko, K. Shimada, S. Shin, A. Kimura, ACS Nano, 14(7), 9059 (2020); https://doi.org/10.1021/acsnano.0c04145.

[19] K. Okamoto, K. Kuroda, Z. S. Aliyev, M. B. Babanly, I. R. Amiraslanov, Phys.Rev.B. (American Phys.Soc.), 86(19), 195304 (2012); https://doi.org/10.1103/PhysRevB.86.195304.

[20] T. V. Menshchikova, S. V. Eremeev, V. M. Kuznetsov, E. V. Chulkov, Mater., 13(20), 4481 (2020); https://doi.org/10.3390/ma13204481.

[21] P. Mal, B. Das, G. Bera, G. R. Turpu, C. V. Tomy, P. Das, J. Mater. Sci.: Mater. Electron. (2021); http://doi.org/10.1007/s10854-021-06350-2.

[22] M. B. Babanly, L. F. Mashadiyeva, D. M. Babanly, S. Z. Imamaliyeva, D. B. Taghiyev, Y. A. Yusibov, Russ. J. Inorg. Chem., 64(13), 1649 (2019); https://doi.org/10.1134/S0036023619130035.

[23] L. E. Shelimova, O. G. Karpinskii, V. S. Zemskov, Inorg. Mater. 36(3), 235 (2000); https://doi.org/10.1007/BF02757928.

[24] L. E. Shelimova, O. G. Karpinskii, V. I. Kosyakov, J. Struct. Chem. 41(1), 81 (2000); https://doi.org/10.1007/BF02684732.

[25] C. S. Jung, S. H. Kim, H. S. Im, K. Park, J. Park, J-P. Ahn, S. J. Yoo, J-G. Kim, J. N. Kim, J. H. Shim, Nano Lett., 15(6), 3923 (2015); https://doi.org/10.1021/acs.nanolett.5b00755.

[26] N. X. Abrikosov, G. T. Danilova-Dobryakova, Izv. Akad. Nauk SSSR, Neorg. Mater. 1, 57 (1965).

[27] T. M. Alakbarova, H-J. Meyer, E. N. Orujlu, I. R. Amiraslanov, M. B. Babanly, Ph. Transit., 94(5), 366 (2021); https://doi.org/10.1080/01411594.2021.1937625.

[28] T. M. Alakbarova, H.-J. Meyer, M. B. Babanly, XI International Conference on Kinetics and mechanism of crystallization. Crystallization and materials of the new generation (Ivanova, 2021), p. 114.

[29] A. S. Skoropanov, B. L. Valevsky, V. F. Skums, G. I. Samal, A. A. Vecher, Thermochim. Acta, 90, 331 (1985).

[30] G. S. Hasanova, A. I. Aghazade, D. M. Babanly, S. Z. Imamaliyeva, Y. A. Yusibov, M. B. Babanly, J. Therm. Anal. Calorim., (2021); https://doi.org/10.1007/s10973-021-10975-0.

[31] G. S. Hasanova, A. I. Aghazade, S. Z. Imamaliyeva, Y. A.Yusibov, M. B. Babanly. JOM, 73(5), 1511 (2021); https://doi.org/10.1007/s11837-021-04621-1.

[32] V. P. Vassiliev, V. A. Lysenko, Electrochim. Acta, 222, 1770 (2016); https://doi.org/10.1016/j.electacta.2016.11.075.

[33] E. G. Osadchii , Ya I. Korepanov, N. N. Zhdanov, Instrum. Exp. Tech., 59(2), 302 (2016); https://doi.org/10.1134/S0020441216010255.

[34] V. Vassiliev, W. Gong, "Electrochemical cells with the liquid electrolyte in the study of semiconductor, metallic and oxide systems." Electrochemical Cells – New Advances in Fundamental Researches and Applications. Ed. Yan Shao, IntechOpen, 71 (2012); https://doi.org/10.5772/39007.

[35] S. Z. Imamaliyeva, S. S. Musayeva, D. M. Babanly, Y. I. Jafarov, D. B. Tagiyev, M. B. Babanly, Thermochim. Acta, 679, 178319 (2019); https://doi.org/10.1016/j.tca.2019.178319.

[36] A. G. Morachevsky, G. F. Voronin, V. A. Geyderich, I. B. Kutsenok, Electrochemical methods of investigation in hermodynamics of metal systems. (Moscow: Akademkniga Publ., 2003).

