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Experimental investigation and thermodynamic assessment of phase equilibria in the GaTe–$AgGa_5Te_8$–Te system below 600 K

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Equilibrium *T*–*x* space of the Ag–Ga–Te system in the GaTe–$AgGa_5Te_8$–Te part was divided below 600 K into three-phase regions Ga_2Te_5–$AgGa_5Te_8$–Te, Ga_2Te_3–$AgGa_5Te_8$–Ga_2Te_5, Ga_7Te_{10}–$AgGa_5Te_8$–Ga_2Te_3, Ga_3Te_4–$AgGa_5Te_8$–Ga_7Te_{10}, and GaTe–$AgGa_5Te_8$–Ga_3Te_4 by the electromotive force (EMF) method. To accomplish accurate experimental data, the following electrochemical cells (ECs) were assembled: (−) IE | NE | SSE | R{Ag^+} | PE | IE (+), where IE is the inert electrode (graphite powder), NE is the negative electrode (silver powder), SSE is the solid-state electrolyte (glassy Ag_3GeS_3Br), PE is the positive electrode, R{Ag^+} is the region of PE that contact with SSE. At the stage of cell preparation, PE is a nonequilibrium phase mixture of the well-mixed powdered compounds Ag_2Te, GaTe, Ga_2Te_3, and tellurium, taken in ratios corresponding to two or three different points in each of the mentioned regions. The equilibrium set of phases was formed in the R{Ag^+} region at 600 K for 48 h with the participation of the Ag^+ ions. Silver cations, displaced for thermodynamic reasons from the NE to the PE of the ECs, acted as catalysts, i.e., small nucleation centers of equilibrium phases. Thus, the same electrochemical cell was used both for the synthesis of an equilibrium set of phases in the R{Ag^+} region and subsequent EMF measurements. The spatial position of the established three-phase regions relative to the silver point was used to assign the overall potential-determining reactions of synthesis of the ternary $AgGa_5Te_8$ and binary Ga_2Te_5, Ga_7Te_{10}, Ga_3Te_4 compounds. For the first time, the values of the standard thermodynamic functions (Gibbs energies, enthalpies, and entropies) of these compounds were determined based on the temperature dependencies of the EMF of the ECs.

Keywords: Ag-containing compounds, Thermoelectric materials; Thermodynamic properties, Phase equilibria, Gibbs energy, EMF method.

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Introduction

Phase equilibria in the Ag–Ga–Te system have been investigated by several authors [1–6], using different experimental methods. In particular, Guittard et al. [1] divided the phase space of the Ag–Ga–Te system in the temperature range of 273–1000 K into 9 regions with the participation of binary and ternary compounds. In the binary systems Ag–Te, Ag–Ga, and Ga–Te, the temperature ranges for existence of the compounds Ag_2Te, $Ag_{1.9}Te$, Ag_5Te_3; phases of variable composition ζ, δ; compounds GaTe, Ga_2Te_3, Ga_2Te_5, have been established. Devision of the concentration space of the Ag–Ga–Te system was carried out with the participation of the mentioned binary compounds, phases of mixed composition, and ternary compounds of the quasi-binary system Ag_2Te–Ga_2Te_3: Ag_9GaTe_6, $AgGaTe_2$, and a phase $Ag_xGa_{(4-x)/3}\square_{(2-2x)/3}Te_2$ which is a solid solution for $0.63 < x < 0.75$ [3].

In Ref. [2] Deiseroth et al. synthesized the Ga_7Te_{10}

compound at 1020 K and determined its crystal structure. According to Ref. [4], there are four intermediate compounds in the Ga–Te system. The GaTe and Ga_2Te_3 compounds melt congruently at 1108 K and 1071 K, respectively; Ga_3Te_4 decomposes at 1057 K by the peritectic reaction on liquid *L* and compound Ga_2Te_3; high-temperature modification of the Ga_2Te_5 forms by a eutectoid reaction at 681 K and decomposes by peritectic scheme at 757 K.

