Thermodynamic properties of solid solutions in the $PbSe—AgSbSe_2$ system

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The results of the study of the $PbSe—AgSbSe_2$ system by measuring the emf of concentration chains with respect to PbSe in a temperature range of 300—450 K are presented. The formation in the system of a wide (37—100 mol.% $AgSbSe_2$) region of solid solutions based on $AgSbSe_2$ is shown. The partial thermodynamic functions of PbSe and lead in the alloys are calculated from the equations of the temperature dependences of the emf. The standard thermodynamic functions of formation and standard entropies of solid solutions $(2PbSe)_x(AgSbSe_2)_{1-x}$ (x = 0.4, 0.6, 0.8, and 0.9) are calculated by the integration of the Gibbs—Duhem equation over the $PbSe—AgSbSe_2$ section using the literature data on the corresponding thermodynamic data for compounds PbSe and $AgSbSe_2$.

Key words: $PbSe—AgSbSe_2$ system, thermodynamic properties, EMF method, solid solutions, silver—lead—antimony selenides.

Thermoelectric materials attract increasing attention in the recent decades as alternative power sources.[1—3] Among similar materials, alloys $Ag—A^{IV}—M^{V}—X$ (where A^{IV} is Ge, Sn, and Pb; M^{V} is Sb, and Bi; X is Se and Te) play an important role, being highly efficient thermoelectric materials with an anomalously low thermal conductivity.[4—9] In addition, many silver chalcogenides with A^{IV} and M^{V} elements are characterized by interesting photoelectrical and optical properties,[10—12] and some of them have mixed ion—electron conductivity, due to which they are very promising for use in the production of photoelectrode materials, electrochemical converters of solar energy, *etc.*[13—16]

The development of methods and optimization of the synthesis conditions for new multicomponent materials require reliable data on the phase equilibria and thermodynamic properties of the corresponding systems.[17,18] A number of works on studying the thermodynamic properties of ternary and more complicated silver chalcogenides has recently been published.[19—24] We presented[25—28] the results of the complex study of the phase equilibria and thermodynamic properties of quasi-ternary systems $Ag_2Se—PbSe—Bi_2Se_3$,[25] $Ag_2Te—PbTe—Bi_2Te_3$,[26] $Ag_2Te—SnTe—Bi_2Te_3$,[27] and $Ag_2Te—SnTe—Sb_2Te_3$,[28] in which broad regions of solid solutions along the $A^{IV}X—AgM^{V}X_2$ sections were revealed. They are of significant practical interest as potential thermoelectric materials.

This work is devoted to the study of the thermodynamic properties of solid solutions in the $PbSe—AgSbSe_2$ system. We have previously studied the phase equilibria in this system[29] and showed that the system is quasi-binary, refers to the peritectic type, and is characterized by the formation of a wide region of solid solutions based on $AgSbSe_2$.

Experimental

The thermodynamic study of the $PbSe—AgSbSe_2$ system was carried out by the EMF method with the glycerol electrolyte. This variant of the EMF method is successfully used for thermodynamic investigations of binary and more complicated metallic, semiconductor, and other systems.[30—37]

We composed the concentration chains of the type

$$(-)\ PbSe\ (s)\ |\ \text{liquid electrolyte},$$

$$Pb^{2+}\ |\ (2PbSe)_x(AgSbSe_2)_{1-x}\ (s)\ (+)\ \textbf{(I)}$$

and measured their emf in the temperature range 300—450 K. It has previously been shown[36,37] that for similar systems the concentration (with respect to the lead electrode) chains are irreversible: the emf values continuously decrease during experiments. This is likely caused by a change in the composition of the electrodes due to the chemical interaction between them through the electrolyte.

The initial compounds PbSe and $AgSbSe_2$, which melt congruently at 1354 (see Ref. 38) and 908 K,[39] respectively, were

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primarily synthesized for experiments. The synthesis was carried out by smelting the corresponding elemental components in stoichiometric ratios in evacuated (to ~10^{-2} Pa) and sealed quartz ampules at the temperatures by 50 K higher than the melting points of the corresponding compounds. The following high-purity simple substances (EVOCHEM Advanced Materials GmbH, Germany) were used: silver in granules (Ag-00047; 99.999%), antimony in granules (Sb-00002; 99.999%), lead in granules (Pb-00005; 99.9995%), and selenium in granules (Se-00002; 99.999%). Since the pressure of selenium vapors is high at the melting points of lead selenide, this compound was synthesized in the two-zone regime. The temperature of the hot zone was 1390 K, and that of the cold zone was 900 K, which is somewhat lower than the boiling point of selenium (958 K).[40] The synthesized compounds were identified by DTA and X-ray diffraction analysis (XRD).

