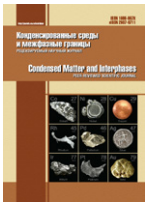

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Thermodynamic study of the BiSI-BiSeI system by the electromotive force method

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Abstract

Objectives: Chalcohalides of arsenic subgroup elements and solid solutions based on them are of great interest as functional materials exhibiting thermoelectric, photoelectric, piezoelectric, optical, and other properties.

Experimental: This paper presents the results of a study of the thermodynamic properties of BiSI, BiSeI, and $BiS_{1-x}Se_xI$ solid solutions using electromotive force (EMF) analysis. For this study, concentration cells of the type

(–) Bi (solid)/liquid electrolyte, Bi^{3+}/(Bi in alloy) (solid) (+)

were constructed and their EMFs were measured in the temperature range of 300-370 K. An ionic liquid, namely, morpholine formate, was used as the electrolyte. To select the compositions of the right-hand electrodes, solid-state equilibria in the BiSI-BiSeI-BiI_3 system were studied using X-ray diffraction analysis. Continuous solid solutions of the BiSI-BiSeI boundary system were shown to form stable tie-line with BiI_3. Using these data and literature information on boundary systems, a fragment of the solid-phase equilibria diagram for the Bi-S-Se-I system was constructed. Based on constructed diagram, the $BiS_{1-x}Se_xI$ solid solutions of various compositions with a 2–3 mol % excess of BiI_3 and $S_{1-x}Se_x$ were selected as electrode-alloys for the aforementioned concentration cells. The partial molar functions of bismuth in the alloys were calculated from the obtained pairs of *E*(mV) and *T*(K) values.

Conclusions: The constructed phase diagram made it possible to determine the virtual reactions of potential formation corresponding to the aforementioned partial molar functions and calculate the standard thermodynamic functions of formation and the standard entropies of bismuth thio- and selenoidide and $BiS_{1-x}Se_xI$ solid solutions. The calculations were performed using literature data on the corresponding standard integral thermodynamic functions of the BiI_3 compound and $S_{1-x}Se_x$ alloys involved in potential-forming reactions. The thermodynamic functions of the BiSI and BiSeI compounds were compared with existing fragmentary literature data, and for solid solutions, they were determined for the first time.

Keywords: Bismuth chalcoiodides, Phase diagram, Solid solutions, EMF method, Thermodynamic functions, Ionic liquid

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1. Introduction

Compounds of the B^VXHal type (B^V = As, Sb, Bi; X = S, Se, Te; Hal = Cl, Br, I) and phases based on them have recently attracted considerable research interest due to their thermoelectric, photoelectric, piezoelectric and optical properties and are considered promising for several practical applications in modern high technologies [1–7]. In addition, a number of compounds of this type are Rashba semiconductors and are considered good candidates for use in spintronic devices [8–11].

The search and development of methods for obtaining new multicomponent phases and materials is based on data from fundamental research on phase equilibria and the thermodynamic properties of the corresponding systems [12–15]. One of the rational approaches to the comprehensive investigation of these characteristics is the incorporation of the electromotive force (EMF) method into the traditional set of experimental methods for studying phase equilibria [15]. The EMF method, being one of the most accurate equilibrium methods of chemical thermodynamics [16–18], is widely used for the comprehensive investigation of phase equilibria and thermodynamic properties of inorganic systems. Thermodynamic data obtained by this method, in addition to internal consistency within an individual phase, are also characterized by mutual consistency of their values for all phases of the system and with the phase diagram [15].

In practical thermodynamic investigations, various modifications of concentration cells with liquid [19–23] and solid electrolytes [24–28] are employed. It should be noted that in most cases, when studying chalcogenide and chalcohalide systems by this method, it is advisable to conduct experiments in the subsolidus region of the phase diagram, i.e., below the melting point of the corresponding chalcogen. The most widely used electrolytes for such measurements have been glycerol solutions of alkali metal salts, the application of which has made it possible to carry out thermodynamic studies even at room temperature [16, 17, 29–31]. A number of studies [32-35] have demonstrated the possibility of using ionic liquids as electrolytes in such low-temperature EMF measurements.

To obtain new sets of mutually consistent data for antimony and bismuth chalcoiodides, we have carried out systematic investigations of phase equilibria and thermodynamic properties of a series of ternary B^V-X-Hal systems [36–40], as well as some more complex systems including these elements [41–45].

This study aimed to investigate solid-phase equilibria in the composition area BiSeI-BiSI-BiI_3 (A) of the quaternary Bi-S-Se-I system and to determine the thermodynamic functions of the ternary BiSI, BiSeI compounds, and $BiS_{1-x}Se_xI$ solid solutions by the EMF method.

The BiSeI-BiSI and $Bi_{19}S_{27}I_3$-"$Bi_{19}Se_{27}I_3$" sections of the indicated system were studied by us in [46, 47]. It was shown that the first is characterized by the formation of a continuous series of solid solutions, and the second – a wide area of solid solutions (up to 70 mol %) based on $Bi_{19}S_{27}I_3$.

2. Experimental

For the thermodynamic study of solid solutions along the BiSI-BiSeI section, concentration cells of the type

(-) Bi (solid) / liquid electrolyte,
Bi^{3+} / (Bi in alloy) (solid) (+) (1)

were assembled and their EMF values were measured in the temperature range of 300–370 K.

As it is known [15], when planning thermodynamic experiments by the EMF method, it is necessary to have reliable data on phase equilibria in the studied system in the temperature range of EMF measurements. Taking this into account, we first carried out experiments to determine the nature of solid-phase equilibria in the BiSI-BiSeI-BiI_3 (A) subsystem. For this purpose, the BiI_3, BiSeI, and BiSI compounds were synthesized. At the same time, high-purity elementary components (not less than 99.999 %) purchased from the Alfa Aesar company were used. The synthesis was carried out by co-melting of stoichiometric amounts of constituent elements, weighed with an accuracy of 10^{-4} g on analytical balances. The synthesis was carried out in evacuated quartz ampoules (~10^{-2} Pa) at temperatures 30–50 K higher than their melting temperatures. Taking into account the high vapor pressure

of elemental iodine, sulfur, and selenium at the synthesis temperatures [48], the synthesis was performed in a two-zone inclined furnace. The temperature in the upper "cold" zone was maintained slightly below the boiling point of iodine, while the temperature in the "hot" zone was set at 30–50 K above the melting point of the synthesized compound. Taking into account that the ternary compounds BiSeI and BiSI melt with decomposition by peritectic reactions, the samples were ground into powder, pressed into tablets, and annealed at 750 K for 300 hours to ensure complete homogenization. The phase purity of all the synthesized initial compounds was verified by X-ray diffraction analysis (XRD) and differential thermal analysis (DTA), and the results coincided with literature data [36, 41, 49].

