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Published in:

TMS 2022 151st Annual Meeting and Exhibition Supplemental Proceedings

DOI:

[10.1007/978-3-030-92381-5_7](https://doi.org/10.1007/978-3-030-92381-5_7)

Published: 01/01/2022

Document Version

Accepted author manuscript

Document License

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[Link to publication](#)

Please cite the original version:

Moroz, M., Tesfaye, F., Demchenko, P., Prokhorenko, M., Pereviznyk, O., Rudyk, B., Soliak, L., Lindberg, D., Reshetnyak, O., & Hupa, L. (2022). Phase Equilibria in the Ag–Ge–Bi–Te System and Thermodynamic Properties of the $n\text{GeTe}\times m\text{Bi}_2\text{Te}_3$ ($n, m = 1-4$) Layered Compounds. In *TMS 2022 151st Annual Meeting and Exhibition Supplemental Proceedings* (1 ed., Vol. 1, pp. 60-73). (Minerals, Metals and Materials Series). Springer International Publishing. https://doi.org/10.1007/978-3-030-92381-5_7

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Phase Equilibria in the Ag–Ge–Bi–Te System and Thermodynamic Properties of the $n\text{GeTe}\cdot m\text{Bi}_2\text{Te}_3$ ($n, m = 1-4$) Layered Compounds

Mykola Moroz,[✉] Fiseha Tesfaye, Pavlo Demchenko, Myroslava Prokhorenko, Orest Pereviznyk, Bohdan Rudyk, Lyudmyla Soliak, Daniel Lindberg, Oleksandr Reshetnyak, Leena Hupa

Abstract

Phase equilibria of the Ag–Ge–Bi–Te system in the part $\text{GeTe–Ag}_8\text{GeTe}_6\text{–Te–Bi}_2\text{Te}_3$ (**I**) were established by the electromotive force (EMF) method with a solid Ag^+ conducting electrolyte. It was shown that the concentration space of (**I**) in the part $4\text{GeTe}\cdot\text{Bi}_2\text{Te}_3\text{–Ag}_8\text{GeTe}_6\text{–Te–Bi}_2\text{Te}_3$ consists of 8 four-phase regions, formed of the layered compounds of the $n\text{GeTe}\cdot m\text{Bi}_2\text{Te}_3$ ($n, m = 1-4$) homologous range, as well as Ag_8GeTe_6 , Bi_2Te_3 , and Te. Equations of overall potential-forming reaction of the decomposition and synthesis of compounds of the homologous range were written for each region. Reactions were performed in the following electrochemical cells (ECCs) $(-)\text{IE} | \text{Ag} | \text{SE} | \text{PE} | \text{IE}(+)$, where IE is the inert electrode (graphite), Ag is the negative (left) electrode, SE is the solid-state Ag^+ ion-conducting electrolyte, PE is the positive (right) electrode. PEs of ECCs were prepared by melting of a mixture of the high-purity elements Ag, Ge, Bi, and Te. The component ratios in samples were determined based on the equations of the potential-forming reactions in respective phase regions. The finely grounded samples were used as PEs of ECCs. The synthesis of an equilibrium set of phases was performed in the part of PE that is in contact with SE of ECC at $T = 580$ K for 50 h. Silver cations that shift from the left to the right electrode acted as the nucleation centers of equilibrium compounds in the corresponding phase regions. Linear dependences E vs T of ECCs in the range of $T = (440-500)$ K were used to calculate values of the Gibbs energies, enthalpies of formation, and entropies of compounds $\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot 3\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot 2.5\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot 2\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, $2\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, $3\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, and $4\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$. The differences in the values of the thermodynamic functions of GeTe-rich and Bi_2Te_3 -rich compounds with respect to $\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$ correlate well with the literature data on the differences of their crystal structures.

Keywords Layered Compounds, Phase equilibria, Thermodynamic properties, EMF method, Gibbs energy

1. Introduction

The $\text{GeTe–Bi}_2\text{Te}_3$ system features the formation of a sequence of the compounds of the formula compositions $n\text{GeTe}\cdot m\text{Bi}_2\text{Te}_3$ ($n = 1-9, m = 1-4$) with layered long-periodic crystal structure [1,2]. All of these compounds belong to class of thermoelectric materials [3–5]. Moreover, the GeBi_2Te_4 is three-dimensional topological insulator [6–8]. According to phase diagram of the $\text{GeTe–Bi}_2\text{Te}_3$ system [2,9], the $3\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, and $\text{GeTe}\cdot 2\text{Bi}_2\text{Te}_3$ compounds are formed by peritectic reactions at 923 K, 857 K, and 837 K, respectively. The $4\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, $2\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, $2\text{GeTe}\cdot 5\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot 3\text{Bi}_2\text{Te}_3$, and $\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3$ compounds were obtained in sub-solidus temperature range by homogenizing melts of a mixture of elements at 570–620 K for the period of 300–500 h [2]. The crystal structure of compounds was established by the results of electron diffraction on thin