Equilibrium alloys $(2PbSe)_x(AgSbSe_2)_{1-x}$ (x = 0.1, 0.2, 0.4, 0.6, 0.7, and 0.9) served as the right electrodes in the chains of type **I**. They were prepared from the preliminarily synthesized initial compounds under vacuum conditions. The compositions were chosen taking into account the data on the phase equilibria in this system.[29] In order to bring the alloys to the equilibrium state as close as possible and to eliminate compositional heterogeneity of the solid solutions, the cast non-homogenized samples obtained by alloy quenching were powdered, thoroughly mixed, pressed in pellets 0.5—0.7 g in weight, and annealed first at 850 K (500 h) and then at 450 K (500 h).

For the preparation of electrodes, PbSe (left electrode) and annealed alloys $(2PbSe)_x(AgSbSe_2)_{1-x}$ were powdered and pressed on molybdenum current leads as pellets with a diameter of ~0.6 cm and a thickness of ~0.3 cm.

A solution of KCl in glycerol (analytical purity grade) with the addition of $PbCl_2$ served as an electrolyte. To prevent the presence of moisture and oxygen in the electrolyte, glycerol was pre-dehydrated and degassed by pumping out at ~400 K and the anhydrous chemically pure salts were used.

The structure of the used electrochemical cell and procedure of its assembling and emf measurements were described in detail.[31,41] The measurements of the emf were performed in an inert atmosphere with a V7-91 high-ohmic digital voltmeter. Prior to measurements, the electrochemical cell was kept at ~350 K for 40—60 h, after which the first equilibrium emf values were obtained. The subsequent measurements were carried out at an interval of 3—4 h after a desired temperature was established. The emf values, which did not differ from each other at a given temperature by more than 0.2 mV regardless the direction of temperature changing, considered to be equilibrium.

Results and Discussion

The dependence of the emf for the chains of type **I** at 300 K on the composition of the PbSe—AgSbSe$_2$ system is presented in Fig. 1. As can be seen from Fig. 1, the emf values for the samples with compositions 10 and 30 mol.% AgSbSe$_2$ remain constant regardless the total composition and are close to zero (3—4 mV). This is consistent with the phase diagram,[29] according to which the alloys with these compositions are two-phase and contain the phase rich in PbSe. The reproducible emf values, which are the monotonic function of the composition, were obtained for the samples with compositions 40, 60, 80, and 90 mol.% AgSbSe$_2$. This result confirms the earlier obtained data[29] on the formation of more than 60 mol.% solid solutions based on AgSbSe$_2$ in the PbSe—AgSbSe$_2$ system.

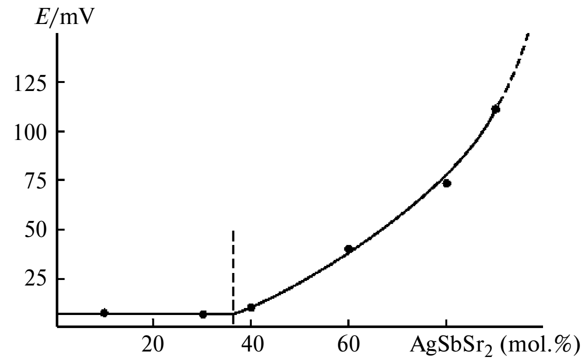

Fig. 1. Dependence of the emf of the chains of type **I** at 300 K on the composition of the PbSe—AgSbSe$_2$ system.

The formation of the solid solutions in the PbSe—AgSbSe$_2$ system was also confirmed by the XRD data. The powder XRD patterns of some annealed PbSe—AgSbSe$_2$ alloys are presented in Fig. 2. As can be seen from Fig. 2, the diffraction patterns of the alloys containing ~40 mol.% AgSbSe$_2$ are qualitatively similar to the diffraction patterns of pure AgSbSe$_2$ with some shift of the reflections. The XRD patterns of the alloys with compositions 10 and 30 mol.% AgSbSe$_2$ consist of diffraction lines of two cubic phases.

