THERMODYNAMIC PROPERTIES OF BISMUTH SESQUISELENIDE AND SESQUITELLURIDE AND THEIR SOLID SOLUTIONS

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The Gibbs free energies, enthalpies and entropies of formation of bismuth selenide Bi_2Se_3 between 308 and 408 K, bismuth telluride Bi_2Te_3 between 308 and 413 K, and their solid solutions between 670 and 840 K are measured using the e.m.f. method. Positive deviations of the activities of components in the solid solutions from the ideal behavior are found. The possibility of ordering effects in the solid solutions at lower temperatures is assumed.

Keywords: *Gibbs free energy, enthalpy, entropy, activity, solid solution, bismuth selenide, bismuth telluride.*

Metal chalcogenides and semiconductor materials on their basis hold much promise for optoelectronics and sensor microdevices. They also include $A_2^{V} B_3^{VI}$-type compounds, such as Bi_2Se_3 and Bi_2Te_3. They have been successfully used in thermoelectric devices for over 50 years. Of great interest are solid solutions based on individual semiconductor compounds because material properties vary widely in multicomponent systems [1–3] thus extending their application. Band-gap energy and lattice parameters usually vary in such semiconductors.

The objective of this paper is to examine the thermodynamic properties of Bi_2Se_3–Bi_2Te_3 solid solutions and individual Bi_2Se_3 and Bi_2Te_3 compounds that bound the solid solution using the e.m.f. method.

The individual compounds are discussed in many papers which consider, in particular, their synthesis, crystal structure, physical parameters, and applications. The thermodynamic properties of Bi_2Se_3 and Bi_2Te_3 have been examined in detail while their $Bi_2(Se_xTe_{1-x})_3$ solid solutions are poorly studied.

Bismuth Sesquiselenide Bi_2Se_3. Selenide Bi_2Se_3 is a compound that is most reach in selenium in the binary Bi–Se system and melts congruently at 979 K [4]. Bi_2Se_3 has rhombohedric lattice of tetradymite type (Bi_2Te_2S) with parameters $a = 413.4$ pm and $c = 2863$ pm [5]. We used the e.m.f. method to measure Bi_2Se_3 thermodynamic properties between 308 and 408 K:

$$(-)\, Bi \mid Bi^{+3} \text{ in electrolyte} \mid [\, Bi_2Se_3 + Se]\, (+). \tag{1}$$

The alloys containing 80 and 90 at.% Se were made by melting of bismuth (99.999%) and selenium (99.999%) at 1000 K for 5 h in Pyrex glass capsules that were evacuated and filed with helium (99.985%). The ingots were annealed at 773 K for 100 h, ground to powder, pressed, and then electrode pellets were sintered at the same temperature for electrochemical measurements. X-ray analysis of the samples has shown a two-phase region $[Bi_2Se_3 + Se]$.

To measure e.m.f., a U-shaped cell of molybdenum glass was used. The cell with electrodes was filled with electrolyte, evacuated to 10^{-2} Pa, filled with helium, and sealed. Dehydrated glycerin with small additions of KCl–NaCl–BiCl$_3$ salt alloy served as electrolyte. The e.m.f. temperature dependence was approximated by linear equation $E = A + BT = \overline{E} + B(T - \overline{T})$, where $\overline{E}$ and $\overline{T}$ are average e.m.f. and temperature. Equation parameters

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were calculated with the least-squares method and presented in a compact form as recommended in [6]: $n = 16$; $\overline{T} = 359.3$ K; $\overline{E} = 247.4$ mV; $B = -8.02 \cdot 10^{-3}$ mV/K; $\sum(T_i - \overline{T})^2 = 14393$ K^2; $\delta_0^2 = 1.17$ (mV)^2.