Alloys of various compositions of system (A) were prepared by melting the synthesized and identified initial compounds at 850 K in vacuumed quartz ampoules, which, after fusion, were subjected to stepwise homogenizing annealing: at 650 K for 300 h and 370 K for 100 h.

Powder diffraction patterns of annealed alloys revealed that all alloys in the studied system consist of two-phase mixtures of $BiS_{1-x}Se_xI$ and BiI_3. As an example, Fig. 1 presents the powder diffraction pattern of a sample with the nominal composition 40 mol % BiSI + 40 mol % BiSeI + 20 mol % BiI_3 (sample 1). Thus, according to the XRD data, the solid-phase equilibria diagram of system (A) at room temperature has the form shown in Fig. 2.

For the correct selection of the compositions of the electrode alloys of cells of type (1), it is advisable to consider the ray lines originating from the bismuth corner (reference electrode) of the concentration tetrahedron Bi-S-Se-I and passing through the BiSI-BiSeI section, on which the investigated $BiS_{1-x}Se_xI$ solid solutions are located. For this purpose, using Fig. 2 and the literature data on the boundary systems BiSI-BiI_3 [36], BiSeI-BiI_3 [41] and the binary S-Se system [49], we constructed a fragment of the solid-phase equilibrium diagram of the indicated quaternary system (Fig. 3). As can be seen, the indicated ray sections (red straight lines), passing through the investigated section (points 1, 2, 3, 4), reach the stable BiI_3-S-Se plane (shaded triangle). In this case, the rays passing through the extreme points 1 and 4, corresponding to the compositions

