

CHEMICAL THERMODYNAMICS  
AND THERMOCHEMISTRY

Thermodynamic Properties of  $\text{AgIn}_2\text{Te}_3\text{I}$  and  $\text{AgIn}_2\text{Te}_3\text{Br}$ ,  
Determined by EMF Method

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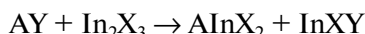
**Abstract**—Differential thermal analysis (DTA), X-ray diffraction (XRD), and electromotive force (EMF) are used to triangulate Ag–In–Te–I(Br) systems in the vicinity of compounds  $\text{AgIn}_2\text{Te}_3\text{I}$  and  $\text{AgIn}_2\text{Te}_3\text{Br}$ . The three-dimensional position of the  $\text{AgIn}_2\text{Te}_3\text{I}$ –InTe– $\text{Ag}_2\text{Te}$ –AgI and  $\text{AgIn}_2\text{Te}_3\text{Br}$ –InTe– $\text{Ag}_3\text{TeBr}$  phase areas with respect to the figurative points of silver is used to create equations of potential-determining chemical reactions. The potential-determining reactions are conducted in (–)C|Ag| $\text{Ag}_3\text{GeS}_3\text{I(Br)}$  glass|D|C(+) electrochemical cells (ECCs), where C stands for inert (graphite) electrodes, Ag and D are ECC electrodes (D denotes alloys of one-, three-, and four-phase areas), and  $\text{Ag}_3\text{GeS}_3\text{I}$  and  $\text{Ag}_3\text{GeS}_3\text{Br}$  glasses are membranes with purely ionic  $\text{Ag}^+$  conductivity. Linear parts of the temperature dependences of the cell EMFs are used to calculate the standard integral thermodynamic functions of saturated solid solutions based on  $\text{AgIn}_2\text{Te}_3\text{I}$  and  $\text{AgIn}_2\text{Te}_3\text{Br}$ , and the relative partial thermodynamic functions of silver in the stoichiometric quaternary compounds.

**Keywords:** phase equilibria, thermodynamic functions, Gibbs energy, EMF method

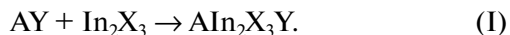
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INTRODUCTION

The possibility of creating quaternary  $\text{CuIn}_2\text{Se}_3\text{Br}$ ,  $\text{CuIn}_2\text{Se}_3\text{I}$ , and  $\text{AgIn}_2\text{Se}_3\text{I}$  compounds with tetrahedral structure was established in [1, 2]. The thermodynamically competitive reaction



is a barrier to the ampoule synthesis of many compounds of the  $\text{AlnX}_3\text{Y}$  family (where A stands for Cu and Ag; X for S, Se, and Te; and Y for Cl, Br, and I), which proceeds according to the scheme



An increase in the external pressure acting on the mixture of binary compounds helps to achieve reaction (I). Many of the quaternary compounds of the  $\text{AlnX}_3\text{Y}$  family are synthesized under external pressures of  $p = 5 \times 10^8$ ,  $20 \times 10^8$ , and  $40 \times 10^8$  Pa at a temperature of 773 K [3]. Under these conditions of synthesis, phases with the following crystalline structures are obtained: structures of a defective zinc blend ( $\text{AgIn}_2\text{Se}_3\text{I}$ ,  $\text{AgIn}_2\text{Te}_3\text{I}$ ,  $\text{CuIn}_2\text{Se}_3\text{I}$ ,  $\text{CuIn}_2\text{Te}_3\text{Cl}$ ,  $\text{CuIn}_2\text{Te}_3\text{Br}$ , and  $\text{CuIn}_2\text{Te}_3\text{I}$ ), spinel ( $\text{AgIn}_2\text{S}_3\text{Cl}$ ,  $\text{AgIn}_2\text{S}_3\text{Br}$ ,  $\text{AgIn}_2\text{Se}_3\text{Cl}$ ,  $\text{AgIn}_2\text{Se}_3\text{Br}$ , and  $\text{AgIn}_2\text{Se}_3\text{I}$ ), and a defective NaCl lattice ( $\text{AgIn}_2\text{Te}_3\text{Cl}$  and