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films, X-ray diffraction on poly- and single-crystal samples. Tellurium atoms are grouped by the principle of dense cubic packing in all compounds. By superimposing layers of tellurium atoms, the packages are formed. In these packages, the octahedral cavities are occupied by germanium and bismuth atoms. Hexagonal elementary cells of compounds are formed from multilayer packages of different types, the planes of which are perpendicular to the c axis. The packets are divided by the *Van der Waals* slits. The number of packages in the unit cell depends on the relative amount of germanium and bismuth tellurides in the compound. In the GeTe-rich compounds ($n/m > 1$), the unit cell is formed from packages with the same number of layers. The packages differ in the placement of Ge and Bi in the cationic layers. In the Bi_2Te_3 -rich compounds ($m/n > 1$), the unit cell consists 5- and 7-layered packets. Compounds of the $n\text{GeTe}\cdot m\text{Bi}_2\text{Te}_3$ ($n, m = 1-4$) homologous range are phases of variable composition [10]. Deviation from the stoichiometric composition of one or more elements significantly affects the numerical values of the thermo-EMF coefficients α , the electrical conductivity σ and the thermal conductivity $k_{\text{tot}} = k_{\text{ph}} + k_{\text{el}}$, where k_{ph} and k_{el} are phonon and electronic components of k_{tot} , respectively, which determine the thermoelectric efficiency of material $Z = \alpha^2 \sigma / k_{\text{tot}}$ [11–13]. The thermoelectric efficiency of compounds of the homologous series depends on the peculiarities of filling octahedral cavities. Layers with mixed cationic filling in the GeBi_2Te_4 [1] and GeBi_4Te_7 [14,15] compounds were established by XRD measurements. The presence of mixed cationic positions causes fluctuations of masses and stresses, which contributes to the strong scattering of phonons. The consequence of the formation of such layers is a decreasing of k_{ph} values. The thermoelectric properties of ternary compounds can be optimized by doping with electroactive impurities. According to Konstantinov et al. [11], a significant increase of the σ and decrease of k_{ph} values of the GeBi_4Te_7 compound can be explained by the intercalation of copper into the space between multilayer packets. Another way to reduce the lattice thermal conductivity in the compounds is the formation of solid solutions with cationic and anionic substitution [12,16].

Herein, we present thermodynamic properties of the layered equilibrium compounds $n\text{GeTe}\cdot m\text{Bi}_2\text{Te}_3$ ($n, m = 1-4$) in the $4\text{GeTe}\cdot\text{Bi}_2\text{Te}_3\text{--Ag}_8\text{GeTe}_6\text{--Te--Bi}_2\text{Te}_3$ part of the Ag–Ge–Bi–Te system below $T = 500$ K, determined by the EMF method described in [17,18]. Information on the thermodynamic properties of the compounds can be used for modeling by CALPHAD methods [19] of the chemical composition of a multinary solid solution based on compounds of homologous series with optimal values of ZT parameter.

2. Experimental Section

The starting materials for synthesis were high-purity elements: Ag, 99.99 wt% (Alfa-Aesar, Germany); Ge, 99.999 wt% (Alfa-Aesar, Germany); Bi, 99.99 wt% (Alfa-Aesar, Germany); S, 99.999 wt% (Alfa-Aesar, Germany); Te, 99.999 wt% (Alfa-Aesar, Germany).

For the EMF measurements [18,20–24], the following electrochemical cells (ECCs) were assembled:



where IE is the inert electrode (graphite), SE is the solid-state electrolyte, PE is the positive (right) electrode. A pure Ag in powder form was used as a negative (left) electrode. As SE we used Ag_2GeS_3 -glass which is the purely Ag^+ ionic conductor material [25–27]. The Ag_2GeS_3 -glass [25,28] was obtained by melt quenching of the corresponding elements from $T = 1200$ K in ice water. The PEs of the ECCs (A) were synthesized by melting of a mixture of the high-purity elements Ag, Ge, Bi, and Te in evacuated quartz glass ampoules at $T = 1070$ K for 5 h. Slowly cooled to room temperature samples were ground into a fine powder with the particle size of ≤ 5 μm and were used as PEs of ECCs. The composition of the pure elements of PEs were calculated based on equations of electrochemical reactions for each of 8 four-phase regions of the $4\text{GeTe}\cdot\text{Bi}_2\text{Te}_3\text{--Ag}_8\text{GeTe}_6\text{--Te--Bi}_2\text{Te}_3$ system. The synthesis of an equilibrium set of phases was performed in the part of the PE that is in contact with SE of ECC at 580 K for 50 h. Ag^+ that shift from the left to the right electrode acted as the nucleation centers of equilibrium compounds in the corresponding phase regions [29].