The Ag_2Te–Ga_2Te_3 cross-section of the Ag–Ga–Te system is characterized by three intermediate compounds: Ag_9GaTe_6, $AgGaTe_2$, and $AgGa_5Te_8$ [3,5,6]. According to Ref. [5], the orthorhombic compound $AgGa_5Te_8$ was obtained by cooling the melt of the calculated amounts of Ag_2Te, Ga_2Te_3, and Te to 873 K, followed by annealing for 1 week. The minimum temperature of the of existence of this compound in the equilibrium *T*–*x* space of the Ag–Ga–Te system is unknown. Based on the a dimensionless figure of merit parameter $ZT=(S^2\sigma)T/k$ (where *S* is the Seebeck coefficient, σ is the electrical conductivity, *k* is the thermal conductivity, and *T* is the absolute temperature), ternary compounds of the Ag–Ga–Te system belong to class of the thermoelectric materials [3,5–8].

The effect of replacing part of the gallium cations of the compound *p*-Ag_9GaTe_6 according to the scheme $Ag_9Ga_{1-\delta}M_\delta Te_6$ (*M* = Cd, Zn, Mg, Nb; δ = 0.05) on the *ZT* values is given in Ref. [6]. In the case of Cd doping, the thermoelectric figure of merit parameter was achieved $ZT \approx 0.6$ at 600 K. Such method of increasing the *ZT* value is ineffective in the case of a thermodynamically unbalanced state of the doping component in the crystal lattice of the compound. The action of such external factors as changes in temperature, pressure, radiation, etc. will contribute to the migration of impurities at the grain boundary, which will lead to a decrease in the *ZT* value of the sample over time. It is possible to avoid a decrease in the *ZT* value during the operation of a doped thermocouple by producing it in the form of an equilibrium solid solution based on a quaternary compound. As an example, for doping of the Ag_9GaTe_6, $AgGaTe_2$, and $AgGa_5Te_8$, it is possible to use quaternary compounds of the Ag_2Te–Ga_2Te_3–AgBr region. This region is part of the Ag–Ga–Te–AgBr system, where the formation of quaternary compounds $Ag_3Ga_{10}Te_{16}Br$, $Ag_3Ga_2Te_4Br$, and $Ag_{27}Ga_2Te_{12}Br_9$ is possible at the intersection points of the cross-sections $AgGa_5Te_8$–AgBr, $AgGaTe_2$–AgBr, Ag_9GaTe_6–AgBr with the tie-line Ga_2Te_3–Ag_3TeBr. There are no any previous reports on quaternary compounds of mentioned composition. The thermodynamic conditions for the formation of quaternary phases likely correspond to the temperature values $T < 600$ K, where there are kinetic obstacles to such a process. Kinetic obstacles to the synthesis of phases from pure substances and binary compounds can be overcome with the participation of a catalyst – Ag^+ ions, as small centers of nucleation of equilibrium phases [9,10]. In order to establish the conditions for the existence of quaternary compounds in the Ag_2Te–Ga_2Te_3–AgBr system, information on compounds in the GaTe–Te part of the Ga–Te system at $T < 600$ K is required.

The purpose of this work was to establish the phase equilibria of the GaTe–$AgGa_5Te_8$–Te system at $T < 600$ K and to determine the standard thermodynamic properties of compounds by the electromotive force (EMF) method.

I. Experimental

The high-purity substances Ag (>99.9 wt.%) and Ga, Te (>99.99 wt.%) were used to synthesize the binary and ternary compounds. Evacuated melts of the Ag_2Te, GaTe, and Ga_2Te_3 compounds, cooled to room temperature, were crushed to a particle size of $\sim 1\cdot 10^{-6}$ m for preparation of the positive electrodes (PE) of electrochemical cells (ECs). Melts of the Ga_7Te_{10}, $AgGaTe_2$, and $AgGa_5Te_8$ compounds cooled to a temperature of 630 K were annealed for 2 weeks, followed by cooling to room temperature with the furnace turned off. The phase composition of the synthesized compounds was analyzed by an X-ray diffraction (XRD) technique. The STOE STADI P diffractometer equipped with a linear position-sensitive detector PSD, in a Guinier geometry (transmission mode, Cu$K\alpha_1$ radiation, a bent Ge(111) monochromator, and $2\theta/\omega$ scan mode) was used for these investigations. The following software programs STOE WinXPOW [11], PowderCell [12], FullProf [13], and databases [14,15] were applied to analyze the obtained results.