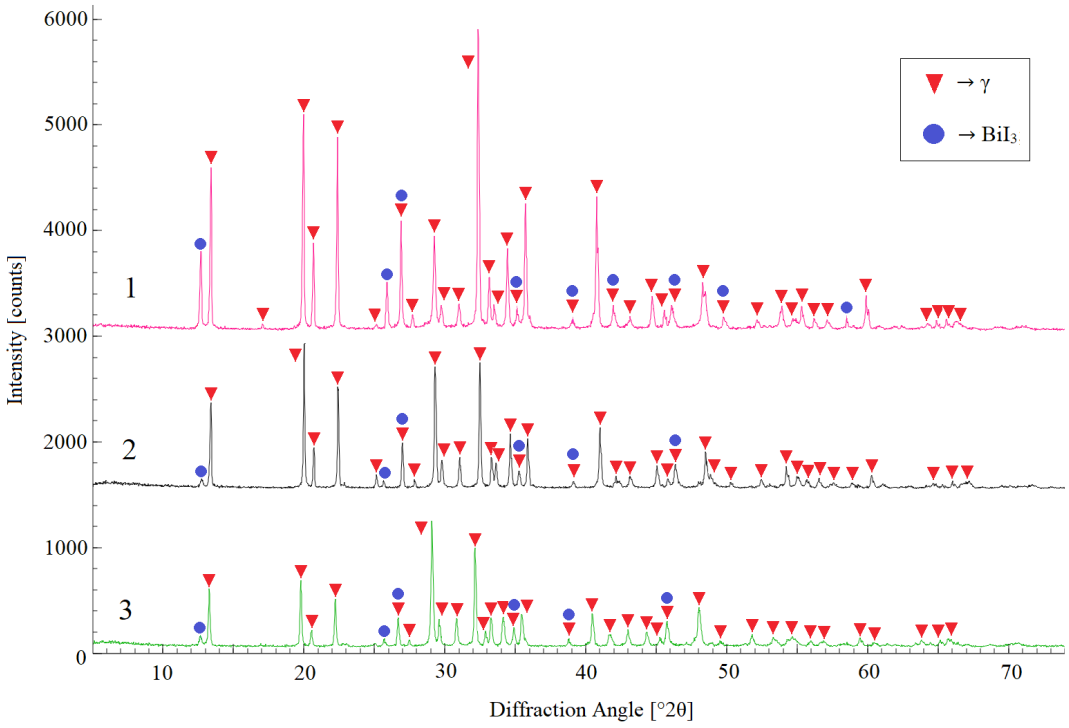

Fig. 1. Powder diffraction patterns of samples 1–3 in Fig. 2

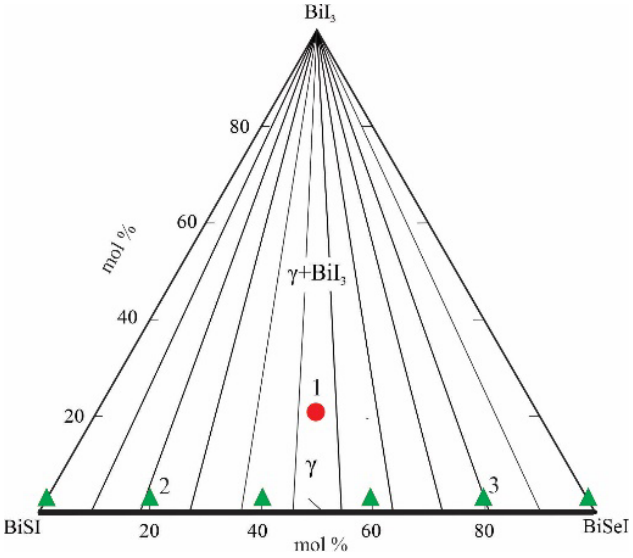

Fig. 2. Solid-phase equilibria diagram of the BiSeI-BiSI-BiI_3 system

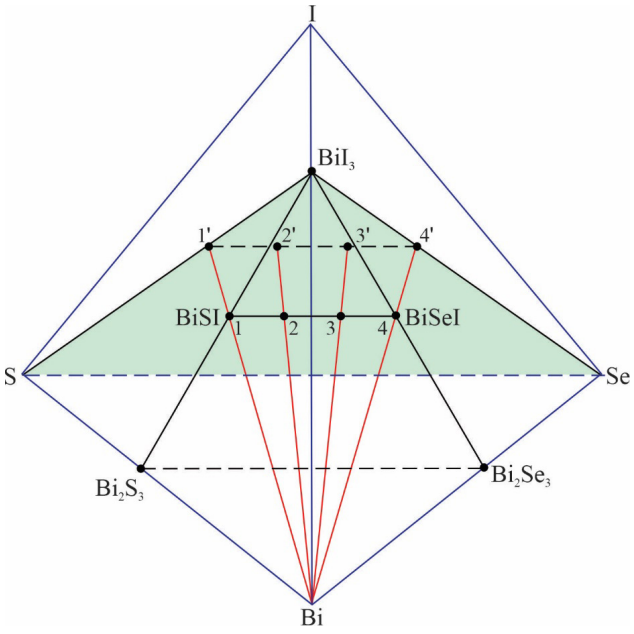

Fig. 3. Fragment of the solid-phase equilibria diagram of the Bi-S-Se-I concentration tetrahedron

of the BiSI and BiSeI compounds, reach the lateral sides BiI_3-S (point 1′) and BiI_3-Se (point 2′), respectively.

The ray lines passing through the intermediate compositions of the BiSI-BiSeI section (for example, points 2 and 3) reach points 2′ and 3′. According to the phase diagram of the S-Se system [49], alloys on the BiI_3-S-Se concentration plane, depending on the S : Se ratio, consist of mixtures of BiI_3 with single- or two-phase alloys of this binary system.

Taking the above into account, $BiS_{1-x}Se_xI$ samples with a small (2–3 mol %) excess of BiI_3 and $S_{1-x}Se_x$ were used as electrode alloys in type (1) cells. All of these samples are compositionally aligned with the above-discussed ray lines and consist of heterogeneous mixtures of $BiS_{1-x}Se_xI$, bismuth triiodide, and $S_{1-x}Se_x$ alloys. To bring the electrode alloys into a state as close as possible to equilibrium, after melting, they were subjected to annealing under the above-mentioned conditions.

Fig. 1 presents the powder diffraction patterns of samples 2 and 3 marked in Fig. 2. As can be seen, both samples exhibit a high degree of crystallinity; their diffraction patterns are identical and consist of reflection lines of γ-solid solutions of 20 and 80 mol % BiSeI compositions [46]. The absence of diffraction lines of BiI_3 and $S_{1-x}Se_x$ alloys is due to their insignificant number.

To prepare the right-hand electrodes of the cells of type (1), the annealed alloys were ground into powder and then pressed into tablets with a diameter of 7 and a thickness of 3–4 mm onto molybdenum current wires.

An ionic liquid (morpholinium formate) with the addition of $BiCl_3$ was used as the electrolyte. To obtain the ionic liquid, morpholine, formic acid, and anhydrous $BiCl_3$ were purchased from Alfa Aesar. The ionic liquid was prepared in accordance with the procedure described in [50]: morpholine was poured into a three-necked round-bottomed flask immersed in an ice-water bath and equipped with a reflux condenser, a dropping funnel for adding acid, and a thermometer to monitor the temperature. Formic acid was slowly (60 min) added dropwise with vigorous stirring. Considering the exothermic nature of this reaction, the temperature of the mixture was maintained below 25 °C using an ice bath. Stirring was continued for 4 h. The residual amine or acid was evaporated under reduced pressure (1–5 mmHg), and the remaining liquid was additionally dried at 80 °C under the same conditions.

To conduct EMF measurements, an electrochemical cell of design described in [32]

was assembled, evacuated, filled with argon to a pressure of ~40 kPa, and placed in a specially made tubular resistance furnace, where it was thermostatted at a temperature of ~360 K for three days. The temperature of the cell was measured using chromel-alumel thermocouples and a mercury thermometer with an accuracy of ±0.5 °C.

The EMF was measured using a high-resistance (input resistance 10^9 Ohm) digital voltmeter Keithley 2100 $6^{1/2}$, in the temperature range of 300–370 K. The choice of the upper limit of measurements is because at higher temperatures, the alloys of the S-Se system melt [49], which leads to a change in the phase composition of the electrode alloys.

The first equilibrium values were obtained after thermostating the cell under the above-mentioned conditions, and subsequent measurements were taken approximately every 4 h after the set temperature was established. Values of EMF were considered equilibrium when repeated measurements at a given temperature differed from each other by no more than 0.5 mV, regardless of the direction of the temperature change.

3. Results and discussion

Fig. 4 shows the EMF measurement data for cells of type (1). As can be seen, the numerical values of EMF decrease monotonically with increasing selenium concentration in the $BiS_{1-x}Se_xI$ solid solutions, and for each sample, its temperature dependence is linear. Considering this, for thermodynamic calculations, the experimental data were processed by the least-squares method, and linear equations of the type

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

recommended in modern thermodynamic literature [16, 17] were obtained. In equation (2), n is the number of pairs of E and T values; S_E and S_b are the variances of individual EMF measurements and the b-factor, respectively. $\overline{T}$ – is the average absolute temperature; t is the Student's criterion. At a confidence level of 95 % and a number of experimental points $n \geqslant 20$, the Student's t-test is $t \geqslant 2$. The resulting equations of type (2) are presented in Table 1.