The temperature dependence of e.m.f. is described by the following equation between 308 and 408 K:

$$E = 0.2503 - 8 \cdot 10^{-6} \cdot T \text{ (V)}.$$

Gibbs energy of Bi_2Se_3 formation from solid components by reaction $2Bi_{(T)} + 3Se_{(T)} \rightarrow Bi_2Se_{3(T)}$ is as follows over this temperature range:

$$\Delta_f G^0 = -2zFE = -144940 + 4.63 \cdot T \text{ (J/mole)},$$

where z is bismuth ionic charge in the electrolyte ($z = +3$ [7]) and F is Faraday constant. Gibbs energy, enthalpy, and entropy of Bi_2Se_3 formation are $\Delta_f G^0 = -143.27 \pm 0.32$ kJ/mole, $\Delta_f H^0 = -144.9 \pm 3.8$ kJ/mole, and $\Delta_f S^0 = -4.6 \pm \pm 10.5$ J/(K $\cdot$ mole) at 360 K (average temperature).

The thermodynamic characteristics of Bi_2Se_3 that we determined agree well with published data within the error of measurement (Table 1).

A substantial difference of the standard formation enthalpy of Bi_2Se_3 determined in [12] by combustion in a calorimetric bomb from that of other studies and the value recommended in [17, 18] ($\Delta_f H^0$ (298.15 K) = −28.0 kJ/mole at.) may result from the inaccurate identification of bismuth combustion products.

Bismuth Sesquitelluride Bi_2Te_3. Telluride Bi_2Te_3 is a compound that is most reach in tellurium in the binary Bi–Te system and melts congruently at 860 K [4]. At temperatures close to the melting point, Bi_2Te_3 has a small homogeneity region: 59.8–60.2 at.% Te at 773 K and 59.7–60.1 at.% Te at 883 K. Below 700 K, this compound is a linear

TABLE 1. Thermodynamic Characteristics of Bismuth Selenide Formation from Solid Components at 298.15 K

$\Delta_f G^0$, kJ/mole at.	$\Delta_f H^0$, kJ/mole at.	$\Delta_f S^0$, J/(K $\cdot$ mole at.)	Method	T, K	References
−28.71 ± 0.07*	−29.0 ± 0.8	−0.9 ± 2.1	e.m.f.	308–408	Authors
−30.32	−30.7 ± 3.3	−1.3 ± 5.8	e.m.f.	555–583	[7, 8]
−28.22	−28.5 ± 0.4	−1.1	e.m.f.	310–411	[9]
	−30.5		C**		[10]
	−28.03 ± 0.13		C		[11]
	−11.63 ± 1.25		C		[12]
	−28.4 ± 1.2		VP***	735–897	[13, 14]
	−27.1 ± 1.2		C		[15]
	−31 ± 2		C		[16]

* Extrapolation. ** Calorimetry. *** Vapor pressure measurement.

TABLE 2. Thermodynamic Characteristics of Bismuth Telluride Formation

$\Delta_f G^0$, kJ/mole at. (T, K)	$\Delta_f H^0$, kJ/mole at.	$\Delta_f S^0$, J/ (K $\cdot$ mole at.)	Method	T, K	References
−17.47 ± 0.18 (360)	−19.9 ± 1.9	−6.7 ± 5.3	e.m.f.	308–413	Authors
−16.56 (298)	−17.4	−2.5	e.m.f.	555–585	[7, 8]
−15.73 ± 0.04 (673)	−20.4 ± 0.8	−7.0 ± 1.3	e.m.f.	643–683	[20, 21]
−15.68 (700 K)	−38.5 ± 8.4	−32.6 ± 3.1	e.m.f.	655–766	[22]
	−15.7 ± 0.8		C	298	[11]
	−16.82 ± 0.67		C	298	[23, 24]
	−4.6		C	853	[25]
	−16.1 ± 1.0		VP	298	[14]
	−13.1 ± 1.0		VP	298	[26]

phase. Bi_2Te_3 has rhombohedric lattice of tetradymite type with parameters a = 438.35 (5) pm and c = 3048.7 pm [19]. We used the e.m.f. method to measure Bi_2Te_3 thermodynamic properties between 308 and 413 K:

$$(-)\ Bi\ |\ Bi^{+3}\ in\ electrolyte\ |\ [Bi_2Te_3 + Te]\ (+). \tag{2}$$
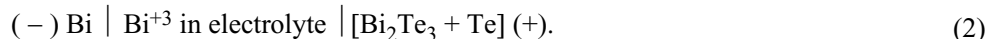
Alloys containing 70, 80, and 90 at.% Te were made of bismuth (99.999%) and T-V3-grade tellurium (99.996%) in the same way as bismuth selenide was (capsule synthesis). The ingots were annealed at 643 K (100 h). X-ray analysis has shown a two-phase region $[Bi_2Te_3 + Te]$.