The modified EMF method [16] was used both to establish the phase equilibria in the GaTe–$AgGa_5Te_8$–Te region below 600 K and to determine the thermodynamic parameters of compounds. For these measurements, a certain number of ECs were assembled:

$$(-)\ \mathrm{IE}\ |\ \mathrm{NE}\ |\ \mathrm{SSE}\ |\ \mathrm{R\{Ag^+\}}\ |\ \mathrm{PE}\ |\ \mathrm{IE}\ (+),$$

where IE is the inert electrode (graphite powder), NE is the negative electrode (silver powder), SSE is the solid-state electrolyte (glassy Ag_3GeS_3Br), R{Ag^+} is the region of PE that contacts with SSE. At the stage of cell preparation, PE is the nonequilibrium phase mixture of the well-mixed powdered binary compounds Ag_2Te, GaTe, Ga_2Te_3, and pure substance tellurium. Compositions of these mixtures covered the entire concentration space of the GaTe–$AgGa_5Te_8$–Te system. An equilibrium set of phases was formed in the R{Ag^+} region at 600 K for 48 h. The Ag^+ ions, displaced for thermodynamic reasons from the NE to the PE electrodes of the ECs, acted as catalysts, i.e., small nucleation centers of equilibrium phases [9,10].

The experiments were performed in a resistance furnace described in Ref. [17]. A fluoroplastic base with a hole with a diameter of 2 mm was used to assemble the ECs. The powder components of ECs were pressed at pressure 10^8 Pa into the hole under a load of (2.0±0.1) tons to a density of $\rho = (0.93\pm0.02)\cdot\rho_0$, where ρ_0 is the experimentally determined density of cast samples. The assembled cells were placed in a quartz tube with nozzles for the purging of argon gas. The argon gas had a direction from the NE to PE of ECs at the rate of $(10.0\pm0.2)\ \mathrm{cm^3\cdot min^{-1}}$. The temperature of ECs was maintained by an electronic thermostat with ±0.5 K accuracy. The EMF (*E*) values of the cells (accuracy ±0.3 mV) were determined by a Picotest M3500A digital voltmeter with an input impedance of $>10^{12}$ Ohms. The reproducibility of the EMF versus temperature dependences ($E(T)$) of ECs in heating-cooling cycles was a criterion for completing the formation of the equilibrium set of phases in the R{Ag^+} region.

II. Results and discussion

The $AgGa_5Te_8$ compound was not obtained by cooling the melt to 630 K followed by annealing for 2 weeks. The diffraction pattern of powder sample is shown in Fig. 1.

The presence of the $Ag_xGa_{0.67}Te$ phase (structure type (ST) ZnS, space group (SG) $F\text{–}43m$) and minor impurities of non-identified phase have been established by the XRD method. The refined unit-cell parameter $a = 0.59786(5)$ nm is greater than $a \sim 0.587 \div 0.590$ nm for $Ga_{0.67}Te$, thus indicated the formation of solid solution. Such a metastable, for kinetic reasons, combination of the mentioned phases was confirmed by an attempt to implement the reaction $AgGaTe_2 + 2Ga_2Te_3 = AgGa_5Te_8$. For this reason, a well-mixed mixture of the $AgGaTe_2$ and $2Ga_2Te_3$ compounds was evacuated, kept for 2 weeks at 630 K and cooled to room temperature. According to the XRD results, the orthorhombic $AgGa_5Te_8$ compound also was not obtained, Fig. 2. The sample contained characteristic peaks of the phases $Ag_xGa_{0.67}Te$ (ST ZnS, SG $F\text{–}43m$), $AgGaTe_2$ (ST $CuFeS_2$, SG $I\text{–}42d$), and the pure Te (ST Se, SG $P3_121$).

Thus, results of the XRD shown that the orthorhombic $AgGa_5Te_8$ compound decomposes at a certain value of the temperature in the range of 630–873 K. The existence of the $AgGa_5Te_8$ compounds in two temperature ranges was also established by the results of triangulation of the concentration space of the GaTe–$AgGa_5Te_8$–Te system by the EMF method and calculation of the thermodynamic properties of compounds. Other examples of the existence of silver-based ternary and quaternary compounds in two temperature ranges are presented in Ref. [18–21].