From the data in Table 1, using the thermodynamic relations [16, 17]:

$$\Delta\overline{G}_{Bi} = -zFE \quad (3)$$

$$\Delta\overline{H}_{Bi} = -z\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa \quad (4)$$

$$\Delta\overline{S}_{Bi} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb \quad (5)$$

(F = Faraday constant, 96485 C·mol^{-1}; z = cation charge, Bi^{3+}), the relative partial Gibbs free energy, enthalpy, and entropy of bismuth in the

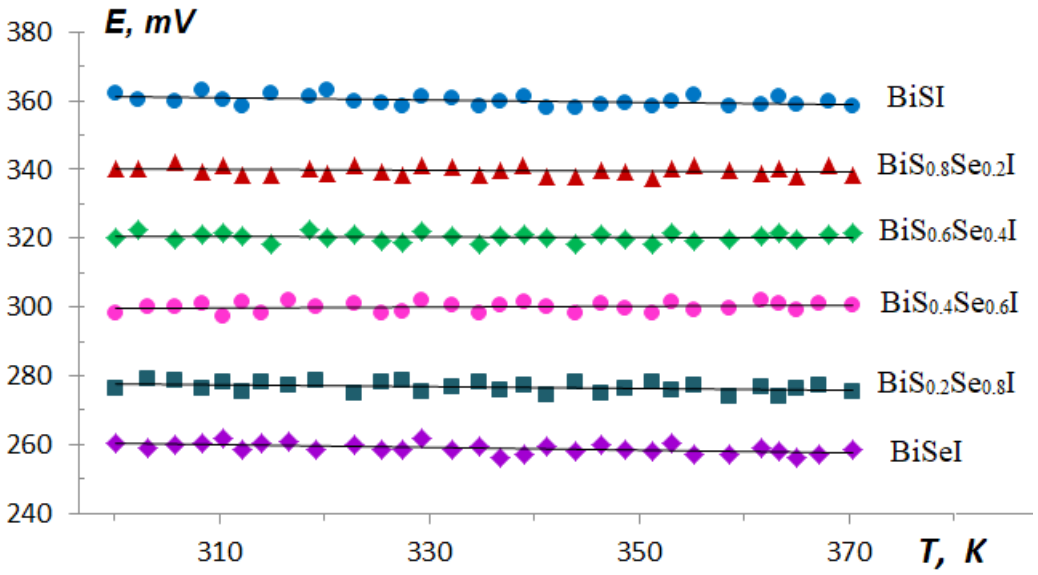

Fig. 4. EMF measurement data for type (1) cells for $BiS_{1-x}Se_xI$ alloys

Table 1. Equations for the temperature dependences of EMF for $BiS_{1-x}Se_xI$ alloys of various compositions in the temperature range 300–370 K

Phase	E, mV = $a + bT \pm 2\tilde{S}_E(T)$
BiSI	$370.35 - 0.0308T \pm 2\left[\frac{1.80}{30} + 1.4 \cdot 10^{-4}(T - 336.6)^2\right]^{1/2}$
$BiS_{0.8}Se_{0.2}I$	$344.48 - 0.0145T \pm 2\left[\frac{1.41}{30} + 1.1 \cdot 10^{-4}(T - 336.6)^2\right]^{1/2}$
$BiS_{0.6}Se_{0.4}I$	$322.13 - 0.0055T \pm 2\left[\frac{1.52}{30} + 1.2 \cdot 10^{-4}(T - 336.6)^2\right]^{1/2}$
$BiS_{0.4}Se_{0.6}I$	$296.54 + 0.0101T \pm 2\left[\frac{1.84}{30} + 1.4 \cdot 10^{-4}(T - 335.4)^2\right]^{1/2}$
$BiS_{0.2}Se_{0.8}I$	$279.70 - 0.0103T \pm 2\left[\frac{1.69}{30} + 1.3 \cdot 10^{-4}(T - 335.4)^2\right]^{1/2}$
BiSeI	$272.09 - 0.0394T \pm 2\left[\frac{1.48}{30} + 1.1 \cdot 10^{-4}(T - 335.4)^2\right]^{1/2}$

Table 2. Partial molar functions of bismuth in $BiS_{1-x}Se_xI$ alloys at 298 K

Phase	$-\Delta\overline{G}_{Bi}$	$-\Delta\overline{H}_{Bi}$	$\Delta\overline{S}_{Bi}$, J·K^{-1}·mol^{-1}
	kJ·mol^{-1}		
BiSI	104.54±0.15	107.20±1.5	-8.93±3.41
$BiS_{0.8}Se_{0.2}I$	98.46±0.13	99.71±1.01	-4.20±3.01
$BiS_{0.6}Se_{0.4}I$	92.77±0.13	93.24±1.05	-1.60±3.13
$BiS_{0.4}Se_{0.6}I$	86.71±0.15	85.84±1.16	2.94±3.44
$BiS_{0.2}Se_{0.8}I$	80.07±0.14	80.96±1.11	-2.99±3.30
BiSeI	75.36±0.13	78.76. ±1.04	-11.39±3.09

alloys were calculated. The resulting partial molar functions are presented in Table 2, and their concentration dependence graphs are shown in Fig. 5.

As can be seen from Fig. 5, all three functions are continuous functions of composition, which is in accordance with the formation of continuous solid solutions in the studied system.

To calculate the integral thermodynamic functions of BiSI, BiSeI compounds, and $BiS_{1-x}Se_xI$ solid solutions of various compositions, we determined the equations of potential-forming reactions using the schematic solid-phase equilibria diagram of the Bi-S-Se-I system (Fig. 3) [15]. It is easy to show that for BiSI and BiSeI compounds, they have the form:

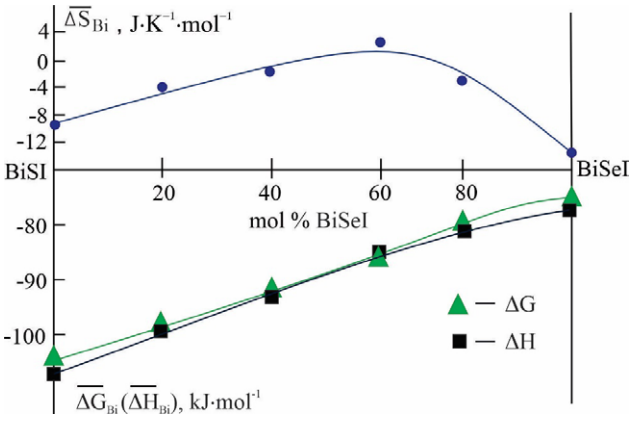

Fig. 5. Concentration dependences of the partial molar functions of bismuth in the BiSI-BiSeI system at 300 K

Bi (solid) + 0.5 BiI_3 (solid) + 1.5S (solid) = = 1.5 BiSI (solid) (6)

Bi (solid) + 0.5BiI_3 (solid) + 1.5Se (solid) = = 1.5BiSeI (solid) (7)