The thermodynamic properties of Bi_2Te_3 were examined using the same procedure as for Bi_2Se_3. The e.m.f. temperature dependence of galvanic element (2) was approximated by a compact linear equation with n = 17; $\overline{T}$ = = 358.8 K; $\overline{E}$ = 151.0 mV; B = $-57.6 \cdot 10^{-3}$ mV/K; $\sum (T_i - \overline{T})^2$ = 19963 K^2; δ_0^2 = 9.37 (mV)^2.

The e.m.f. temperature dependence of galvanic element (2) is described by the following equation between 308–413 K:

$$E = 0.1716 - 57.6 \cdot 10^{-6} \cdot T\ (V),$$

giving

$$\Delta_f G^0\ (Bi_2Te_3) = -2zFE = -99365 + 33.35 \cdot T\ (J/mole).$$

The Gibbs energy, enthalpy and entropy of Bi_2Te_3 formation from solid components are $\Delta_f G^0$ = = -87.36 ± 0.92 kJ/mole, $\Delta_f H^0$ = -99.4 ± 9.5 kJ/mole, and $\Delta_f S^0$ = -33.4 ± 26.4 J/(K $\cdot$ mole) at average temperature (360 K). The results shown in Table 2 are comparable with published data. Our data agree well with those obtained in [20, 21] using the e.m.f. method, but they substantially differ from the results from vapor pressure measurements and calorimetry.

Solid Solutions Bi_2Se_3–Bi_2Te_3. The phase diagram of the quasibinary Bi_2Se_3–Bi_2Te_3 system was first plotted in [27]. It is established that a continuous series of solid solutions forms in this system and no ternary compounds are found. Subsequent studies of structural and physical properties and phase equilibria [28–34] confirmed the existence of a continuous series of solid solutions above 773 K. However, the Bi_2Se_3–Bi_2Te_3 solid solution undergoes some changes below 600 K whose nature is different according to different researchers. It is believed in [29] that the solid solution is ordered at these temperatures and ternary hexagonal Bi_2Te_2Se compound is formed. It is assumed in [32] that the solid solution is not ordered at low temperatures but, on the contrary, disintegrates into two new ones with rhombohedric structure of tetradymite type.

Information on the thermodynamic properties of the Bi_2Se_3–Bi_2Te_3 system is limited to calorimetric data on the formation enthalpies of solid solutions [35, 36]. However, the results of these studies are contradictory: the formation enthalpy of solid solutions is negative according to [35] and is positive according to [36]. We are not aware of data on Gibbs energies or formation entropies of the Bi_2Se_3–Bi_2Te_3 solid solutions.

The thermodynamic properties of alloys in the quasibinary Bi_2Se_3–Bi_2Te_3 system were examined by e.m.f. measurements between 670 and 840 K:

$$[Bi_2Te_3 + Te]\ |\ KCl–LiCl–BaCl_2–BiCl_3\ |\ [Bi_2Se_3–Bi_2Te_3 + Te]. \tag{3}$$

To make three-component samples, addition alloys were first melted whose composition corresponded to those of binary Bi_2Se_3 and Bi_2Te_3 compounds. They were synthesized from the same materials and in the same conditions as the individual components were. Polycrystalline Bi_2Se_3 and Bi_2Te_3 samples were broke to small pieces and ground in agate pounder. The resulting fine powders were mixed to produce samples of Bi_2Se_3–Bi_2Te_3 alloys. Six compositions containing 20.0, 40.0, 50.0, 60.0, 70.0, and 80.0 mole% Bi_2Te_3 were made. Pellets 10 mm in diameter were pressed of the thoroughly stirred mixtures and then placed in Pyrex capsules. The capsules with samples were evacuated to 10^{-2} Pa, filled with helium of high purity, and sealed. The samples were sintered and annealed at 773 K. The alloys containing 20.0, 40.0, 60.0, and 70.0 mole% Bi_2Te_3 were held at this temperature for 1600 h and alloys containing 50.0 and 80.0 mole% Bi_2Te_3 for 2210 h.