The division of the concentration space of the Ag–

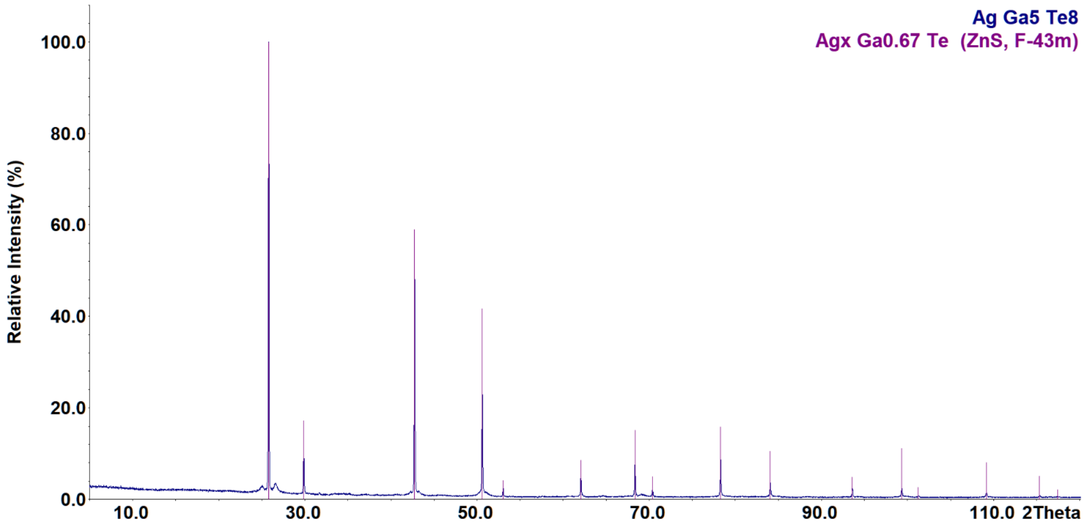

Fig. 1. X-ray powder diffraction pattern of the sample with nominal composition $AgGa_5Te_8$, obtained by cooling the melt to 630 K. Compositions of the sample and identified phase (with structure type and space group indicated) are shown in the upper right corner.

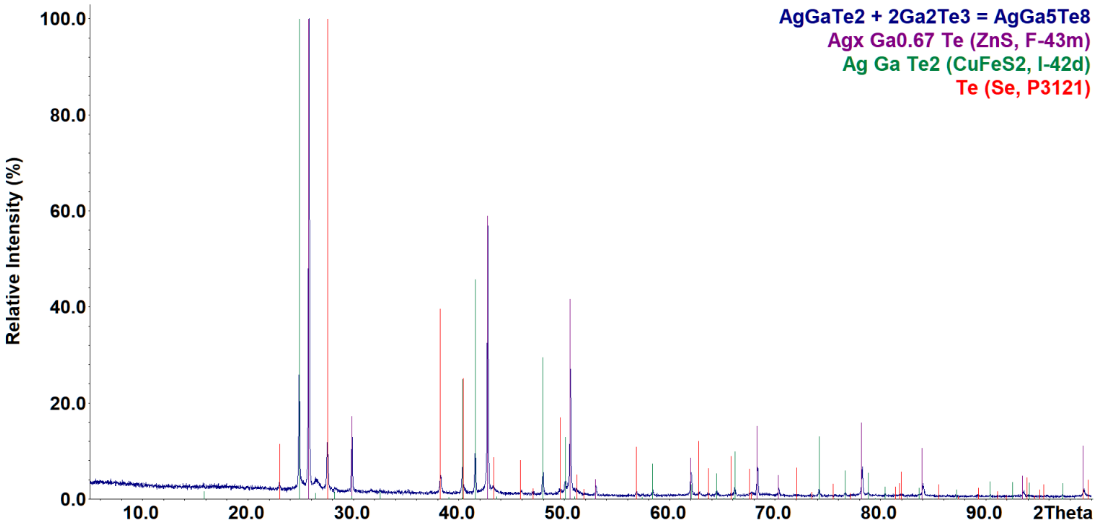

Fig. 2. X-ray powder diffraction pattern of the sample with nominal composition $AgGa_5Te_8$, obtained by solid-state synthesis mixture of the $AgGaTe_2$ and $2Ga_2Te_3$ compounds. Compositions of the sample and identified phases (with structure type and space group indicated) are shown in the upper right corner.