In accordance with these equations, the standard Gibbs free energy of formation and the enthalpy of formation of the specified ternary compounds were calculated using the relations:

$$\Delta_f Z^0(\mathrm{BiSI}) = \frac{2}{3}\Delta\overline{Z}_{\mathrm{Bi}} + \frac{1}{3}\Delta_f Z^0(\mathrm{BiI_3}) \quad (8)$$

$$\Delta_f Z^0(\mathrm{BiSeI}) = \frac{2}{3}\Delta\overline{Z}_{\mathrm{Bi}} + \frac{1}{3}\Delta_f Z^0(\mathrm{BiI_3}) \quad (9)$$

where $Z \equiv G$, H, and the standard entropies are according to

$$S^0(\mathrm{BiSI}) = \frac{2}{3}[\Delta\overline{S}_{\mathrm{Bi}} + S^0(\mathrm{Bi})] + \frac{1}{3}S^0(\mathrm{BiI_3}) + S^0(\mathrm{S}) \quad (10)$$

$$S^0(\mathrm{BiSeI}) = \frac{2}{3}[\Delta\overline{S}_{\mathrm{Bi}} + S^0(\mathrm{Bi})] + \frac{1}{3}S^0(\mathrm{BiI_3}) + S^0(\mathrm{Se}). \quad (11)$$

On the other hand, as shown above, the ray lines passing through different compositions of γ-solid solutions reach the BiI_3-S-Se concentration triangle. Therefore, the overall potential-forming reaction for them has the form

Bi (solid) + 0.5BiI_3 (solid) + 1.5($S_{1-x}Se_x$) (solid) = = 1.5 $BiS_{1-x}Se_xI$ (solid) (12)

According to equation (12), the standard thermodynamic functions of solid solution formation are calculated using the relations:

$$\Delta_f Z^0(\mathrm{BiS_{1-x}Se_x}) = \frac{2}{3}\Delta\overline{Z}_{\mathrm{Bi}} + \frac{1}{3}\Delta_f Z^0(\mathrm{BiI_3}) + +\Delta_f Z^0(\mathrm{S_{1-x}Se_x}), \quad (13)$$

and the standard entropies are –

$$S^0(\mathrm{BiS_{1-x}Se_x}) = \frac{2}{3}[\Delta\overline{S}_{\mathrm{Bi}} + S^0(\mathrm{Bi})] + \frac{1}{3}S^0(\mathrm{BiI_3}) + S^0(\mathrm{S_{1-x}Se_x}). \quad (14)$$

In calculations using equations (8)–(11) and (13)–(14), the values of standard entropies of bismuth, sulfur, and selenium recommended in modern reference literature (S^0(Bi) = 56.90±0.42, S^0(S) = 31.92±0.21, S^0(Se) = 42.13±0.21 J·mol^{-1}·K^{-1}) [51] were used, as well as the standard integral thermodynamic functions of BiI_3 compounds and binary $S_{1-x}Se_x$ alloys (x = 0.2, 0.4, 0.6, 0.8). For $S_{1-x}Se_x$ alloys, the values of $\Delta_f H^0$ and $\Delta_f S^0$ were taken from [52], and the standard entropy was calculated by combining the data from [52] with the above-given values of the standard entropies of elemental sulfur and selenium (Table 3). For BiI_3, the values of the functions $\Delta_f H^0$ and S^0 given in the reference books [53, 54] were used, and $\Delta_f G^0$ was calculated based on them (Table 4).

The obtained values of the standard integral thermodynamic functions are presented in Table 4. As can be seen, our data on ternary compounds are very close to those given in [32]. Thermodynamic data for $BiS_{1-x}Se_xI$ solid solutions have been determined for the first time. Their analysis shows a consistent decrease in the numerical values of the Gibbs free entropy and enthalpy with increasing selenium concentration. The behavior of the functions $\Delta_f S^0$ and S^0 is different: the formation of solid solutions is accompanied by an increase in the values of these functions from the stoichiometric compositions of the ternary compounds and passes through a maximum at approximately the composition $BiS_{0.4}Se_{0.6}I$, which is apparently associated with the contribution of the configurational entropy of the solid solutions.

Table 3. Standard integral thermodynamic functions of $S_{1-x}Se_x$ alloys [52]

Phase	$-\Delta_f G^0$ (298 K)	$-\Delta_f H^0$ (298 K)	$\Delta_f S^0$ (298 K)	S^0 (298 K)
	kJ·mol^{-1}		J·K^{-1}·mol^{-1}	
$S_{0.8}Se_{0.2}$	0.54	-0.8	4.5	38.5±0.3
$S_{0.6}Se_{0.4}$	0.84	-0.8	5.5	41.5±0.3
$S_{0.4}Se_{0.6}$	0.88	-1.0	6.3	44.4±0.3
$S_{0.2}Se_{0.8}$	0.69	-0.8	5.0	45.1±0.3

Table 4. Standard integral thermodynamic functions of the BiI_3, BiSI, BiSeI compounds and $BiS_{1-x}Se_xI$ solid solutions

Фаза	$\Delta_f G^0$(298 K)	$\Delta_f H^0$(298 K)	$\Delta_f S^0$ (298 K)	S^0 (298 K)
	kJ·mol^{-1}		J·K^{-1}·mol^{-1}	
BiI_3 [53, 54]	148.8±8.0	150.6±6.3	–	224.7±6.3
BiSI [32]	119.5±2.7	121.2±2.5	–	141.1±3.9
BiSI	119.3±2.8	121.7±2.9	−8.1±4.3	138.8±4.8
$BiS_{0.8}Se_{0.2}I$	115.3±2.8	115.9±2.8	−2.0±4.3	148.0±4.8
$BiS_{0.6}Se_{0.4}I$	112.3±2.8	111.6±2.9	2.3±4.2	152.7±4.7
$BiS_{0.4}Se_{0.6}I$	108.2±2.9	106.4±3.0	6.0±4.3	158.9±4.9
$BiS_{0.2}Se_{0.8}I$	103.7±2.9	103.5±3.0	0.7±4.4	154.6±4.9
BiSeI	99.8±2.8	102.7±2.8	−9.7±4.2	147.4±4.6
BiSeI [32]	100.0±2.8	102.4±2.5	–	148.6±3.6