The temperature dependences of the emf for the samples from the homogeneity region of the studied system are presented in Fig. 3. They are nearly linear and, therefore, the experimental data were processed by least squares in the approximation of the linear temperature dependence of the emf using the Microsoft Office Excel 2003 computer program. The calculation steps for the $(2PbSe)_{0.1}(AgSbSe_2)_{0.9}$ alloy are presented in Table 1.

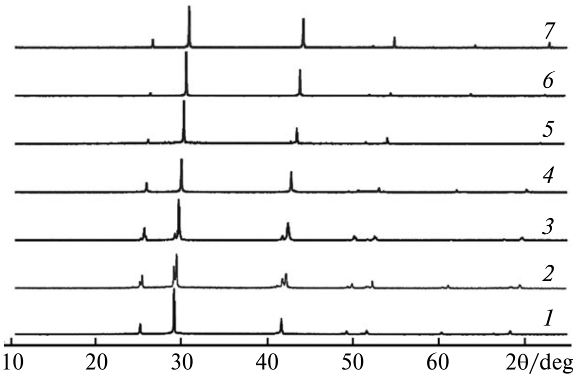

Fig. 2. Powder XRD patterns for the initial compounds and some alloys of the PbSe—AgSbSe$_2$ system: PbSe (*1*), 10 mol.% AgSbSe$_2$ (*2*), 30 mol.% AgSbSe$_2$ (*3*), 40 mol.% AgSbSe$_2$ (*4*), 60 mol.% AgSbSe$_2$ (*5*), 80 mol.% AgSbSe$_2$ (*6*), and AgSbSe$_2$ (*7*).

Table 1. Experimental temperature (T_i) and emf (E_i) values and the data related to the calculation steps of the equation $E = a + bT \pm t\left[(S_E^2/n) + S_b^2 \cdot (T-\bar{T})^2\right]^{1/2}$ for the sample $(2PbSe)_{0.1}(AgSbSe_2)_{0.9}$

T_i/K	E_i/mV	$(T_i - \bar{T})$/K	$E_i(T_i - \bar{T})$/mV K	$(T_i - \bar{T})^2$/K^2	$\tilde{E}$	$E_i - \tilde{E}$	$(E_i - \tilde{E})^2$/mV^2
					mV		
301.2	112.7	−72.84	−8209.44	5306.15	112.27	0.43	0.19
305.7	112.5	−68.34	−7688.63	4670.81	112.51	−0.01	0.00
310.2	112.8	−63.84	−7201.53	4075.97	112.74	0.06	0.00
315.8	113.6	−58.24	−6616.44	3392.29	113.04	0.56	0.31
319.4	113.0	−54.64	−6174.70	2985.89	113.23	−0.23	0.05
325.7	113.4	−48.34	−5482.13	2337.08	113.56	−0.16	0.03
331.1	114.4	−42.94	−4912.72	1844.13	113.85	0.55	0.30
335.6	113.6	−38.44	−4367.16	1477.89	114.09	−0.49	0.24
340.3	115.0	−33.74	−3880.48	1138.61	114.33	0.67	0.44
347.1	114.2	−26.94	−3076.93	725.94	114.69	−0.49	0.24
351.5	115.6	−22.54	−2606.01	508.20	114.93	0.67	0.45
355.7	114.4	−18.34	−2098.48	336.48	115.15	−0.75	0.56
362.4	115.1	−11.64	−1340.15	135.57	115.50	−0.40	0.16
365.5	115.2	−8.54	−984.19	72.99	115.67	−0.47	0.22
369.3	116.3	−4.74	−551.65	22.50	115.87	0.43	0.19
372.1	115.5	−1.94	−224.45	3.78	116.01	−0.51	0.26
379.8	116.5	5.76	670.65	33.14	116.42	0.08	0.01
386.3	116.5	12.26	1427.90	150.23	116.76	−0.26	0.07
393.3	116.9	19.26	2251.10	370.82	117.13	−0.23	0.05
398.2	118.3	24.16	2857.73	583.54	117.39	0.91	0.82
403.5	117.5	29.46	3461.16	867.70	117.67	−0.17	0.03
408.1	117.3	34.06	3994.85	1159.86	117.92	−0.62	0.38
413.8	117.3	39.76	4663.46	1580.59	118.22	−0.92	0.84
415.7	118.4	41.66	4932.15	1735.28	118.32	0.08	0.01
422.6	118.1	48.56	5734.54	2357.75	118.68	−0.58	0.34
426.8	118.8	52.76	6267.49	2783.27	118.90	−0.10	0.01
434.5	119.7	60.46	7236.66	3655.01	119.31	0.39	0.15
438.6	120.0	64.56	7746.80	4167.56	119.53	0.47	0.22
443.3	120.2	69.26	8324.65	4796.49	119.78	0.42	0.18
448.2	120.7	74.16	8950.71	5499.21	120.03	0.67	0.44