Ga–Te system in the GaTe–$AgGa_5Te_8$–Te part below 600 K into separate three-phase regions is shown in Fig. 3. The following basic rules of the EMF method [22–25] were used for this triangulation:

1) within a specific phase region, the EMF value of the cell does not depend on the phase composition of the PE;

2) ECs with PE of different phase regions are characterized by different EMF values at $T = \text{const}$, Table. 1;

3) the three-phase region further away from the figurative point of Ag is characterized by a higher EMF value at a specific temperature.

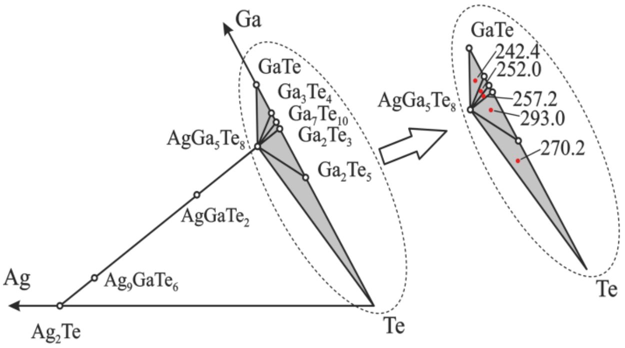

Fig. 3. Division of the concentration space of the GaTe–$AgGa_5Te_8$–Te system at T<600 K. Red dots indicate compositions of the PE of ECs and EMF (mV) values of the ECs at 400.4 K.

Table.

Measured values of temperature (T) and EMF (E) of the ECs with PE of different phase regions at pressure P=10^5 Pa. Standard *uncertainties u* are $u(T)$ = 0.5 K, $u(P)$ = 10^4 Pa, and $u(E)$ = 0.3 mV.

T/K	Phase regions		T/K	Phase regions	
	(I)	(II)		(III)	(IV)
	$E_{(I)}$/mV	$E_{(II)}$/ mV		$E_{(III)}$/ mV	$E_{(IV)}$/ mV
400.4	270.2	293.0	350.3	251.5	246.8
405.4	271.0	293.5	355.3	252.0	247.3
410.4	271.7	294.1	360.3	252.7	247.8
415.4	272.4	294.7	365.4	253.3	248.4
420.3	273.2	295.2	370.4	254.0	249.0
425.3	274.0	295.9	375.4	254.6	249.5
430.3	274.7	296.5	380.4	255.2	250.0
435.2	275.5	297.2	385.4	255.8	250.5
440.2	276.2	297.7	390.4	256.3	251.0
445.2	277.1	298.3	395.4	256.8	251.5
450.1	277.7	298.7	400.4	257.2	252.0
455.1	278.5	299.3	405.4	257.7	252.5

The spatial position of three-phase regions Ga_2Te_5–$AgGa_5Te_8$–Te (I), Ga_2Te_3–$AgGa_5Te_8$–Ga_2Te_5 (II), Ga_7Te_{10}–$AgGa_5Te_8$–Ga_2Te_3 (III), and Ga_3Te_4–$AgGa_5Te_8$–Ga_7Te_{10} (IV) relative to the silver point was used to establish the overall potential-determining reactions:

$$2Ag + 5Ga_2Te_5 = 2AgGa_5Te_8 + 9Te, \qquad (R1)$$

$$4Ag + 9Ga_2Te_3 + Ga_2Te_5 = 4AgGa_5Te_8, \qquad (R2)$$

$$Ag + 6Ga_2Te_3 = AgGa_5Te_8 + Ga_7Te_{10}, \qquad (R3)$$

$$Ag + 2Ga_7Te_{10} = AgGa_5Te_8 + 3Ga_3Te_4. \qquad (R4)$$

Reactions (R1)–(R4) were carried out in the PE of ECs, the phase mixtures correspond to phase regions (I)–(IV), respectively. According to reactions (R1)–(R4), the ratios of binary compounds and pure tellurium for the assemble the PE of ECs were established. In particular, the compounds $AgGa_5Te_8$, Ga_2Te_5, Ga_7Te_{10}, and Ga_3Te_4 are present in the PE compositions in the following ratios of mixtures of the binary compounds and the simple substance Te: $0.5Ag_2Te + 2.5Ga_2Te_3$, $Ga_2Te_3 + 2Te$, $GaTe + 3Ga_2Te_3$, and $GaTe + Ga_2Te_3$, respectively.