4. Conclusions

Thus, we present new, consistent sets of thermodynamic data for the phases of the BiSI-BiSeI system, obtained by measuring the EMF of concentration cells with an ionic liquid as the electrolyte relative to a bismuth electrode. To rationally plan experiments and process their results, a solid-phase equilibria diagram of the BiSI-BiSeI-BiI_3 system and a fragment of the phase diagram of the Bi-S-Se-I system in the corresponding region were constructed using X-ray diffraction (XRD). The relative partial Gibbs free energy, enthalpy, and entropy of bismuth in the alloys were calculated from the EMF measurements. Based on the schematic phase diagram of the Bi-S-Se-I system, the virtual potential-forming reactions responsible for the indicated partial molar quantities were established. Using the obtained equations of potential-forming reactions, the standard thermodynamic functions of formation and the standard entropy of BiSI and BiSeI compounds, as well as $BiS_{1-x}Se_xI$ solid solutions of compositions x = 0.2, 0.4, 0.6, 0.8, were calculated. The thermodynamic functions of BiSI and BiSeI compounds are in good agreement with the literature, whereas those for solid solutions have been determined for the first time.

Contribution of the authors

A. A. Qurbanov – literature search, experimental research, participation in writing the original text. E. J. Ahmadov – processing of experimental data, participation in writing the article. G. M. Shukurova – participation in research and discussion of results. I. J. Alverdiev – scientific supervision, participation in discussion of results and text editing. Y. I. Jafarov – development of methodology of thermodynamic experiments and participation in text editing.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Mistewicz K., Das T. K., Nowacki B., … Masiuchok O. Bismuth sulfoiodide (BiSI) nanorods: synthesis, characterization, and photodetector application. *Scientific Reports*. 2023;13: 8800. https://doi.org/10.1038/s41598-023-35899-7

2. Peng B., Xu K., Zhang H., … Soukoulis C. M. 1D SbSeI, SbSI, and SbSBr with high stability and novel properties for microelectronic, optoelectronic, and thermoelectric applications. *Advanced Theory and Simulation*. 2018;1(1): 1700005. https://doi.org/10.1002/adts.201700005

3. Ganose A. M., Butler K. T., Walsh A., Scanlon D. O. Relativistic electronic structure and band alignment of BiSI and BiSeI: candidate photovoltaic materials. *Journal of Materials Chemistry A*. 2016;4: 2060–2068. https://doi.org/10.1039/C5TA09612J

4. Koc H., Palaz S., Mamedov A. M., Ozbay E. Optical, electronic, and elastic properties of some $A^5B^6C^7$ ferroelectrics (A=Sb, Bi; B=S, Se; C=I, Br, Cl): first principle calculation. *Ferroelectrics*. 2017;511: 22–34. https://doi.org/10.1080/00150193.2017.1332967

5. Xiong G. H., Liu T., Huang H. H., Wang J. Thermoelectric properties of Janus BiXI (X = S and Se) monolayers: a first-principles study. *Journal of Applied Physics*. 2024;136(18): 185102. https://doi.org/10.1063/5.0221109

6. Khan W., Hussain S., Minar J., Azam S. Electronic and thermoelectric properties of ternary chalcohalide semiconductors: first principles study. *Journal of Electronic Materials*. 2018;47: 1131–1139. https://doi.org/10.1007/s11664-017-5884-z

7. Govindaraj P., Venugopal K. Intrinsic ultra-low lattice thermal conductivity in orthorhombic BiSI: an excellent thermoelectric material. *Journal of Alloys and Compounds*. 2022;929: 167347. https://doi.org/10.1016/j.jallcom.2022.167347

8. Guo S. D., Guo X. S., Liu Z. Y., Quan Y. N. Large piezoelectric coeffcients combined with high electron mobilities in Janus monolayer XTeI (X=Sb and Bi): a first-principle study. *Journal of Applied Physics*. 2020;127(6): 064302. https://doi.org/10.1063/1.5134960

9. Zhuang H. L., Cooper V. R., Xu H., Ganesh P., Hennig R. G., Kent P. R. C. Rashba effect in single-layer antimony telluroiodide SbTeI. *Physical Review B*. 2015;92: 115302. https://doi.org/10.1103/PhysRevB.92.115302

10. Landolt G., Eremeev S. V., Koroteev Y. M., … Dil J. H. Disentanglement of surface and bulk rashbaspin splittings in noncentrosymmetric BiTeI. *Physical Review Letters*. 2012;109: 116403. https://doi.org/10.1103/PhysRevLett.109.116403

11. Li T., Xu Y., Li M., … Ju W. A study of the Rashba effect in two-dimensional ternary compounds ABC monolayers (A = Sb, Bi; B = Se, Te; C = Br; I). *Physical Chemistry Chemical Physics*. 2023;25: 3182–3189. https://doi.org/10.1039/D2CP05002A

12. Babanly M. B., Yusibov Y. A., Imamaliyeva S. Z., Babanly D. M., Alverdiyev I. J. Phase diagrams in the development of the argyrodite family compounds and solid solutions based on them. *Journal of Phase Equilibria and Diffusion*. 2024;45: 228–255. https://doi.org/10.1007/s11669-024-01088-w

13. Babanly M. B., Mashadieva L. F., Imamaliyeva S. Z., Babanly D. M., Taghiyev D. B., Yusibov Y. A. Complex copper-based chalcogenides: a review of phase equilibria and thermodynamic properties. *Condensed Matter and Interphases*. 2024;26(4): 579–619. https://doi.org/10.17308/kcmf.2024.26/12367

14. Babanly M. B., Mashadiyeva L. F., Babanly D. M., Imamaliyeva S. Z., Tagiev D. B., Yusibov Yu. A. Some issues of complex studies of phase equilibria and thermodynamic properties in ternary chalcogenide systems involving emf measurements (Review). *Russian Journal of Inorganic Chemistry*. 2019;64(13): 1649–1671. https://doi.org/10.1134/S0036023619130035

15. Babanly M. B., Mashadiyeva L. F., Babanly D. M., Imamaliyeva S. Z., Tagiev D. B., Yusibov Yu. A. Some issues of complex studies of phase equilibria and thermodynamic properties in ternary chalcogenide systems involving emf measurements (Review). *Russian Journal of Inorganic Chemistry*. 2019;64(13): 1649–1671. https://doi.org/10.1134/S0036023619130035

16. Morachevsky A. G., Voronin G. F., Geyderich V. A. Kutsenok I. B. *Electrochemical methods of investigation in hermodynamics of metal systems**. Moscow: Akademkniga Publ.; 2003. 334 p. (In Russ.)