**Note:* T_i and E_i are the measured temperatures and emf; $\bar{T}$ = 374.04 K, $\bar{E}$ = 116.1 mV are the average values of the temperature and emf; $T_i - \bar{T}$ is the difference between the measured and average temperatures; $\tilde{E}$ are the emf values calculated by Eq. (2); $\Sigma E(T_i - \bar{T})$ = 3104.77 mV K; $\Sigma(T_i - \bar{T})^2$ = 58774.7 K^2; and $\Sigma(E_i - \tilde{E})^2$ = 7.21 mV^2.

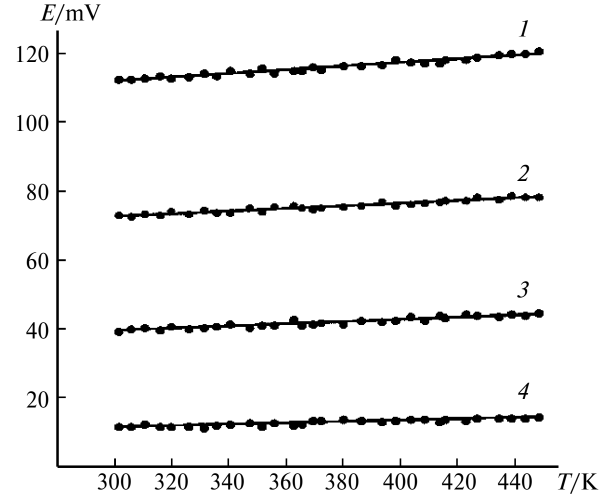

Fig. 3. Temperature dependences of the emf for solid solutions $(2PbSe)_{1-x}(AgSbSe_2)_x$ of the compositions x = 0.9 (*1*), 0.8 (*2*), 0.6 (*3*), and 0.4 (*4*).

The obtained linear equations are presented in Table 2 in the following recommended[30,31] form:

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

where n is the number of pairs of the E and T values; S_E and S_b are the dispersions of individual measurements of the emf and coefficient b, respectively; $\bar{T}$ is the average absolute temperature; and t is Student's criterion. The latter is $t \le 2$ at a confidence interval of 95% and the number of experimental points $n \ge 20$.

The partial molar thermodynamic functions of PbSe ($\Delta\bar{Z}_{PbSe}$, $Z = G$ or H) in the alloys at 298.15 K (Table 3) were calculated using the data of Table 2 by the equations[30]

$$\Delta\bar{G}_{PbSe} = -zFE, \tag{2}$$

$$\Delta\bar{S}_{PbSe} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb, \tag{3}$$

Table 2. Temperature dependences of the emf of the concentration chains of type **I** for the $PbSe—AgSbSe_2$ alloys

Content of $AgSbSe_2$ (mol.%)	E (mV) $= a + bT \pm tS_E(T)$
90	$96.36 + 0.0528T \pm 2[(0.26/30) + 4.4 \cdot 10^{-6}(T - 374.04)^2]^{1/2}$
80	$61.48 + 0.0380T \pm 2[(0.16/30) + 2.8 \cdot 10^{-6}(T - 374.04)^2]^{1/2}$
60	$31.58 + 0.0302T \pm 2[(0.36/30) + 6.2 \cdot 10^{-6}(T - 375.50)^2]^{1/2}$
40	$8.06 + 0.0129T \pm 2[(0.25/30) + 4.6 \cdot 10^{-6}(T - 375.50)^2]^{1/2}$

$$\Delta\bar{H}_{\mathrm{PbSe}} = -zF\left[E + T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa, \quad (4)$$

where F is the Faraday number, and z is the charge of the ion (Pb^{2+}) of the potential forming component. These functions represent the difference in the partial molar thermodynamic functions of lead in the solid solutions $(2PbSe)_x(AgSbSe_2)_{1-x}$ ($\Delta\bar{Z}_{\mathrm{Pb}}$) and in pure PbSe ($\Delta\bar{Z}'_{\mathrm{Pb}}$):

$$\Delta\bar{Z}_{\mathrm{PbSe}} = \Delta\bar{Z}_{\mathrm{Pb}} - \Delta\bar{Z}'_{\mathrm{Pb}}. \quad (5)$$