Processing of the E versus T experimental dependences was performed by the least squares method [26,27] and presented in the form of Eq. (1):

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

where a and b are coefficients of linear equation, k_{St} is the Student's parameter [28], n is the number of experimental pairs E_i and T_i, u_E^2 and u_b^2 are the statistical dispersions of the E and b quantities, respectively.

Listed in the Table 1 the experimental values of E and T were used to calculate the coefficients and statistical dispersions of Eq. (1) in the phase regions (I)–(IV). The results of calculations are listed in the Table 2.

The Gibbs energies ($\Delta_r G$), enthalpies ($\Delta_r H$), and entropies ($\Delta_r S$) of the reactions (R1)–(R4) were calculated by the following thermodynamic equations:

$$\Delta_r G = -n\,\mathrm{F}\,E, \qquad (2)$$

$$\Delta_r H = -n\,\mathrm{F}\,[E - (dE/dT)\,T], \qquad (3)$$

$$\Delta_r S = n\,\mathrm{F}\,(dE/dT). \qquad (4)$$

where n is the number of electrons involved in the reactions (R1)–(R4), F is the Faraday's constant, and E is the EMF of the ECs.

The values of the thermodynamic functions of reactions (R1)–(R4) in the standard state (T = 298 K and P = 10^5 Pa) were calculated according to Eqs. (2)–(4) and are listed in the Table 3.

The Gibbs energies of reactions (R1) and (R2) are related to the Gibbs energies of compounds by Eqs. (5) and (6):

$$\Delta_{r(R1)}G^\circ = 2\Delta_f G^\circ_{AgGa_5Te_8} - 5\Delta_f G^\circ_{Ga_2Te_5}, \qquad (5)$$

$$\Delta_{r(R2)}G^\circ = 4\Delta_f G^\circ_{AgGa_5Te_8} - 9\Delta_f G^\circ_{Ga_2Te_3} - \Delta_f G^\circ_{Ga_2Te_5}. \quad (6)$$

By solving the system of equations (5) and (6) we obtained:

$$\Delta_f G^\circ_{Ga_2Te_5} = \frac{\Delta_{r(R2)}G^\circ - 2\Delta_{r(R1)}G^\circ}{9} + \Delta_f G^\circ_{Ga_2Te_3}. \qquad (7)$$

Equations for determining the enthalpy of formation and entropy of the Ga_2Te_5 compound were obtained in a

Table 2.

The coefficients and statistical dispersions of E versus T dependencies of the ECs.

Phase regions	$E = a + bT \pm k_{St}\sqrt{\left(\frac{u_E^2}{n} + u_b^2(T - \bar{T})^2\right)}$
(I)	$E = 209.34 + 151.97 \times 10^{-3}T \pm 2.179\sqrt{\left(\frac{2.37 \times 10^{-3}}{12} + 6.72 \times 10^{-7}(T - 427.78)^2\right)}$
(II)	$E = 245.88 + 117.57 \times 10^{-3}T \pm 2.179\sqrt{\left(\frac{6.63 \times 10^{-3}}{12} + 1.88 \times 10^{-6}(T - 427.78)^2\right)}$
(III)	$E = 211.32 + 114.97 \times 10^{-3}T \pm 2.179\sqrt{\left(\frac{2.00 \times 10^{-2}}{12} + 5.56 \times 10^{-6}(T - 377.88)^2\right)}$
(IV)	$E = 210.42 + 103.93 \times 10^{-3}T \pm 2.179\sqrt{\left(\frac{2.54 \times 10^{-3}}{12} + 7.07 \times 10^{-7}(T - 377.88)^2\right)}$

Table 3.

The values of standard thermodynamic properties of the reactions (R1)–(R4). Uncertainties for $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ are standard uncertainties.