Components of the ECCs in powder form were pressed at 10^8 Pa through a 2 mm diameter hole arranged in the fluoroplast matrix up to the density $\rho = (0.93 \pm 0.02) \cdot \rho_0$, where ρ_0 is the experimentally determined density of cast samples. Three-fold thermal cycling of ECCs in the temperature between 400 and 500 K was performed to eliminate possible defects due to plastic deformation during sample pressing [30,31]. The heating and cooling rates were $2 \text{ K} \cdot \text{min}^{-1}$.

Experiments were performed in a horizontal resistance furnace, similar to that described in [32,33]. As protective atmosphere, we used a continuously flowing highly purified (99.99 vol%) Ar(g) at 0.12 MPa, with a flow rate of $2 \cdot 10^{-3} \text{ m}^3 \cdot \text{h}^{-1}$ from the left to right electrode of the ECCs. The temperature was maintained with an accuracy of ± 0.5 K. The EMF of the cells were measured by the compensation method with high-resistance universal U7-9 digital voltmeter with input impedance of $> 10^{12} \Omega$. The equilibrium in ECCs at each temperature was achieved within ≤ 3 h. After equilibrium has been attained, the EMF values were constant or their variation did not exceed ± 0.2 mV. The criterion for achieving the equilibrium state is the reproducibility of the E vs T dependences in the heating-cooling cycles. In our previous works [34,35] we have described in details the scheme of ECCs and procedure of the EMF measurements.

3. Results and Discussion

The division of concentration space of the Ag–Ge–Bi–Te system in the part $4\text{GeTe}\cdot\text{Bi}_2\text{Te}_3\text{--Ag}_8\text{GeTe}_6\text{--Te--Bi}_2\text{Te}_3$ (**II**) into 8 four-phase regions is shown in Fig. 1 and corresponding phase regions is listed in Table 1.

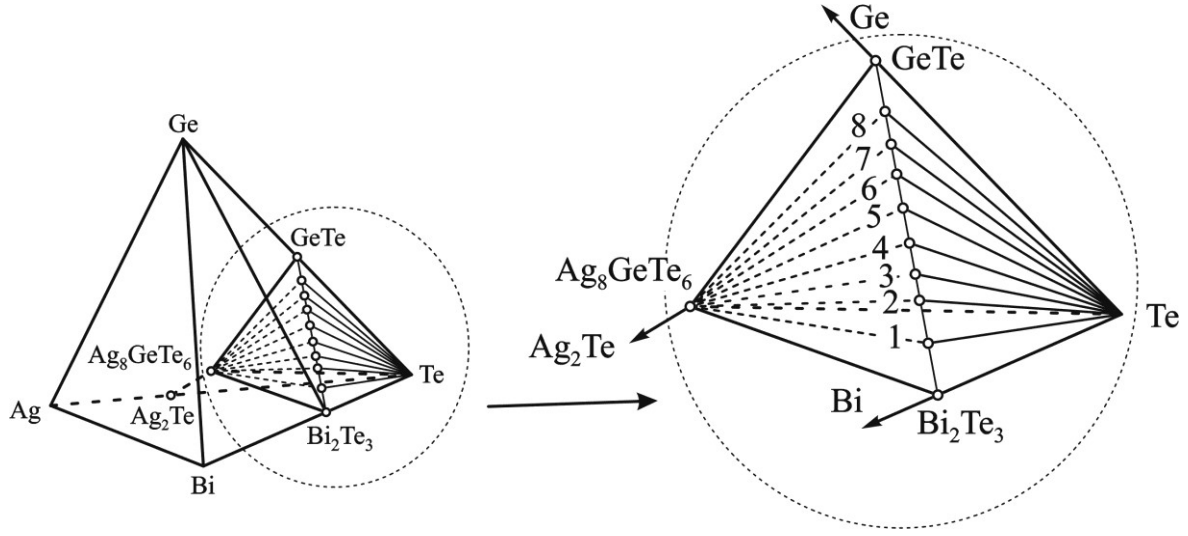


Fig. 1 The phase equilibria of the Ag–Ge–Bi–Te system in the $4\text{GeTe}\cdot\text{Bi}_2\text{Te}_3\text{--Ag}_8\text{GeTe}_6\text{--Te--Bi}_2\text{Te}_3$ part, below $T = 500$ K. 1 is $\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3$, 2 is $\text{GeTe}\cdot 3\text{Bi}_2\text{Te}_3$, 3 is $\text{GeTe}\cdot 2.5\text{Bi}_2\text{Te}_3$, 4 is $\text{GeTe}\cdot 2\text{Bi}_2\text{Te}_3$, 5 is $\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, 6 is $2\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, 7 is $3\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, and 8 is $4\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$

Table 1 Ternary phase regions of the Ag–Ge–Bi–Te system in the $4\text{GeTe}\cdot\text{Bi}_2\text{Te}_3\text{--Ag}_8\text{GeTe}_6\text{--Te--Bi}_2\text{Te}_3$ part and the EMF values of ECCs in corresponding phase regions at 460 K