The annealed ingots were cut into parts for microstructural, x-ray, and thermodynamic analyses. According to microstructural and x-ray analyses, the samples were one-phase after long-term annealing.

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A part of the ingot intended for thermodynamic analyses was ground to powder in agate pounder. A small amount of elemental tellurium (99.996 wt.% Te) was added to the ground powder of the Bi_2Se_3–Bi_2Te_3 solid solution, thoroughly mixed and pressed into pellets 6 mm in diameter for electrochemical measurements. A tungsten–rhenium wire for current contact was pressed into pellets. The pellets were placed in molybdenum glass capsules, evacuated to 10^{-2} Pa, filled with helium of high purity, and sealed. The samples were sintered at 700 K for 24 h.

A eutectic mixture of anhydrous potassium, lithium, and barium chlorides that was smelted in vacuum (10^{-1} Pa) and had the melting temperature at 593 K [37] was used as electrolyte. All salts were qualified as chemically pure. Bismuth trichloride was first dehydrated in slow heating in vacuum with gradually increasing temperature to ~400 K, and lithium chloride by holding in a drying cabinet with gradually increasing temperature until it was completely dehydrated. It took about 100 h to completely dry LiCl. Bismuth ionic charge in electrolyte was taken equal to +3.

The reversible transfer of bismuth from Bi_2Te_3, which is in equilibrium with tellurium, to the solid solution, which is also equilibrium with tellurium, is voltage-generating process for galvanic element (3). The e.m.f. determines the activity and partial Gibbs energy of Bi_2Te_3 as a component of the solid solution of this composition (Bi solubility in Te over a range of research temperatures is negligibly small [4], i.e., $a_{Te} = 1$), and Bi_2Te_3 thermodynamic functions in the solid solution are determined by common equations with the e.m.f. method:

$$\Delta\overline{G}_{Bi_2Te_3} = RT\ln\alpha_{Bi_2Te_3} = -zFE,$$

$$\Delta\overline{S}_{Bi_2Te_3} = zF \cdot dE/dT = zF \cdot B,$$

$$\Delta\overline{H}_{Bi_2Te_3} = -zF(\overline{E} - B\overline{T}) = -zFA.$$

Table 3 summarizes the parameters of these equations calculated with the least-squares method.

The partial thermodynamic functions of bismuth selenide were determined by the graphical integration of Gibbs–Duhem equation and integral functions by adding partial values as follows:

$$\Delta\overline{\Phi}_{Bi_2Se_3} = \int_0^{x_{Bi_2Te_3}} x_{Bi_2Te_3}/(1 - x_{Bi_2Te_3})\ d(\Delta\overline{\Phi}_{Bi_2Te_3}),$$

$$\Delta\Phi_{Bi_2Se_3} = x_{Bi_2Te_3} \cdot \Delta\overline{\Phi}_{Bi_2Te_3} + (1 - x_{Bi_2Te_3}) \cdot \Delta\overline{\Phi}_{Bi_2Se_3},$$

where $\Delta\Phi$ is ΔG^{ex}, ΔH, or ΔS.

Tables 4 to 6 summarize the thermodynamic functions for the formation of Bi_2Se_3–Bi_2Te_3 solid solutions from binary compounds. Moderate positive deviations of activities from Raoult law (Fig. 1) are typical of these solutions (Fig. 1). There is some similarity in the thermodynamic behavior of Bi_2Se_3–Bi_2Te_3 solid solutions and Se–Te molten alloys, which also have small positive deviations from Raoult law (Fig. 2) as established in [38, 39]. Note that we observed such similarity previously for ZnTe–CdTe and ZnTe–HgTe solid solutions and Zn–Cd and Zn–Hg liquid solutions [40].