Reactions	$-\Delta_r G^\circ$	$-\Delta_r H^\circ$	$\Delta_r S^\circ$
	kJ mol^{-1}		J (mol K)$^{-1}$
(R1)	49.14 ± 0.05	40.40 ± 0.15	29.33 ± 0.34
(R2)	108.42 ± 0.15	94.90 ± 0.49	45.38 ± 1.15
(R3)	23.70 ± 0.04	20.39 ± 0.19	11.09 ± 0.50
(R4)	23.29 ± 0.04	20.30 ± 0.15	10.03 ± 0.35

similar way:

$$\Delta_f H^\circ_{Ga_2Te_5} = \frac{\Delta_{r(R2)}H^\circ - 2\Delta_{r(R1)}H^\circ}{9} + \Delta_f H^\circ_{Ga_2Te_3}, \qquad (8)$$

$$S^\circ_{Ga_2Te_5} = \frac{\Delta_{r(R2)}S^\circ - 2\Delta_{r(R1)}S^\circ}{9} + 2S^\circ_{Te} + S^\circ_{Ga_2Te_3}. \qquad (9)$$

The corresponding reactions to determine the standard thermodynamic properties $\Delta_f G^\circ$, $\Delta_f H^\circ$, and S° of the AgGa$_5$Te$_8$, Ga$_7$Te$_{10}$, and Ga$_3$Te$_4$ compounds were written in a similar way using reactions (R2)–(R4) with the corresponding stoichiometric numbers.

For the first time, the standard thermodynamic quantities for compounds of the GaTe–AgGa$_5$Te$_8$–Te system were determined using Eqs. (7)–(9) and thermodynamic data of pure substances (Ag, Ga, Te) and the binary compound Ga$_2$Te$_3$ [29]. The results of calculations are listed in the Table. 4.

The temperature dependences of the Gibbs energies of the formation of compounds of the GaTe–AgGa$_5$Te$_8$–Te system are described by Eqs. (10)–(13):

$$\Delta_f G_{Ga_2Te_5}/(\text{kJ mol}^{-1}) = -(276.5 \pm 4.6) + (18.1 \pm 0.3) \times 10^{-3}T/\text{K}, \qquad (10)$$

$$\Delta_f G_{AgGa_5Te_8}/(\text{kJ mol}^{-1}) = -(711.3 \pm 8.8) + (30.9 \pm 0.4) \times 10^{-3}T/\text{K}, \qquad (11)$$

$$\Delta_f G_{Ga_7Te_{10}}/(\text{kJ mol}^{-1}) = -(958.4 \pm 11.7) + (58.6 \pm 0.7) \times 10^{-3}T/\text{K}, \qquad (12)$$

$$\Delta_f G_{Ga_3Te_4}/(\text{kJ mol}^{-1}) = -(408.6 \pm 7.9) + (25.4 \pm 0.4) \times 10^{-3}T/\text{K}. \qquad (13)$$

The obtained $\Delta_f G^\circ_{Ga_2Te_5}$, $\Delta_f G^\circ_{AgGa_5Te_8}$, $\Delta_f G^\circ_{Ga_7Te_{10}}$, and $\Delta_f G^\circ_{Ga_3Te_4}$ values do not deny the hypothetical reactions of the synthesis of compounds under standard conditions:

$$Ga_2Te_3 + 2Te = Ga_2Te_5, \qquad (R5)$$

$$Ag_2Te + 5Ga_2Te_3 = 2AgGa_5Te_8, \qquad (R6)$$

$$GaTe + 3Ga_2Te_3 = Ga_7Te_{10}, \qquad (R7)$$

$$GaTe + Ga_2Te_3 = Ga_3Te_4. \qquad (R8)$$

The calculated Gibbs energies values of the reaction (R5)–(R8) $\Delta_{r(R5)}G^\circ = -1.2$ kJ mol^{-1}, $\Delta_{r(R6)}G^\circ = -19.6$ kJ mol^{-1}, $\Delta_{r(R7)}G^\circ = -9.3$ kJ mol^{-1}, and $\Delta_{r(R8)}G^\circ = -9.2$ kJ mol^{-1} are negative. Thus,

Table 4.
The values of standard (T=298 K and P=10^5 Pa) thermodynamic properties of compounds of the GaTe–$AgGa_5Te_8$–Te system. Uncertainties for $\Delta_f G^\circ$, $\Delta_f H^\circ$, and S° are standard uncertainties.