$\text{AgIn}_2\text{Te}_3\text{Br}$ ) [3]. In [4], the conditions of and results from the synthesis of  $\text{AgIn}_2\text{Se}_3\text{Br}$ ,  $\text{AgIn}_2\text{Te}_3\text{I}$ , and  $\text{AgIn}_2\text{Te}_3\text{Br}$  in evacuated ampoules by the scheme (I) were described. Alloys with lattices of defective wurtzite, sphalerite, and spinel retained their external appearance and crystal structure for a year under normal conditions. Alloys with defective NaCl lattices transitioned to the X-ray amorphous state under the described conditions.  $\text{AgIn}_2\text{X}_3\text{Y}$  compounds belong to the group of silver-containing chalcogenide crystalline  $\text{Ag}_3\text{SI(Br)}$  and glass-like  $\text{Ag}_3\text{GeS}_3\text{I(Br)}$  phases in which halide anions, along with silver, exhibit properties of a mobile quasi-liquid [5].

A great many binary and ternary intermediate compounds of the Ag–In–Te–I(Br) system contain a number of quasi-quaternary systems in the four-element area [6–12]. Experimental difficulties in determining the boundaries of such systems can be overcome by simulating the  $T$ – $x$  phase diagram using the CALPHAD approach and data on the thermodynamic properties of phases [13, 14].

In this work, we present the results from experimental determination of the phase area boundaries of  $\text{AgIn}_2\text{Te}_3\text{I(Br)}$  compounds, and from calculating integral thermodynamic functions for saturated solid solu-

tions based on these quaternary compounds and relative partial thermodynamic functions of the silver in stoichiometric alloys of them. Some data on the thermodynamic properties of  $\text{AgIn}_2\text{Te}_3\text{I}$  can be found in [15].

## EXPERIMENTAL

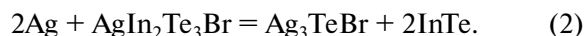
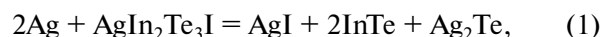
High-purity elemental substances (Ag, 99.99 wt %; In, 99.99 wt %; Te, 99.999 wt %) and compounds (AgI and AgBr, 99.96 wt %) were used. Calculated amounts of elements and compounds were sealed in quartz glass ampoules evacuated to a residual pressure of less than 1 Pa. Binary compounds  $\text{InTe}$ ,  $\text{In}_2\text{Te}_3$ , and  $\text{Ag}_2\text{Te}$  were prepared by cooling the melts of mixtures of the elements at a rate of 2 K/min. Quaternary compounds  $\text{AgIn}_2\text{Te}_3\text{I}$  and  $\text{AgIn}_2\text{Te}_3\text{Br}$  were obtained via solid-phase synthesis from powdered mixtures of AgI, AgBr, and  $\text{In}_2\text{Te}_3$  at 820 K for 20 days [4]. Three- and four-phase alloys of the positive electrodes of electrochemical cells (ECCs) were obtained from a mixture of the compounds produced by equations of the potential-determining reactions under the conditions described for the quaternary phases.  $\text{Ag}_3\text{GeS}_3\text{I}$  and  $\text{Ag}_3\text{GeS}_3\text{Br}$  glasses were obtained by quenching a molten mixture of the elemental substances and compounds AgI and AgBr in ice-cold water at  $T = 1150$  K. The phase composition of the alloys was monitored by means of differential thermal analysis (DTA) and X-ray diffraction (XRD). The DTA curves were recorded on a H307-1 XY instrument equipped with two chromel-alumel thermocouples, using a resistance heating furnace. The heating (cooling) rate in the DTA of the alloys was 6 to 8 K/min, and the error of temperature measurement did not exceed  $\pm 5$  K. A STOE STADI P diffractometer with a PSD linear position-sensitive detector operating in the transmission mode according to a modified Guinier geometry was used in our XRD studies ( $\text{CuK}_{\alpha 1}$  radiation, bent Ge (111) monochromator, and  $2\theta/\omega$  scanning mode). The diffraction arrays were processed using the STOE WinX<sup>POW</sup> (version 2.21) [16] and PowderCell (version 2.3) [17] software packages.