TABLE 3. E.M.F. Measurement of Galvanic Elements (3)

$x_{Bi_2Te_3}$	n	$\overline{E}$, mV	$\overline{T}$, K	B, mV/K	$\sum(T - \overline{T})^2$, (K)^2	δ_0^2, (mV)^2
0.200	15	27.39	767	0.01385	49556	$4.7 \cdot 10^{-3}$
0.400	15	14.25	767	−0.00054	49556	$7.19 \cdot 10^{-3}$
0.500	15	11.01	767	−0.00268	49556	$6.2 \cdot 10^{-3}$
0.600	15	8.74	754	−0.00174	41595	$12.5 \cdot 10^{-3}$
0.700	15	6.49	754	0.00124	41595	$11.1 \cdot 10^{-3}$
0.800	15	4.11	754	0.00265	41595	$7.1 \cdot 10^{-3}$
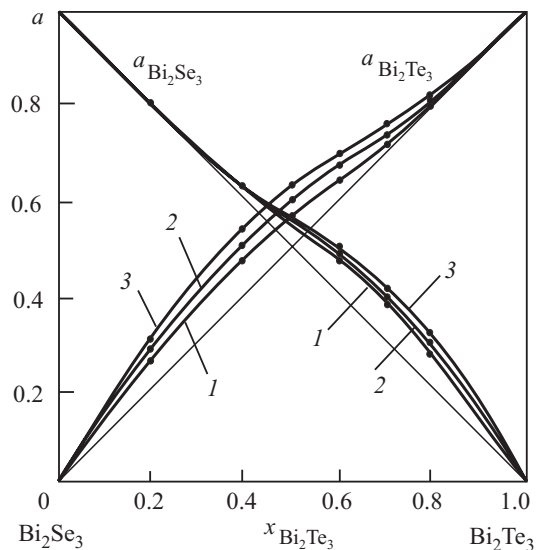
Fig. 1
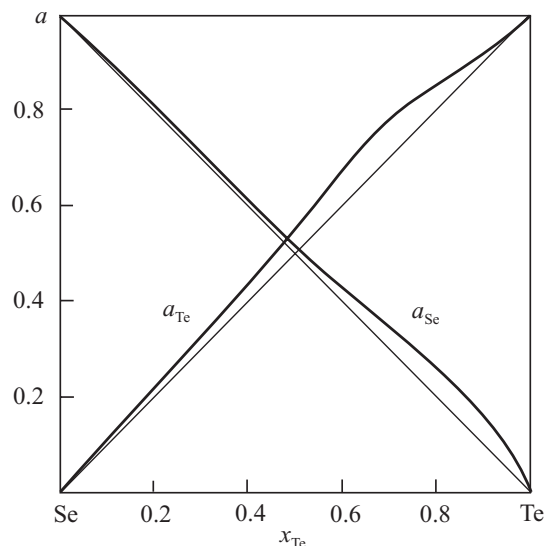
Fig. 2

Fig. 1. Activity of components in the Bi_2Se–Bi_2Te_3 quasibinary system at 673 (*1*), 750 (*2*), and 833 K (*3*)

Fig. 2. Activity of components in the Se–Te binary system at 923 K, according to [38]

TABLE 4. Activities (at 673, 750, and 833 K) and Partial Thermodynamic Values for Bi_2Te_3 in the Formation of Bi_2Se_3–Bi_2Te_3 Solid Solutions (at 750 K)

$x_{Bi_2Te_3}$	$a_{Bi_2Te_3}$			$\Delta\overline{G}_{Bi_2Te_3}$	$\Delta G_{Bi_2Te_3}^{-ex}$	$\Delta\overline{H}_{Bi_2Te_3}$	$\Delta\overline{S}_{Bi_2Te_3}$	$\Delta S_{Bi_2Te_3}^{-ex}$
	673 K	750 K	833 K	J/mole			J/(K · mole)	
0.2	0.259	0.283	0.306	−7871 ± 11	2165	−4854 ± 69	4.02 ± 0.08	−9.36
0.4	0.477	0.516	0.552	−4126 ± 14	1588	−4243 ± 85	−0.16 ± 0.09	−7.77
0.5	0.558	0.599	0.636	−3195 ± 13	1126	−3780 ± 79	−0.78 ± 0.09	−6.54
0.6	0.631	0.668	0.698	−2516 ± 18	668	−2909 ± 120	−0.52 ± 0.14	−4.77
0.7	0.718	0.739	0.759	−1886 ± 17	339	−1609 ± 113	0.37 ± 0.13	−2.60
0.8	0.818	0.827	0.835	−1207 ± 13	184	−611 ± 90	0.79 ± 0.10	−1.06