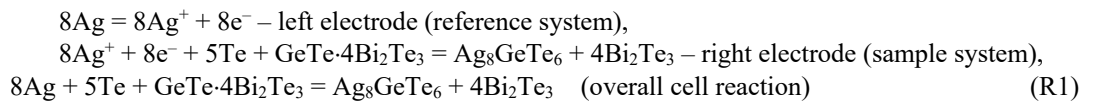
Number of the phase region	Phase region	E / mV
PR(1)	$\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--Bi}_2\text{Te}_3$	237.83
PR(2)	$\text{GeTe}\cdot 3\text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--GeTe}\cdot 4\text{Bi}_2\text{Te}_3$	241.40
PR(3)	$\text{GeTe}\cdot 2.5\text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--GeTe}\cdot 3\text{Bi}_2\text{Te}_3$	245.58
PR(4)	$\text{GeTe}\cdot 2\text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--GeTe}\cdot 2.5\text{Bi}_2\text{Te}_3$	250.18
PR(5)	$\text{GeTe}\cdot \text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--GeTe}\cdot 2\text{Bi}_2\text{Te}_3$	253.81
PR(6)	$2\text{GeTe}\cdot \text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--GeTe}\cdot \text{Bi}_2\text{Te}_3$	263.19
PR(7)	$3\text{GeTe}\cdot \text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--}2\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$	267.64
PR(8)	$4\text{GeTe}\cdot \text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--}3\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$	280.12

The division of (**II**) are based on our investigations of the phase regions boundaries by the EMF as well as the data published in [36–38]. The correctness of the division of the equilibrium concentration space in Fig. 1 is confirmed by the following:

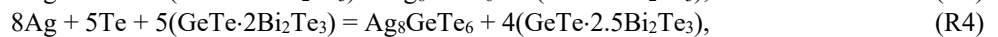
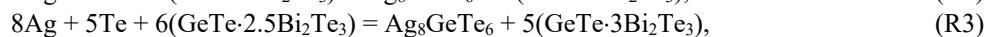
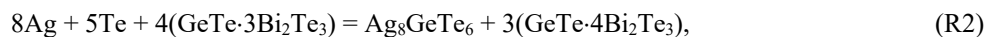
a) the ECCs with positive electrodes of three-phase regions are characterized by different EMF values at constant temperature in the range 445–500K,

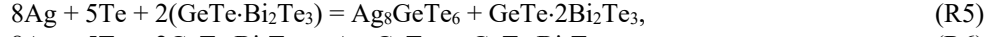
b) the three-phase region that is more distant from the point of silver is characterized by higher EMF value [18], see Table 1.

The established division of (**II**) relative to the position of Ag can be used for the calculation of thermodynamic properties of the ternary compounds, equilibrium in these phase regions. The $\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3\text{--Te--Ag}_8\text{GeTe}_6\text{--Bi}_2\text{Te}_3$ phase region (PR(1)) is the nearest to the point of Ag. For this region the electrochemical process of the synthesis of compounds Ag_8GeTe_6 and Bi_2Te_3 from Ag, Te, and $\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3$ can be expressed by:



In the positive electrodes, the overall cell reactions of ECCs (A) in the PR(2)–(8) can be expressed as:





In accordance with reactions (R1)–(R8), the composition of the PE of the ECCs were determined by the following Ag : Ge : Bi : Te component ratios 4 : 1 : 8 : 18, 4 : 4 : 24 : 45, 2 : 3 : 15 : 28, 4 : 5 : 20 : 40, 4 : 2 : 4 : 13, 2 : 1 : 1 : 5, 4 : 3 : 2 : 11, and 2 : 2 : 1 : 6, respectively.

The measured EMF values (E) of the ECCs at different temperatures (T) are listed in Table 2 and plotted in Fig. 2. The upper and lower limits of the temperature range of the measurements were determined by the linear part of the E vs T dependences that were reproducible in the heating-cooling cycles.

Table 2 The measured values of temperature and EMF of the ECCs from different phase regions of the Ag–Ge–Bi–Te system