Potential-determining processes were conducted in a (-)C|Ag| $\text{Ag}_3\text{GeS}_3\text{I(Br)}$  glass|D|C(+) electrochemical cell (C denotes inert (graphite) electrodes, Ag and D are ECC electrodes, D is made from alloys of one-, three-, and four-phase areas, and the  $\text{Ag}_3\text{GeS}_3\text{I}$  and  $\text{Ag}_3\text{GeS}_3\text{Br}$  glasses are membranes with purely ionic  $\text{Ag}^+$  conductivity). Like  $\text{Ag}_3\text{GeS}_3\text{I}$  glass [19],  $\text{Ag}_3\text{GeS}_3\text{Br}$  glass [18] belongs to the class of quaternary superionic materials [20, 21]. The equilibrium state in ECC ( $E = \text{const}$ ) was achieved for times of 2 to 4 h. Equilibrium was considered to be achieved when the EMF values were stable or their changes did not exceed  $\pm 2$  mV.

The powdered components of the cells were pressed ( $p \sim 10^8$  Pa) into holes 2 mm in diameter made in a Teflon base until a density of  $\rho = (0.93 \pm 0.02)\rho_0$  was reached, where  $\rho_0$  is the experimentally determined density of the cast alloys. To eliminate plastic deformation defects in the pressed alloys, heating and cooling thermal cycles in the range of 400 to 480 K were repeated 5 times at a rate of 2 K/min. The electrochemical cells were heated in a resistance furnace similar to the one described in [22], which was filled with a mixture of  $\text{H}_2$  and Ar in a molar ratio of 1 : 9 at  $p = 10^5$  Pa. The gas flow was directed from the positive to the negative ECC electrodes. The gas flow rate was about  $2 \times 10^{-3}$  m<sup>3</sup>/h. The accuracy of maintaining the cell temperature was  $\pm 0.5$  K. EMF measurements were performed using the U7-9 electrometer voltmeter with an input impedance of more than  $10^{12}$   $\Omega$ . Temperature dependences  $E(T)$  of the EMF of the cells were investigated using the technique described in [23].

## RESULTS AND DISCUSSION

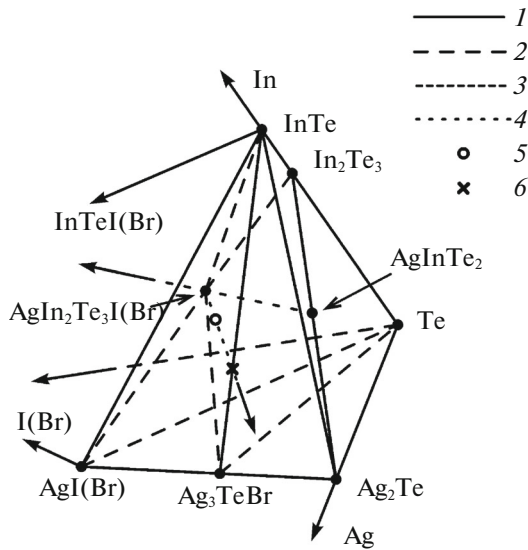
The triangulation of the Ag–In–Te–I(Br) systems in the vicinity of the  $\text{AgIn}_2\text{Te}_3\text{I}$  and  $\text{AgIn}_2\text{Te}_3\text{Br}$  compounds is shown in Fig. 1 by two-phase equilibria lines. The line positions were established in [11, 12, 24], and in our studies of the alloys via EMF, DTA, and XRD. The spatial position of the  $\text{Ag}_2\text{Te}$ – $\text{InTe}$ – $\text{AgIn}_2\text{Te}_3\text{I}$ –AgI (I) and  $\text{Ag}_3\text{TeBr}$ – $\text{InTe}$ – $\text{AgIn}_2\text{Te}_3\text{Br}$  (II) phase areas relative to the figurative point of silver allowed us to use EMF method to determine the thermodynamic properties of quaternary phases [25]. According to Fig. 1, the ECC chemical reactions involving quaternary phases are described by the equations