TABLE 5. Activities (at 673, 750, and 833 K) and Partial Thermodynamic Values for Bi_2Se_3 in the Formation of Bi_2Se_3–Bi_2Te_3 Solid Solutions (at 750 K)

$x_{Bi_2Te_3}$	$a_{Bi_2Se_3}$			$\Delta\overline{G}_{Bi_2Se_3}$	$\Delta G_{Bi_2Se_3}^{-ex}$	$\Delta\overline{H}_{Bi_2Se_3}$	$\Delta\overline{S}_{Bi_2Se_3}$	$\Delta S_{Bi_2Se_3}^{-ex}$
	673 K	750 K	833 K	J/mole			J/(K · mole)	
0.8	0.805	0.806	0.806	−1345	50	−46	1.73	−0.13
0.6	0.627	0.630	0.634	−2881	304	−326	3.41	−0.84
0.5	0.552	0.559	0.565	−3627	696	−712	3.89	−1.88
0.4	0.474	0.490	0.506	−4448	1265	−1801	3.53	−4.09
0.3	0.373	0.407	0.434	−5605	1904	−4292	1.75	−8.26
0.2	0.251	0.290	0.327	−7719	2317	−7452	0.36	−13.03

TABLE 6. Integral Thermodynamic Functions of Formation of Bi_2Se_3–Bi_2Te_3 Solid Solutions at 750 K

$x_{Bi_2Te_3}$	ΔG	ΔG^{ex}	ΔG^{0*}	ΔH	ΔH^{0*}	ΔS	ΔS^{ex}	ΔS^{0*}
	J/mole					J/(K · mole)		
0.2	−2650	473	−130660	−1008	−136810	2.19	−1.97	−8.2
0.4	−3379	818	−117980	−1893	−128590	1.98	−3.61	−14.1
0.5	−3411	911	−111300	−2246	−124380	1.55	−4.21	−17.4
0.6	−3289	907	−104470	−2466	−120050	1.10	−4.50	−20.8
0.7	−3002	809	−97480	−2414	−115440	0.78	−4.30	−24.0
0.8	−2509	611	−90280	−1979	−110450	0.71	−3.45	−26.9

*From solid bismuth, selenium, and tellurium.

The formation enthalpy of the solid solutions is negative (Table 6). The $\Delta_f H$ values obtained in [35] by calorimetric dissolution in molten bismuth are also negative but are more exothermic than our results from e.m.f. measurements. The minimal value of this function, according to our data and [35], corresponds to Bi_2Te_2Se.

The results indicate that the activities of Bi_2Se_3–Bi_2Te_3 quasibinary system components decrease at lower temperatures (Fig. 1). This is evidence that the thermodynamic stability of solid solutions increases. Considering that the enthalpy of formation is also negative, we can conclude that the solid solutions may be ordered at lower temperatures. This conclusion agrees with the paper [29], which established ternary Bi_2Te_2Se compound.