T/K	$E_{(\text{R1})}/\text{mV}$	$E_{(\text{R2})}/\text{mV}$	$E_{(\text{R3})}/\text{mV}$	$E_{(\text{R4})}/\text{mV}$	$E_{(\text{R5})}/\text{mV}$	$E_{(\text{R6})}/\text{mV}$	$E_{(\text{R7})}/\text{mV}$	$E_{(\text{R8})}/\text{mV}$
	PR (1)	PR (2)	PR (3)	PR (4)	PR (5)	PR (6)	PR (7)	PR (8)
445.2	234.6	237.8	241.4	245.7	248.9	259.6	263.9	276.6
450.1	235.7	239.1	242.7	247.2	250.6	260.8	265.1	277.7
455.1	236.7	240.2	244.1	248.8	252.2	262.0	266.3	278.9
460.0	237.8	241.4	245.6	250.2	253.8	263.2	267.6	280.1
465.0	238.8	242.6	247.2	251.7	255.4	264.5	268.9	281.3
469.9	239.9	243.9	248.6	253.3	257.1	265.8	270.3	282.6
474.8	240.9	245.2	250.0	254.8	259.0	267.1	271.7	283.8
479.8	242.0	246.4	251.3	256.3	260.5	268.3	272.9	284.7
484.7	243.1	247.6	252.4	258.0	262.1	269.6	274.0	285.8
489.6	244.0	248.8	253.6	259.5	263.6	270.8	275.2	287.1
494.5	245.1	249.9	255.3	261.0	265.2	272.1	276.5	288.3
499.4	246.1	251.0	256.7	262.5	266.8	273.3	277.6	289.3

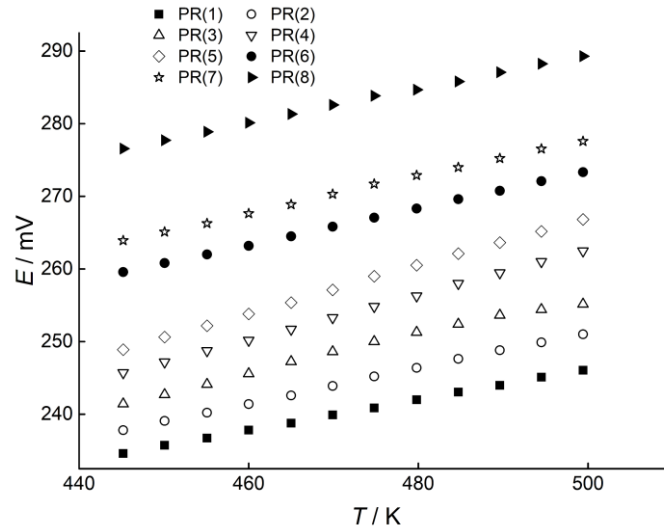


Fig. 2 Temperature dependences of EMF (E) on temperature (T) of the ECCs with PEs of the phase regions PR(1)–(8). The phase regions are defined in Table 1

The treatment of the E vs T dependencies for reactions (R1)–(R8) in the range 446 – 499 K was performed by the least-squares method [39] and can be express as [40]:

$$E = a + bT \pm k \sqrt{\left(\frac{u_E^2}{n} + u_b^2(T - \bar{T})^2\right)}, \quad (1)$$

where n is number of experimental pairs E_i and T_i , $\bar{T} = \frac{\sum T_i}{n}$.

The measured E vs T values for the PR(1)–(8) presented in Table 2 were used to calculate the coefficients (a , b , and k) and dispersions (u_E and u_b) of Eq. 1. The obtained results are listed in Table 3.

Table 3 EMF (mV) vs T (K) relations of the ECCs of type (A) for PR(1)–(8) of the Ag–Ge–Bi–Te system in the range of 446–499 K

Phase region	$E = a + bT \pm k \sqrt{\left(\frac{u_E^2}{n} + u_b^2(T - \bar{T})^2\right)}$
PR(1)	$E_{(R1)} = 140.63 + 211.21 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{2.40 \cdot 10^{-3}}{12} + 6.91 \cdot 10^{-7}(T - 472.34)^2\right)}$
PR(2)	$E_{(R2)} = 128.45 + 245.68 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{7.33 \cdot 10^{-3}}{12} + 2.11 \cdot 10^{-6}(T - 472.34)^2\right)}$
PR(3)	$E_{(R3)} = 116.75 + 280.15 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{3.11 \cdot 10^{-2}}{12} + 8.94 \cdot 10^{-6}(T - 472.34)^2\right)}$
PR(4)	$E_{(R4)} = 107.30 + 310.75 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{4.89 \cdot 10^{-3}}{12} + 1.41 \cdot 10^{-6}(T - 472.34)^2\right)}$
PR(5)	$E_{(R5)} = 101.49 + 331.21 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{1.24 \cdot 10^{-2}}{12} + 3.56 \cdot 10^{-6}(T - 472.34)^2\right)}$
PR(6)	$E_{(R6)} = 146.18 + 254.58 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{2.68 \cdot 10^{-3}}{12} + 7.72 \cdot 10^{-7}(T - 472.34)^2\right)}$
PR(7)	$E_{(R6)} = 149.97 + 255.88 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{1.54 \cdot 10^{-2}}{12} + 4.42 \cdot 10^{-6}(T - 472.34)^2\right)}$
PR(8)	$E_{(R6)} = 171.91 + 235.23 \cdot 10^{-3}T \pm 2.179 \sqrt{\left(\frac{1.23 \cdot 10^{-2}}{12} + 3.53 \cdot 10^{-6}(T - 472.34)^2\right)}$

Thermodynamic properties of the layered compounds were calculated based on overall potential-forming reactions (R1)–(R8), the equations of the temperature dependences of EMF $E_{(R1)}-E_{(R8)}$, and the standard thermodynamic properties of the pure elements and Ag_8GeTe_6 , Bi_2Te_3 compounds [18,41]. The calculations were performed according to the methodology proposed by Osadchii et al. [42].