The equations are written in approximation of the slight differences in the positions of the figurative points of the compounds and their saturated solid solutions in the Gibbs tetrahedron. The ECC positive electrodes were made from mixtures of powdered alloys of the compounds in the molar ratio determined by Eqs. (1) and (2). Temperature dependences  $E_{1,2}(T)$  of the EMF values of cells with the D positive electrodes for the I and II phase areas are shown in Fig. 2. The inflection of  $E_1(T)$  near  $T \approx 419$  K was caused by the polymorphic transformations  $\alpha\text{-AgI} \xrightarrow{419 \text{ K}} \beta\text{-AgI}$  [20] and  $\alpha\text{-Ag}_2\text{Te} \xrightarrow{418 \text{ K}} \beta\text{-Ag}_2\text{Te}$  [26].

The linear parts of the  $E_{1,2}$  (mV)– $T$  (K) plots are described by the equations

$$E_1 = (164.67971 \pm 0.86451) + (0.16850 \pm 0.00186)T \quad (445 \leq T \leq 485), \quad (3)$$



**Fig. 1.** Triangulation of the Ag–In–Te–I(Br) system in the vicinity of the  $\text{AgIn}_2\text{Te}_3\text{I}(\text{Br})$  compounds, where (1, 2) denote the lines of two-phase equilibria, (3, 4) denote the Ag– $\text{AgIn}_2\text{Te}_3\text{I}(\text{Br})$  and  $\text{AgInTe}_2$ – $\text{InTeI}(\text{Br})$  secant lines, (5) is the figurative point of the alloys of the ECC positive electrodes, and (6) is the point of intersection between the Ag– $\text{AgIn}_2\text{Te}_3\text{I}(\text{Br})$  secant and the  $\text{AgI}(\text{Br})$ – $\text{InTe}$ – $\text{Ag}_2\text{Te}$  plane.

$$E_2 = (142.07304 \pm 0.78859) + (0.20809 \pm 0.00172)T \quad (432 \leq T \leq 484). \quad (4)$$

The nonlinearity of the  $E_{1,2}(T)$  dependences below 419 K was a result of the kinetic barriers to achieving the equilibrium of the I and II D phase areas, due to the uncontrolled behavior of reactions (1) and (2)

[27]. The deviations from the linear track of the  $E_{1,2}(T)$  dependence above 480 K were presumably caused by changes in the area of the existence of the phases.

The changes in the Gibbs energy of reactions (1) and (2) ( $\Delta_f G_{T,(1),(2)}$ , J/mol), and the EMF value changes (V) in the external circuit ( $E_{(1),(2)}(T)$ ) under the conditions of electrochemical equilibrium in ECC ( $p, T, E = \text{const}$ ) are related by the following equations:

$$-\Delta_f G_{T,(1),(2)} = nFE_{(1),(2)}(T), \quad (5)$$

where  $n = 2$  is the number of electrons that participate in reactions (1) and (2), and  $F = 96485.3 \text{ C/mol}$  is the Faraday number.

According to Eqs. (1) and (2),

$$\begin{aligned} \Delta_f G_{T,(1)} &= \Delta_f G_{T,\beta\text{-Ag}_2\text{Te}} + 2\Delta_f G_{T,\text{InTe}} \\ &+ \Delta_f G_{T,\beta\text{-AgI}} - \Delta_f G_{T,\beta\text{-AgIn}_2\text{Te}_3\text{I}}, \end{aligned} \quad (6)$$