REFERENCES

1. N. Kh. Abrikosov, V. F. Bankina, L. V. Poretskaya, et al., *Semiconductors, Their Production and Properties* [in Russian], Nauka, Moscow (1967), p. 176.
2. *Solid Solutions in Semiconductor Systems: Handbook* [in Russian], Nauka, Moscow (1978).
3. G. R. Miller, Li Che-Yu, and C. W. Spenser, "Properties of Bi_2Te_3–Bi_2Se_3 alloys," *J. Appl. Physics*, **34**, No. 5, 1398–1400 (1963).
4. T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak (ed.), *Binary Alloy Phase Diagrams* (in 3 vols.), Metals Park, ASM, Ohio (1990), p. 3589.
5. S. N. Chizhevskaya, L. E. Shelimova, and I. A. Zaitseva, "Critical assessment and agreement of data on the Bi–Se phase diagram," *Neorg. Mater.*, **30**, No. 11, 1379–1387 (1994).
6. "Recommendations of the Scientific Council on Chemical Thermodynamics and Thermochemistry of USSR Academy of Sciences," *Zh. Fiz. Khim.*, **46**, No. 11, 2975–2979 (1972).
7. B. T. Melekh, *Research into Some Physical and Chemical Properties of Tellurides and Selenides of Group IV and V Elements* [in Russian], Author's Abstract of PhD Thesis, Moscow (1968), p. 23.
8. B. T. Melekh and S. A. Semenkovich, "Thermodynamic properties of telluride and selenide of trivalent bismuth," *Izv. AN SSSR. Neorg. Mater.*, **4**, No. 8, 1346–1348 (1968).
9. V. P. Vasil'ev, A. P. Somov, A. V. Nikol'skaya, and Ya. I. Gerasimov, "E.m.f. research of thermodynamic properties of bismuth selenide," *Zh. Fiz. Khim.*, **42**, No. 3, 675–677 (1968).
10. L. A. Andreeva and A. A. Kudryavtsev, "Formation heat of bismuth selenide (Bi_2Se_3)," *Tr. MKhTI im. D. I. Mendeleeva*, **49**, 25–27 (1965).
11. B. W. Howlett, S. Misra, and M. B. Beᴠer, "On the thermodynamic properties of the compounds Sb_2Se_3, Bi_2Se_3, Sb_2Te_3 and Bi_2Te_3," *Trans. Metall. Soc. AIME*, **230**, Nо. 10, 1367–1372 (1964).
12. G. Gattow and A. Schneider, "Die bildungswärmen der wismuthchalkogenide," *Angew. Chem.*, **67**, No. 11, 306–307 (1955).
13. Z. Boncheva-Mladenova, A. S. Pashinkin, and A. V. Novoselova, "Determination of saturated steam pressure of solid bismuth selenide," *Izv. AN SSSR. Neorg. Mater.*, **4**, No. 7, 1027–1031 (1968).

14. Z. Boncheva-Mladenova, *Evaporation and Oxidation of Bismuth and Stibium Tellurides and Bismuth Selenide* [in Russian], Author's Abstract of PhD Thesis, Moscow (1969), p. 15.

15. T. A. Stolyarova, N. M. Gavrilov, and N. Ya. Nekrasov, "Thermodynamic properties of bismuth selenide," *Geokhimiya*, **9**, No. 9, 1367–1374 (1990).

16. H. Bros, R. Castanet, and H. V. Kehiaian, "Etude calorimetrique du systeme bismuth–selenium," *High Temp. High Pressures*, **8**, No. 3, 271–278 (1976).

17. K. S. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworth, London (1974), p. 854.

18. S. A. Semenkovich, K. B. Sadykov, and N. G. Bekledova, "Optical and electrophysical study of chemical reactions in solids," *Izv. AN TSSR, Ser. Fiz. Tekhn. Khim. Geol. Nauk*, No. 2, 17–29 (1989).

19. S. N. Chizhevskaya, L. E. Shelimova, S. V. Zemskov, et al., "Critical assessment of agreement of data on the Bi–Te phase diagram," *Neorg. Mater.*, **30**, No. 1, 3–11 (1994).

20. Ya. I. Gerasimov, A. V. Nikolskaya, V. A. Geiderikh, et al., "E.m.f. study of thermodynamic properties of some semiconductor alloys," in: *Chemical Bonds in Semiconductors and Solids* [in Russian], Nauka i Tekhnika, Minsk (1965), pp. 113–121.

21. Ya. I. Gerasimov and A. V. Nikol'skaya, "Thermodynamic properties of bismuth telluride (Bi_2Te_3) and stibium telluride (Sb_2Te_3)," in: *Metallurgy and Physics of Semiconductors* [in Russian], Izd. AN SSSR, Moscow (1961), pp. 30–33.

22. C.-C. Liu and J. C. Angus, "Electromotive force investigation of the bismuth–tellurium," *J. Electrochem. Soc.*, **116**, No. 8, 1054–1060 (1969).

23. A. S. Skoropanov, *Formation Enthalpies of Binary and Ternary Metal Alloys with Quantitative Thermographic Analysis* [in Russian], Author's Abstract of PhD Thesis, Minsk (1975), p. 22.