The Gibbs energies, entropies, and enthalpies of the reactions (R1)–(R8) can be calculated by combining the measured EMF values of each ECCs and the thermodynamic Eqs. (2)–(4):

$$\Delta_r G = -n \cdot F \cdot E, \quad (2)$$

$$\Delta_r H = -n \cdot F \cdot [E - (dE/dT)T], \quad (3)$$

$$\Delta_r S = n \cdot F \cdot (dE/dT), \quad (4)$$

where $n = 8$ is the number of electrons involved in the reactions (R1)–(R8), $F = 96485.33289 \text{ C}\cdot\text{mol}^{-1}$ is Faraday constant, and E in V is the EMF of the ECCs.

The thermodynamic functions of reactions (R1)–(R8) at 298 K were calculated using Eqs. (2)–(4) in the approximation $\left(\frac{\partial \Delta_r H}{\partial T}\right)_p = 0$ and $\left(\frac{\partial \Delta_r S}{\partial T}\right)_p = 0$ [20,22]. The results of the calculations are presented in Table 4.

Table 4 Standard thermodynamic values of the reactions (R1)–(R8) in the ECCs at 298 K^a

Reaction	$-\Delta_r G^\circ$	$-\Delta_r H^\circ$	$\Delta_r S^\circ$
	kJ·mol ⁻¹		J·(mol·K) ⁻¹
(R1)	157.1 ± 0.3	108.6 ± 0.7	163.0 ± 1.4
(R2)	155.7 ± 0.5	99.2 ± 1.2	189.6 ± 2.5
(R3)	154.6 ± 0.9	90.1 ± 2.4	216.2 ± 5.1
(R4)	154.3 ± 0.4	82.8 ± 1.0	239.9 ± 2.0
(R5)	154.5 ± 0.6	78.4 ± 1.5	255.7 ± 3.2
(R6)	171.4 ± 0.3	112.8 ± 0.7	196.5 ± 1.5
(R7)	174.6 ± 0.7	115.8 ± 1.7	197.5 ± 3.5
(R8)	186.8 ± 0.6	132.7 ± 1.5	181.6 ± 3.2

^a Uncertainties for $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ are standard uncertainties

Standard Gibbs energy and entropy of reaction (R1) are related to the Gibbs energy of formation and entropy of compounds and pure elements the following equations:

$$\Delta_{\text{r(R1)}}G^{\circ} = \Delta_{\text{f}}G_{\text{Ag}_8\text{GeTe}_6}^{\circ} + 4\Delta_{\text{f}}G_{\text{Bi}_2\text{Te}_3}^{\circ} - \Delta_{\text{f}}G_{\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3}^{\circ}, \quad (5)$$

$$\Delta_{\text{r(R1)}}H^{\circ} = \Delta_{\text{f}}H_{\text{Ag}_8\text{GeTe}_6}^{\circ} + 4\Delta_{\text{f}}H_{\text{Bi}_2\text{Te}_3}^{\circ} - \Delta_{\text{f}}H_{\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3}^{\circ}, \quad (6)$$

$$\Delta_{\text{r(R1)}}S^{\circ} = S_{\text{Ag}_8\text{GeTe}_6}^{\circ} + 4S_{\text{Bi}_2\text{Te}_3}^{\circ} - 8S_{\text{Ag}}^{\circ} - S_{\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3}^{\circ} - 5S_{\text{Te}}^{\circ}. \quad (7)$$

It follows from Eqs. (5)–(7) that:

$$\Delta_{\text{f}}G_{\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3}^{\circ} = \Delta_{\text{f}}G_{\text{Ag}_8\text{GeTe}_6}^{\circ} + 4\Delta_{\text{f}}G_{\text{Bi}_2\text{Te}_3}^{\circ} - \Delta_{\text{r(R1)}}G^{\circ}, \quad (8)$$

$$\Delta_{\text{f}}H_{\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3}^{\circ} = \Delta_{\text{f}}H_{\text{Ag}_8\text{GeTe}_6}^{\circ} + 4\Delta_{\text{f}}H_{\text{Bi}_2\text{Te}_3}^{\circ} - \Delta_{\text{r(R1)}}H^{\circ}, \quad (9)$$

$$S_{\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3}^{\circ} = S_{\text{Ag}_8\text{GeTe}_6}^{\circ} + 4S_{\text{Bi}_2\text{Te}_3}^{\circ} - 8S_{\text{Ag}}^{\circ} - 5S_{\text{Te}}^{\circ} - \Delta_{\text{r(R1)}}S^{\circ}. \quad (10)$$

For $\text{GeTe}\cdot 3\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot 2.5\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot 2\text{Bi}_2\text{Te}_3$, $\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, $2\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, $3\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$, and $4\text{GeTe}\cdot \text{Bi}_2\text{Te}_3$ compounds the corresponding reactions to determine $\Delta_{\text{f}}G^{\circ}$, $\Delta_{\text{f}}H^{\circ}$, and S° can be written similar to Eqs. (8)–(10) with their respective moles.