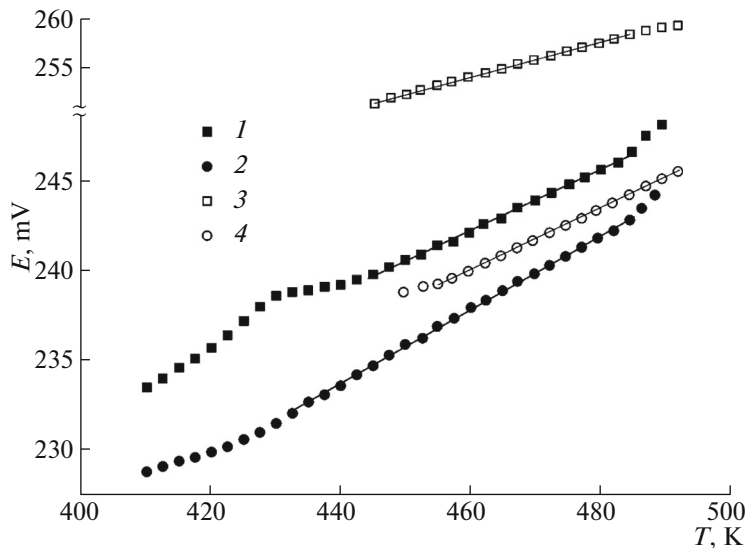
$$\begin{aligned} \Delta_f G_{T,(2)} &= \Delta_f G_{T,\beta\text{-Ag}_3\text{TeBr}} \\ &+ 2\Delta_f G_{T,\text{InTe}} - \Delta_f G_{T,\text{AgIn}_2\text{Te}_3\text{Br}}, \end{aligned} \quad (7)$$

where  $\Delta_f G_{T,\beta\text{-Ag}_2\text{Te},\beta\text{-AgI},\text{InTe},\text{Ag}_3\text{TeBr},\text{AgIn}_2\text{Te}_3\text{I},\text{AgIn}_2\text{Te}_3\text{Br}}$  is the Gibbs energy of the formation of phases ( $\text{kJ mol}^{-1}$ ) from the elemental substances at temperature  $T$  (K).

In light of Eqs. (5)–(7), we obtain

$$\begin{aligned} \Delta_f G_{T,\text{AgIn}_2\text{Te}_3\text{I}} &= \Delta_f G_{T,\beta\text{-Ag}_2\text{Te}} + 2\Delta_f G_{T,\text{InTe}} \\ &+ \Delta_f G_{T,\beta\text{-AgI}} + 2FE_{(1)}, \end{aligned} \quad (8)$$

$$\begin{aligned} \Delta_f G_{T,\text{AgIn}_2\text{Te}_3\text{Br}} &= \Delta_f G_{T,\text{Ag}_3\text{TeBr}} \\ &+ 2\Delta_f G_{T,\text{InTe}} + 2FE_{(2)}. \end{aligned} \quad (9)$$



**Fig. 2.** Temperature dependences of EMF of the  $(-)\text{C}|\text{Ag}|\text{Ag}_3\text{GeS}_3\text{I}(\text{Br}) \text{ glass}|\text{D}|\text{C}(+)$  for the (1)  $\text{Ag}_2\text{Te}$ – $\text{InTe}$ – $\text{AgIn}_2\text{Te}_3\text{I}$ – $\text{AgI}$  and (2)  $\text{Ag}_3\text{TeBr}$ – $\text{InTe}$ – $\text{AgIn}_2\text{Te}_3\text{Br}$  D-phase areas, and for the (3)  $\text{AgIn}_2\text{Te}_3\text{I}$  and (4)  $\text{AgIn}_2\text{Te}_3\text{Br}$  stoichiometric compounds.