Phases	$-\Delta_f G^\circ$	$-\Delta_f H^\circ$	S°	[Ref.]
	kJ mol^{-1}		J (mol K)$^{-1}$	
Ag	0	0	42.677	[29]
Ga	0	0	40.828	[29]
Te	0	0	49.497	[29]
Ga_2Te_3	269.892	274.889	213.384	[29]
Ga_2Te_5	271.1 ± 3.4	276.5 ± 4.6	310.9 ± 4.5	Present study
$AgGa_5Te_8$	702.1 ± 7.8	711.3 ± 8.8	611.9 ± 7.6	Present study
Ga_7Te_{10}	940.9 ± 10.9	958.4 ± 11.7	722.2 ± 8.8	Present study
Ga_3Te_4	401.0 ± 5.9	408.6 ± 7.9	295.1 ± 4.7	Present study

presented in the Table 4 values of the thermodynamic functions of compounds do not contradict the thermodynamics laws.

Conclusions

The phase space of the GaTe–$AgGa_5Te_8$–Te system below 600 K is characterized by the following compounds: GaTe, Ga_3Te_4, Ga_7Te_{10}, Ga_2Te_3, Ga_2Te_5, and $AgGa_5Te_8$. The two-phase tie-lines connecting the $AgGa_5Te_8$ with binary compounds and tellurium divide the GaTe–$AgGa_5Te_8$–Te system into five separate three-phase regions. Based on the division, the compositions of the positive electrodes of the electrochemical cells were established. For the first time, the values of the standard thermodynamic functions (Gibbs energies, enthalpies, and entropies) of the $AgGa_5Te_8$, Ga_2Te_5, Ga_7Te_{10}, and Ga_3Te_4 compounds were determined by the EMF method. The obtained values of the Gibbs energies of the formation of compounds do not contradict the thermodynamics laws. Based on the results of X-ray phase analysis and EMF measurements of the electrochemical cells, it was concluded that the $AgGa_5Te_8$ compound exists in two temperature ranges.

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Експериментальні дослідження та термодинамічна оцінка фазових рівноваг системи GaTe–$AgGa_5Te_8$–Te нижче 600 К

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Методом ЕРС здійснено триангуляцію рівноважного за T<600 К $T–x$ простору системи Ag–Ga–Te в частині GaTe–$AgGa_5Te_8$–Te на трифазні ділянки Ga_2Te_5–$AgGa_5Te_8$–Te, Ga_2Te_3–$AgGa_5Te_8$–Ga_2Te_5, Ga_7Te_{10}–$AgGa_5Te_8$–Ga_2Te_3, Ga_3Te_4–$AgGa_5Te_8$–Ga_7Te_{10} та GaTe–$AgGa_5Te_8$–Ga_3Te_4. Для отримання достовірних експериментальних даних виготовляли електрохімічні комірки (ЕХК) структури: (−) IE | NE | SSE | R{Ag^+} | PE | IE (+), де IE – інертний електрод (графіт); NE – негативний електрод ЕХК; SSE – твердий електроліт (скло Ag_3GeS_3Br); PE – позитивний електрод ЕХК виготовлений як нерівноважна фазова суміш добре перемішаних, дрібнодисперсних подвійних сполук Ag_2Te, GaTe, Ga_2Te_3 та Te, взятих у співвідношеннях, що відповідають двом або трьом різним точкам кожної із зазначених ділянок; R{Ag^+} – частина PE, що контактує з SSE. Рівноважний набір фаз формувався в R{Ag^+} при 600 К впродовж 48 год. за участі каталізатора Ag^+. Йони аргентуму Ag^+, що змістилися за термодинамічними причинами з лівого до правого електрода ЕХК, виконували роль малих центрів зародження рівноважних фаз. Таким чином, одна і таж електрохімічна комірка використовувалась як для синтезу рівноважного набору фаз в області R{Ag^+} так і наступних ЕРС вимірювань. Просторове положення встановлених ділянок відносно точки аргентуму використано для з'ясування рівнянь потенціаловизначаючих реакцій синтезу потрійної $AgGa_5Te_8$ та подвійних Ga_2Te_5, Ga_7Te_{10}, Ga_3Te_4 сполук. За температурними залежностями ЕРС комірок вперше розраховано значення термодинамічних функцій зазначених сполук в стандартному стані.

Ключові слова: аргентумвмісні сполуки, термоелектричні матеріали, термодинамічні властивості, фазові рівноваги, енергія Гіббса, метод ЕРС.