By combining Eqs. (8)–(10) using thermodynamic data of the pure elements [41], compounds Ag_8GeTe_6 [18], Bi_2Te_3 [41], and the thermodynamic data listed in Table 4, the standard Gibbs energies, enthalpies of formations, and entropies of the layered tetradymite-like compounds of the homologous series $n\text{GeTe}\cdot m\text{Bi}_2\text{Te}_3$ were calculated. A comparative summary of the calculated values is shown in Fig. 3 and listed in Table 5.

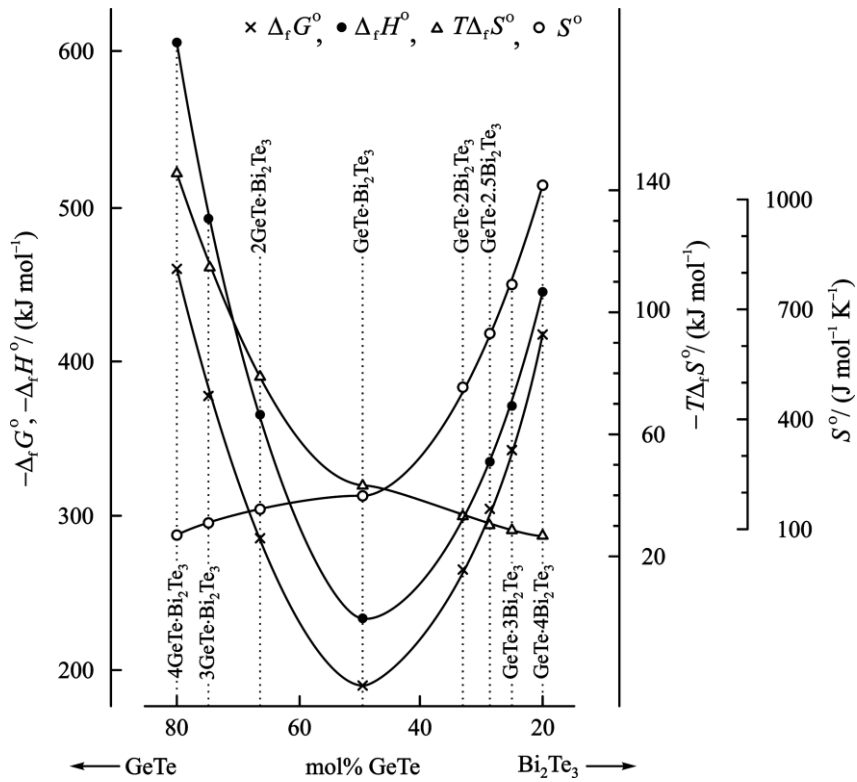


Fig. 3 Concentration changes of thermodynamic functions of the layered tetradymite-like compounds of the $\text{GeTe}\text{--}\text{Bi}_2\text{Te}_3$ system

The temperature dependences of the Gibbs energies of formation of the layered compounds are described as:

$$\Delta_{\text{f}}G_{\text{GeTe}\cdot 4\text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(446.3 \pm 3.0) + (90.8 \pm 0.8) \cdot 10^{-3}T/\text{K}, \quad (11)$$

$$\Delta_{\text{f}}G_{\text{GeTe}\cdot 3\text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(371.2 \pm 5.9) + (96.4 \pm 0.9) \cdot 10^{-3}T/\text{K}, \quad (12)$$

$$\Delta_{\text{f}}G_{\text{GeTe}\cdot 2.5\text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(335.2 \pm 10.5) + (103.7 \pm 1.1) \cdot 10^{-3}T/\text{K}, \quad (13)$$

$$\Delta_{\text{f}}G_{\text{GeTe}\cdot 2\text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(300.7 \pm 12.0) + (115.6 \pm 1.4) \cdot 10^{-3}T/\text{K}, \quad (14)$$

$$\Delta_{\text{f}}G_{\text{GeTe}\cdot \text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(233.8 \pm 12.2) + (147.4 \pm 2.3) \cdot 10^{-3}T/\text{K}, \quad (15)$$

$$\Delta_{\text{f}}G_{2\text{GeTe}\cdot \text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(366.2 \pm 21.6) + (267.6 \pm 6.5) \cdot 10^{-3}T/\text{K}, \quad (16)$$

$$\Delta_{\text{f}}G_{3\text{GeTe}\cdot \text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(495.6 \pm 34.5) + (388.7 \pm 9.3) \cdot 10^{-3}T/\text{K}, \quad (17)$$

$$\Delta_{\text{f}}G_{4\text{GeTe}\cdot \text{Bi}_2\text{Te}_3}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1}) = -(608.2 \pm 48.4) + (493.8 \pm 15.6) \cdot 10^{-3}T/\text{K}. \quad (18)$$