**Table 1.** Standard integral thermodynamic functions of the Ag–In–Te–I(Br) system phases

Phase	$-\Delta G_{298}^{\circ}$ , kJ/mol	$-\Delta H_{298}^{\circ}$ , kJ/mol	$\Delta S_{298}^{\circ}$ , J/(mol K)	$T\Delta S_{298}^{\circ}$ , kJ/mol	Reference
InTe	71.478	71.965	-1.634	–	[28]
$\beta$ -AgI	67.443	63.214	14.19	–	
AgBr	97.06	100.57	-11.77	–	
$\beta$ -Ag <sub>2</sub> Te	38.8 ± 3.3	26.1 ± 1.9	42.8 ± 9.0	–	[22]
Ag <sub>3</sub> TeBr	136.1	127.3	29.4	–	[24]
AgIn <sub>2</sub> Te <sub>3</sub> I	207.7 ± 3.5	201.4 ± 1.9	21.2 ± 9.5	6.3 ± 2.9	Present studies
AgIn <sub>2</sub> Te <sub>3</sub> Br	242.1 ± 0.3	246.3 ± 0.2	-14.1 ± 0.4	-4.2 ± 0.2	
AgIn <sub>2</sub> Te <sub>3</sub> I*	29.7 ± 0.5	28.8 ± 0.3	3.1 ± 1.4	0.9 ± 0.4	
AgIn <sub>2</sub> Te <sub>3</sub> Br*	34.6 ± 0.1	35.2 ± 0.1	-2.0 ± 0.1	-0.6 ± 0.1	

\* Values of the thermodynamic functions are averaged over a mole of phase atoms.

Since  $\Delta_f G_{T,\beta\text{-Ag}_2\text{Te}} = (-26.0129 \pm 1.858) - (42.8 \pm 9) \times 10^{-3}T$  [22],  $\Delta_f G_{T,\text{InTe}} = -71.965 + 1.634 \times 10^{-3}T$ ,  $\Delta_f G_{T,\beta\text{-AgI}} = -63.214 - 14.19 \times 10^{-3}T$  [28],  $\Delta_f G_{T,\text{Ag}_3\text{TeBr}} = -127.26 - 29.40 \times 10^{-3}T$  [24],  $2FE_1 = (31.779 \pm 0.167) + (32.516 \pm 0.359) \times 10^{-3}T$ , and  $2FE_2 = (24.920 \pm 0.152) + (40.156 \pm 0.332) \times 10^{-3}T$ , we derive the following expressions from Eqs. (8) and (9):

$$\Delta_f G_{T,\text{AgIn}_2\text{Te}_3\text{I}} = (-201.4 \pm 1.9) - (21.2 \pm 9.5) \times 10^{-3}T \quad (445 \leq T \leq 485), \quad (10)$$

$$\Delta_f G_{T,\text{AgIn}_2\text{Te}_3\text{Br}} = (-246.3 \pm 0.2) - (-14.1 \pm 0.4) \times 10^{-3}T \quad (432 \leq T \leq 484). \quad (11)$$

Equations (10) and (11) express the temperature dependences of the Gibbs energy of formation of saturated solid solutions of the quaternary compounds from the elemental substances in the I and II phase areas.

The linear parts of the temperature dependence of the EMF values of cells with positive electrodes made from alloys of the AgIn<sub>2</sub>Te<sub>3</sub>I and AgIn<sub>2</sub>Te<sub>3</sub>Br quaternary compounds (Fig. 2) are described by the equations ( $E$ , mV;  $T$ , K)

$$E_{(3)} = (177.01276 \pm 0.41916) + (0.16783 \pm 0.000872)T \quad (445 \leq T \leq 485), \quad (12)$$

$$E_{(4)} = (160.80788 \pm 0.41974) + (0.17212 \pm 0.000879)T \quad (455 \leq T \leq 492). \quad (13)$$

The temperature dependences of the partial Gibbs energy (kJ mol<sup>-1</sup>) of silver in the stoichiometric quaternary compounds were calculated according to [25] using Eq. (5) at  $n = 1$ :

$$\Delta_f \bar{G}_{T,\text{Ag,AgIn}_2\text{Te}_3\text{I}} = (-17.08 \pm 0.04) - (15.36 \pm 0.09) \times 10^{-3}T \quad (445 \leq T \leq 485), \quad (14)$$

$$\Delta_f \bar{G}_{T,\text{Ag,AgIn}_2\text{Te}_3\text{Br}} = (-15.52 \pm 0.04) - (16.61 \pm 0.09) \times 10^{-3}T \quad (432 \leq T \leq 484). \quad (15)$$