24. A. A. Vecher, L. A. Mechkovskii, and A. S. Skoropanov, "Formation heats of some tellurides," *Izv. AN SSSR. Neorg. Mater.*, **10**, No. 12, 2140–2143 (1974).

25. G. Morgan, Y. Feutelais, B. Legendre, et al., "Thermodynamic behavior of Bi–Te alloys," *Z. Metallkunde*, **81**, No. 1, 44–48 (1990).

26. Z. Boncheva-Mladenova, A. S. Pashinkin, and A. V. Novoselova, "Pressure of saturated steam of solid bismuth telluride," *Izv. AN SSSR. Neorg. Mater.*, **4**, No. 2, 291–292 (1968).

27. J. P. Mc Hugh and W. A. Tiller, "Solid–liquid phase equilibria in the pseudo-binary system Bi_2Te_3–Bi_2Se_3," *Trans. Metallurg. Soc. AIME*, **215**, No. 4, 651–655 (1959).

28. G. R. Miller, Li Che-Yu, and C. W. Spencer, "Properties of Bi_2Te_3–Bi_2Se_3 alloys," *J. Appl. Physics*, **34**, No. 5, 1398–1400 (1963).

29. V. F. Bankina and N. Kh. Abrikosov, "System Bi_2Te_3–Bi_2Se_3," *Zh. Neorg. Khim.*, **9**, No. 4, 931–936 (1964).

30. G. N. Gordyakova, A. N. Gorbacheva, and S. S. Sinani, "Thermodynamic properties of unalloyed bismuth telluride and solid solutions in the Bi_2Te_3–Bi_2Se_3 system," *Izv. AN SSSR. Neorg. Mater.*, **4**, No. 7, 1191–1192 (1968).

31. N. Kh. Abrikosov and M. M. Stasova, "Solid solutions based on bismuth and stibium tellurides and bismuth selenides," *Izv. AN SSSR. Neorg. Mater.*, **21**, No. 12, 2011–2015 (1985).

32. J.-C. Tedenac, G. Brun, B. Liautard, et al., "Phase equilibria in multicomponent chalcogenides. Application of phase diagrams in semiconductor science," *Powder Metall. Met. Ceram.*, **36**, No. 1–2, 3–14 (1997).

33. T. E. Svechnikova, H. M. Maksimova, N. V. Polikarpova, and P. P. Konstantinov, "Thermoelectric properties of monocrystals of $Bi_2Te_{2.85}Se_{0.15}$ solid solutions alloyed with copper," *Neorg. Mater.*, **34**, No. 3, 277–280 (1998).

34. T. E. Svechnikova, N. M. Maksimova, and P. P. Konstantinov, "Alloying of monocrystals of Bi_2Te_3-based solid solutions with bismuth sulfide," *Neorg. Mater.*, **34**, No. 3, 302 (1998).

35. S. Misra and M. B. Bever, "On the solid solutions of bismuth telluride and bismuth selenide," *J. Phys. Chem. Sol.*, **25**, 1233–1241 (1964).

36. R. Blachnik and U Rabe, "Mischungesenthalpien von flΰssigen Vb-seleniden mit Vb-telluriden," *J. Less-Common Metals*, **64**, No. 2, 295–298 (1979).

37. B. G. Korshunov, V. V. Safonov, and D. V. Drobot, *Phase Diagrams of Chloride Systems* [in Russian], Khimiya, Leningrad (1972), p. 383.

38. F. L. Konopel'ko, Yu. N. Sveshnikov, and D. K. Belashenko, "Thermodynamic activity of components in Te–Se melts," *Izv. AN SSSR. Neorg. Mater.*, **9**, No. 6, 935–937 (1973).

39. N. Mouloudj, G. Petot-Ervas, C. Petot, and B. Legendre, "Etude des proprietes thermodynamiques des alliages liquids selenium–tellure. Partie I. Determination des propriétés thermodynamiques par la mèthode des f.e.m. de piles," *Thermochim Acta.*, **136**, 87–102 (1998).

40. L. V. Goncharuk and V. R. Sidorko, "Thermodynamic properties of some solid solutions formed with $A^{II}B^{IV}$ and $A^{II}B^{V}$ semiconductor compounds," *Powder Metall. Met. Ceram.*, No. 7–8, 79–84 (1996).