17. Babanly M. B., Yusibov Y. A. Electrochemical methods in thermodynamics of inorganic systems*. Baku: BSU Publ.; 2011. 306 p. (in Russ.)

18. Ipser H., Mikula A., Katayama I. Overview: The emf method as a source of experimental thermodynamic data. *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry*. 2010;34(3): 271–278. https://doi.org/10.1016/j.calphad.2010.05.001

19. Voronin M. V., Osadchii E. G. Determination of thermodynamic properties of silver selenide by the galvanic cell method with solid and liquid electrolytes. *Russian Journal of Electrochemistry*. 2011;47(4): 420–426. https://doi.org/10.1134/S1023193511040203

20. Levanov A. V., Isaikina O. Y., Lunin V. V. Determining the potential of a silver/silver chloride electrode at different temperatures. *Russian Journal of Physical Chemistry A*. 2019;93: 770–773. https://doi.org/10.1134/S0036024419040186

21. Vassiliev V., Gong W. Electrochemical cells with the liquid electrolyte in the study of semiconductor, metallic and oxide systems. *Electrochemical Cells – New Advances in Fundamental Researches and Applications*. InTech. 2012. pp. 71–102. https://doi.org/10.5772/39007

22. Mammmadov F. M., Imamaliyeva S. Z., Akhmedov E. J., Tagiyev D. B., Babanly M. B. Thermodynamic properties of iron-gallium sulfides. *Russian Journal of Physical Chemistry A*. 2024;68(14): 3522–3529. https://doi.org/10.1134/S0036024424703126

23. Mammadov F. M., Babanly D. M., … Babanly M. B. Solid-phase relations in the FeSe-Ga_2Se_3-Se system and thermodynamic investigation of the $FeGa_2Se_4$ compound and $(FeSe)_{1-x}(Ga_2Se_3)_x$ solid solutions. Chemical Thermodynamics and Thermal Analysis. 2025;19: 100207. https://doi.org/10.1016/j.ctta.2025.100207

24. Kristavchuk A. V., Zabolotskaya A. V., Voronin M. V., Chareev D. A., Osadchii E. G. Temperature dependence of tellurium fugacity for the kotulskite (PdTe)–merenskyite ($PdTe_2$) equilibrium determined by the method of a solid-state galvanic cell. *Physics and Chemistry of Minerals*. 2021;48: 16. https://doi.org/10.1007/s00269-021-01141-x

25. Osadchii E. G., Voronin M. V. Thermodynamic properties of $RuTe_2$ evaluated by emf measurements on a solid state electrochemical cell. *Inorganic Materials*. 2024;60(3): 832–837. https://doi.org/10.1134/S0020168524701061

26. Moroz M. V., Tesfaye F., Demchenko P., Prokhorenko M., Prokhorenko, S., Reshetnyak O. Non-activation synthesis and thermodynamic properties of ternary compounds of the Ag-Te-Br system. *Thermochimica Acta*. 2021;698: 178862. https://doi.org/10.1016/j.tca.2021.178862

27. Moroz M., Tesfaye F., Demchenko P., … Gladyshevskii R. Synthesis, thermodynamic properties, and structural characteristics of multicomponent compounds in the Ag-Ni-Sn-S system. *JOM*. 2023;75: 2016–2025. https://doi.org/10.1007/s11837-023-05784-9

28. Alverdiev I. D., Imamalieva S. Z., Babanly D. M. Yusibov Yu. A., Tagiev D. B., Babanly M. B. Thermodynamic study of siver-tin selenides by the emf method with Ag_4RbI_5 solid electrolyte. *Russian Journal of Electrochemistry*. 2019;55: 467–474. https://doi.org/10.1134/S1023193519050021

29. Imamaliyeva S. Z., Mehdiyeva I. F., Qasymov V. A., Babanly D. M., Taghiyev D. B., Babanly M. B. Solid-phase equilibria and thermodynamic properties of phases in the Tm–Te system. *Russian Journal of Physical Chemistry A*.

2021;95(4): 926–932. https://doi.org/10.1134/S0036024421050149

30. Imamaliyeva S. Z., Babanly D. M., Zlomanov V. P., Taghiyev D. B., Babanly M. B. Thermodynamic properties of terbium tellurides. *Condensed Matter and Interphases*. 2020;22(4): 453–459. https://doi.org/10.17308/kcmf.2020.22/3116

31. Mammadov F. M., Babanly D. M., Imamaliyeva S. Z., Zeynalova G. S., Ahmadov E. I., Babanly M. B. Solid-phase equilibria in the FeS-In_2S_3-S system, thermodynamic properties of the $FeIn_2S_4$ compound and $(FeS)_{1-x}(In_2S_3)_x$ solid solutions. *The Journal of Chemical Thermodynamics*. 2026;213: 107585. https://doi.org/10.1016/j.jct.2025.107585

32. Imamaliyeva S. Z., Musayeva S. S., Babanly D. M., Jafarov Y. I., Taghiyev D. B., Babanly M. B. Determination of the thermodynamic functions of bismuth chalcoiodides by emf method wıth morpholinium formate as electrolyte. *Thermochimica Acta*. 2019;679: 178319. https://doi.org/10.1016/j.tca.2019.178319

33. Aliev Z. S., Musayeva S. S., Imamaliyeva S. Z., Babanly M. B. Thermodynamic study of antimony chalcoiodides by emf method with an ionic liquid. *Journal of Thermal Analysis and Calorimetry*. 2018;133: 1115–1120. https://doi.org/10.1007/s10973-017-6812-4