The integral thermodynamic functions of saturated solid solutions of the quaternary phases and the relative partial thermodynamic functions of silver in alloys of the stoichiometric quaternary compounds, calculated using Eqs. (10), (11) and (14), (15) in the approximation

$$\left(\frac{\partial \Delta_f H}{\partial T}\right)_p = \left(\frac{\partial \Delta_f S}{\partial T}\right)_p = 0, \quad (16)$$

are included in Tables 1 and 2. Tables 1 and 2 contain products  $T\Delta S_{298}^{\circ}$  to compare the entropy and energy parameter ( $\Delta H_{298}^{\circ}$ ) contributions to the  $\Delta G_{298}^{\circ}$  values. Saturated solid solutions of the quaternary compounds differ in the value and sign of entropy  $\Delta S_{298}^{\circ}$  of the reaction of formation of phases from the elemental substances. The negative  $\Delta S_{298,\text{AgIn}_2\text{Te}_3\text{Br}}^{\circ}$  value is presumably due to a reduction in the dispersity of alloy grains and an increase in the symmetry of the elementary cell during the formation of the solid solution [29]. The reason for the different properties of the solid phase solutions is apparently the geometric factor, i.e., the difference between the ionic radii of halide anions I<sup>-</sup> (0.219 nm) and Br<sup>-</sup> (0.196 nm) [30].

A comparison of values of the integral thermodynamic functions of the quaternary phases per one mole of atoms (Table 1) and values of the partial thermodynamic functions of silver in the compounds (Table 2) testifies to the quasi-free state of some of Ag<sup>+</sup> ions within the lattice unit cell of the phases [31]. The existence of ionic conductivity of the phase alloys and the correctness of inequality  $\sigma_{\text{AgIn}_2\text{Te}_3\text{Br}} > \sigma_{\text{AgIn}_2\text{Te}_3\text{I}}$  are predicted.

**Table 2.** Relative partial thermodynamic functions of silver in the alloys of stoichiometric compounds at 298 K

Compound	$-\Delta\bar{G}_{\text{Ag}}$ , kJ/mol	$-\Delta\bar{H}_{\text{Ag}}$ , kJ/mol	$\Delta\bar{S}_{\text{Ag}}$ , J/(mol K)	$T\Delta S_{298}^{\circ}$ , kJ/mol
AgIn <sub>2</sub> Te <sub>3</sub> I	21.66 ± 0.05	17.08 ± 0.04	15.36 ± 0.09	4.58 ± 0.03
AgIn <sub>2</sub> Te <sub>3</sub> Br	20.47 ± 0.05	15.52 ± 0.04	16.61 ± 0.09	4.95 ± 0.03

## CONCLUSIONS

Equations for the temperature dependences of the Gibbs energies of the formation of saturated solid solutions of compounds AgIn<sub>2</sub>Te<sub>3</sub>I and AgIn<sub>2</sub>Te<sub>3</sub>Br from elementary substances and the temperature dependences of the relative partial thermodynamic functions of silver in stoichiometric alloys of quaternary compounds were derived. The values of the integral thermodynamic functions of saturated solid solutions of the quaternary phases and the relative partial thermodynamic functions of silver in stoichiometric AgIn<sub>2</sub>Te<sub>3</sub>I and AgIn<sub>2</sub>Te<sub>3</sub>Br under standard conditions were approximated with Eq. (16). Based on our analysis of the values of the integral thermodynamic functions of the quaternary phases and the partial thermodynamic functions of silver in the stoichiometric compounds, the quasi-free state of some of Ag<sup>+</sup> ions within the lattice unit cell of the phases was deduced. The ionic conductivity of the phase alloys and the correctness of the inequality  $\sigma_{\text{AgIn}_2\text{Te}_3\text{Br}} > \sigma_{\text{AgIn}_2\text{Te}_3\text{I}}$  were predicted.

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