[37] N. B. Babanly, E. N., Orujlu, S. Z. Imamaliyeva, Y. A. Yusibov, M. B. Babanly, J. Chem. Thermodyn., 128,78 (2019); https://doi.org/10.1016/j.jct.2018.08.012.

[38] L. F. Mashadiyeva, D. M. Babanly, Y. A. Yusibov, D. B. Tagiyev, M. B. Babanly, Russ. J. Electrochem., 57(3), 281 (2021); https://doi.org/10.1134/S1023193521030083.

[39] M. Moroz, F. Tesfaye, P. Demchenko, M. Prokhorenko, S. Prokhorenko, O. Reshetnyak, D. Lindberg, L. Hupajom, JOM 73(5), 1487 (2021); https://doi.org/10.1007/s11837-021-04619-9)

[40] M. Moroz, F. Tesfaye, P. Demchenko, M. Prokhorenko, S. Prokhorenko, O. Reshetnyak, Thermochim. Acta, 698, 178862(1–7) (2021); https://doi.org/10.1016/j.tca.2021.178862)

[41] M. Moroz, F. Tesfaye, P. Demchenko, M. Prokhorenko, N. Yarema, D. Lindberg, O. Reshetnyak, L. Hupa, Energies. 14(5), 1314(1–15) (2021); https://doi.org/10.3390/en14051314.

[42] N. K. Abrikosov, V. F. Bankina, L. V. Poretskaya, L. E. Shelimova, E. V. Skudnova, Semiconducting II–VI, IV–VI, and V–VI Compounds, (Springer US., 1969).

[43] N. K. Abrikosov, V. F. Bankina, Inorg. Chem. USSR 3, 659 (1958).

[44] R. F. Brebrick, The Chemistry of Extended Defects in Nonmetallic Solids, (American Elsevier Publ Co., Amsterdam, 1970).

[45] D. M. Babanly, G. M. Velieva, S. Z. Imamaliyeva, Russ. J. Phys. Chem. 91, 1170 (2017); https://doi.org/10.1134/S0036024417070044.

[46] T. M. Alakbarova, New mater. compd. appl., 5, 59 (2021).

[47] V. S. Iorish, V. S. Yungman, Database of thermal constants of substances, (Digital version, Eds., 2006)

[48] O. Kubaschewski, C. B. Alcock, P. J Spenser, Materials Thermochemistry, (Pergamon Press, 1993).

[49] I. Barin, Thermochemical Data of Pure Substances, (Wiley-VCH Verlag GmbH & Co., 2008).

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Твердофазні рівноваги в системі GeBi$_2$Te$_4$-Bi$_2$Te$_3$-Te та термодинамічні властивості сполук гомологічного ряду GeTe·mBi$_2$Te$_3$

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Систему GeBi$_2$Te$_4$-Bi$_2$Te$_3$-Te досліджено рентгенофазовим методом та вимірюванням ЕРС обернених концентраційних кіл типу

(-) GeTe (твердий стан) │гліцерин +KCl │ Ge-Bi-Te (твердий стан) (+)
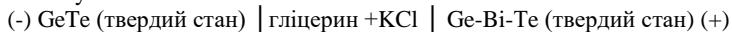
у температурному діапазоні 300-450 K. Показано, що у зазначеному діапазоні температур елементний телур утворює лінії зв'язку із усіма телуридними фазами системи. За даними вимірювань ЕРС, де розраховано часткові термодинамічні функції GeTe в сплавах, отримано рівняння температурних залежностей ЕРС для всіх фазових областей. Парціальні молярні функції германію в сплавах визначали шляхом поєднання отриманих даних із термодинамічними функціями GeTe. За цими даними та діаграмою твердофазної рівноваги системи GeBi$_2$Te$_3$-Bie$_2$Te розраховано стандартну вільну енергію Гіббса та ентальпію утворення, а також стандартну ентропію сполук GeBi$_2$Te$_4$, GeBi$_4$Te$_7$, GeBi$_6$Te$_{10}$ та твердих розчинів на основі Bi$_2$Te$_3$, а також відповідні термодинамічні функції Bi$_2$Te$_3$.

Ключові слова: Германію-бісмуту телуриди, фазові діаграми, тверді розчини, метод EMF, термодинамічні властивості.