Table 5 Summary of the standard thermodynamic properties of layered tetradymite-like compounds of the GeTe–Bi₂Te₃ system at 298 K determined in this work

Phase	$-\Delta_f G^\circ$	$-\Delta_f H^\circ$	$-T\Delta_f S^\circ$	S°
	kJ·mol ⁻¹			J·mol ⁻¹ ·K ⁻¹
GeTe·4Bi ₂ Te ₃	419.2 ± 2.8	446.3 ± 3.0	27.1 ± 0.2	1037.6 ± 29.4
GeTe·3Bi ₂ Te ₃	342.5 ± 5.6	371.2 ± 5.9	28.7 ± 0.3	770.0 ± 22.1
GeTe·2.5Bi ₂ Te ₃	304.3 ± 10.1	335.2 ± 10.5	30.9 ± 0.4	631.8 ± 18.5
GeTe·2Bi ₂ Te ₃	266.3 ± 11.4	300.7 ± 12.0	34.4 ± 0.6	488.9 ± 14.6
GeTe·Bi ₂ Te ₃	189.9 ± 11.7	233.8 ± 12.2	43.9 ± 0.7	195.1 ± 7.1
2GeTe·Bi ₂ Te ₃	286.5 ± 18.2	366.2 ± 21.6	79.7 ± 1.5	155.6 ± 4.8
3GeTe·Bi ₂ Te ₃	379.8 ± 32.5	495.6 ± 34.5	115.8 ± 3.1	115.0 ± 6.9
4GeTe·Bi ₂ Te ₃	461.0 ± 39.2	608.2 ± 48.4	147.2 ± 5.0	90.5 ± 8.1

As can be seen in Fig. 3, the thermodynamic functions of the layered compounds are connected by smooth lines with an inflection at the point of 50 mol% GeTe, that corresponds to the composition of the GeTe·Bi₂Te₃. The depicted dependences correlate well with the results of studies of the crystal structure of the compounds. Compounds of the homologous series are divided into two groups according to the method of forming from slabs the crystal lattice period along the *c* axis [2]. For GeTe-rich compounds, the parameter *c* determines the number of slabs with the same number of layers. The layers differ in the way they fill octahedral cavities with Ge and Bi cations. For Bi₂Te₃-rich compounds, the parameter *c* is determined by a combination of 5- and 7-layer packets, which also differ in the way cations fill octahedral voids. According to Fig. 3, established in [2] compound of the formulaic composition 2GeTe·5Bi₂Te₃ is a high-temperature modification of the GeTe·2.5Bi₂Te₃ compound with a double lattice parameter *c*.

4. Conclusions

The synthesis of the equilibrium set of phases for electrochemical cells of each of the eight phase regions 4GeTe·Bi₂Te₃–Ag₈GeTe₆–Te–Bi₂Te₃ was carried out by melting of pure elements at 1070 K with subsequent annealing of the fine mixture at 550 K for 250 h. The ratios of the components were established according to equations of the overall potential-forming reactions. The equilibrium set of phases determine the value of the EMF of the cell at *constant temperature*. Based on the EMF vs *T* dependences of ECCs, the standard values of Gibbs energies, enthalpies of formation and entropies of compounds of homologous series *n*GeTe·*m*Bi₂Te₃ (*n*, *m* = 1–4) were calculated for the first time. The polymorphism of the compound GeTe·2.5Bi₂Te₃ was established. The 2GeTe·5Bi₂Te₃ compound of the homologous series is actually a high-temperature modification of the GeTe·2.5Bi₂Te₃ phase with a double lattice parameter *c*. The experimental thermodynamic data of the layered compounds determined in this work can be used in thermodynamic modeling of the Ag–Ge–Bi–Te system and contribute to the search for new materials with high *ZT* values in different temperature ranges.

Acknowledgements

This research was supported by the national projects of the Ministry of Education and Science of Ukraine: “Synthesis, physico-chemical and thermodynamic properties of nano sized and nanostructured materials for electrochemical systems” (No. 0120U102184) and “Scientific and experimental bases of manufacturing composite oxide, chalcogenide materials with prolonged service life”. This work was partly supported by the Academy of Finland project (Decision number 311537), as part of the activities of the Johan Gadolin Process Chemistry Centre at Åbo Akademi University.

Conflict of Interest

The authors declare that they have no conflict of interest.

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