34. Hasanova G. S., Aghazade A. I., Babanly D. M., Imamaliyeva S. Z., Yusibov Y. A., M. B. Babanly. Experimental study of the phase relations and thermodynamic properties of BiSe system. *Journal of Thermal Analysis and Calorimetry*. 2022;147: 6403–6414. https://doi.org/10.1007/s10973-021-10975-0

35. Hasanova G. S., Aghazade A. I., Imamaliyeva S. Z., Yusibov Y. A., Babanly M. B. Refinement of the phase diagram of the Bi-Te system and the thermodynamic properties of lower bismuth Tellurides. *JOM*. 2021;73(5): 1511–1521. https://doi.org/10.1007/s11837-021-04621-1

36. Aliev Z. S., Musayeva S. S., Jafarli F. Y., Amiraslanov I. R., Shevelkov A. V. Babanly M. B. The phase equilibria in the Bi–S–I ternary system and thermodynamic properties of the BiSI and $Bi_{19}S_{27}I_3$ ternary compounds. *Journal of Alloys and Compounds*. 2014;610: 522–528. https://doi.org/10.1016/j.jallcom.2014.05.015

37. Babanly M. B., Tedenac J.-C., Aliev Z. S., Balitsky D. V. Phase eqilibriums and thermodynamic properties of the system Bi-Te-I. *Journal of Alloys and Compounds*. 2009;481(1-2): 349–353. https://doi.org/10.1016/j.jallcom.2009.02.139

38. Aliyev Z. S., Musaeva S. S., Babanly D. M., Shevelkov A. V., Babanly M. B. Phase diagram of the Sb-Se-I system and thermodynamic properties of SbSeI. *Journal of Alloys and Compounds*. 2010;505(2): 450–455. https://doi.org/10.1016/j.jallcom.2010.06.103

39. Aliyev Z. S., Babanly M. B. Shevelkov A. V., Babanly D. M., Tedenac J.-C. Phase diagram of the Sb-Te-I system and thermodynamic properties of SbTeI. *International Journal of Materials Research*. 2012;103(3): 290–295. https://doi.org/10.3139/146.110646

40. Aliev Z. S., Musayeva S. S., Babanly M. B. The phase relations in the Sb-S-I system and thermodynamic properties of SbSI. *Journal of Phase Equilibria and Diffusion*. 2017;38(12): 887–896. https://doi.org/10.1007/s11669-017-0601-4

41. Aliev Z. S., Ahmadov E. C., Babanly D. M., Amiraslanov I. R., Babanly M. B. The Bi_2Se_3-Bi_2Te_3-BiI_3 system: synthesis and characterization of the $BiTe_{1-x}Se_xI$ solid solutions. *Calphad*. 2019;66: 101650. https://doi.org/10.1016/j.calphad.2019.101650

42. Ahmadov E. J., Aliev Z. S., Babanly D. M., Imamaliyeva S. Z., Gasymov V. A., Babanly M. B. The quasi-ternary system Bi_2S_3–Bi_2Te_3–BiI_3. *Russian Journal of Inorganic Chemistry*. 2021;66: 538–549. https://doi.org/10.1134/S0036023621040021

43. Ahmadov E. J., Orujlu E. N., Babanly D. M., … Babanly M. B. Phase equilibria of the $Sb_2Te_3+2BiI_3 \leftrightarrow Bi_2Te_3+2SbI_3$ reciprocal system: synthesis and characterization of the cation-substituted $Bi_{1-x}Sb_xTeI$ solid solutions. *Journal of Alloys and Compounds*. 2022;929: 167388. https://doi.org/10.1016/j.jallcom.2022.167388

44. Ahmadov E. J. Physico-chemical interaction in the BiSI–BiTeI system. *Azerbaijan Chemical Journal*. 2020;1: 36–40. https://doi.org/10.32737/0005-2531-2020-1-36-40

45. Ahmadov E. J., Babanly D. M., Aliyev Z. S., Zlomanov V. P. Phase equilibria in the system SbTeI-BiTeI. *New Materials, Compounds and Applications*. 2019;3(2): 87–93. Available at: https://jomardpublishing.com/UploadFiles/Files/journals/NMCA/V3N2/Ahmadov%20et%20al.pdf

46. Qurbanov A., Ahmadov E., Alverdiyev I., Jafarov Y. Phsico-chemical interaction in the BiSI-BiSeI system. *Baku State University Journal of Chemistry and Material Sciences*. 2024;1(4): 6–12. https://doi.org/10.30546/209501.201.2024.1.04.061

47. Qurbanov A. A., Ahmadov E. J., Aghazade A. I., Aghayeva A. R., Gasymov V. A., Alverdiyev I. J. Phase equilibria in the $Bi_{19}S_{27}I_3$-"$Bi_{19}Se_{27}I_3$" system and characterization of solid solutions. *Azerbaijan Chemical Journal*. 2026;2: 145–152. https://doi.org/10.32737/0005-2531-2026-2-145-152

48. Emsley J. *The elements*. Oxford: Clarendon, Oxford University Publ.; 1998. 292 p.

49. Massalski T. B., Okamoto H., Subramanian P. R., Kacprzak L. *Binary alloy phase diagrams*. 2nd ed. Ohio: ASM International, Materials Park Publ.; 1990. 3589 p.

50. Brigouleix C., Anouti M., Jacquemin J., Caillon-Caravanier M., Galiano H., Lemordant D. Physicochemical characterization of morpholinium cation based protic ionic liquids used as electrolytes. *The Journal of Physical Chemistry B*. 2010;114(5): 1757–1766. https://doi.org/10.1021/jp906917v

51. Data base of thermal constants of substances. Digital version. Eds.: Iorish V.S., Yungman V.S., 2006. http://www.chem.msu.ru/cgi-bin/tkv.pl

52. Guan P. W., Shang S. L., Lindwall G., Anderson T., Liu Z. K. First-principles calculations and thermodynamic modeling of the S-Se system and implications for chalcogenide alloys. *Journal of Alloys and Compounds*. 2017;694: 510–521. https://doi.org/10.1016/j.jallcom.2016.10.037

53. Kubaschewski O., Alcock C. B., Spencer P. J. *Materials thermochemistry*. Oxford: New York: Pergamon Publ.; 1993. 363 p.

54. Barin I. *Thermochemical data of pure substances*. Third edition. New York: Willey Publ.; 2008. 1936 p.

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