Compound PbSe is the single one in the Pb—Se system and has an almost constant stoichiometric composition.[38] It can easily been shown[31] that the following equation takes place in such cases:

$$\Delta\bar{Z}'_{\mathrm{Pb}} = \Delta_f Z^\circ(\mathrm{PbSe}). \quad (6)$$

Taking this into account, the partial molar thermodynamic functions of lead in $(2PbSe)_x(AgSbSe_2)_{1-x}$ solid solutions can be calculated by the equation

$$\Delta\bar{Z}_{\mathrm{Pb}} = \Delta\bar{Z}_{\mathrm{PbSe}} + \Delta_f Z^\circ(\mathrm{PbSe}). \quad (7)$$

The $\Delta\bar{Z}_{\mathrm{Pb}}$ values obtained by Eq. (7) are presented in Table 4.

The standard thermodynamic functions of formation of solid solutions $(2PbSe)_x(AgSbSe_2)_{1-x}$ were calculated using the integration of the Gibbs—Duhem equation

$$\Delta_f Z^\circ[(2\mathrm{PbSe})_x(\mathrm{AgSbSe_2})_{1-x}] =$$
$$= (1-x)\int_0^x \frac{\Delta\bar{Z}_{\mathrm{PbSe}}}{(1-x)^2}dx + 2x\Delta_f Z^\circ(\mathrm{PbSe}) + (1-x)\Delta_f Z^\circ(\mathrm{AgSbSe_2}). \quad (8)$$

The inaccuracies were determined by the method of accumulation of errors. The first term of the right part of Eq. (8), which characterizes the thermodynamic functions of formation of solid solutions $(2PbSe)_x(AgSbSe_2)_{1-x}$ from the initial compounds PbSe and $AgSbSe_2$, was calculated by graphical integration.

The literature data on the corresponding standard integral functions of compounds PbSe and $AgSbSe_2$ (Table 5) were used along with our experimental results (see Table 3) in the calculations by Eq. (8).

The values of the standard enthalpies of formation and entropy of PbSe presented in the reference literature[42,43] nearly coincide. The standard Gibbs energy of formation $\Delta_f G$ for this compound calculated by us using the published data[42,43] agrees well with the values recommended by the reference books.[42,44] The data[24] obtained by the EMF method with the solid electrolyte were used for compound $AgSbSe_2$. The thermodynamic values for this compound presented in Ref. 45 are evidently underestimated.

Table 3. Relative partial thermodynamic functions of PbSe in the $PbSe—AgSbSe_2$ alloys at 298.15 K

Content of $AgSbSe_2$ (mol.%)	$-\Delta\bar{G}_{\mathrm{PbSe}}$	$-\Delta\bar{H}_{\mathrm{PbSe}}$	$\Delta\bar{S}_{\mathrm{PbSe}}$ /J K^{-1} mol^{-1}
	kJ mol^{-1}		
90	21.63±0.07	18.59±0.30	10.19±0.81
80	14.05±0.06	11.86±0.24	7.34±0.65
60	7.83±0.09	6.09±0.36	5.82±0.96
40	2.30±0.07	1.56±0.31	2.49±0.83

Table 4. Relative partial thermodynamic functions of lead in the $PbSe—AgSbSe_2$ alloys at 298.15 K

Content of $AgSbSe_2$ (mol.%)	$-\Delta\bar{G}_{\mathrm{Pb}}$	$-\Delta\bar{H}_{\mathrm{Pb}}$	$\Delta\bar{S}_{\mathrm{Pb}}$ /J K^{-1} mol^{-1}
	kJ mol^{-1}		
90	120.2±3.1	118.7±2.4	5.0±2.9
80	112.7±3.1	112.0±2.4	2.3±2.8
60	106.4±3.1	106.2±2.5	0.7±3.1
40	100.9±3.1	101.7±2.4	−2.7±2.9

To conclude, the formation of a wide (more than 60 mol.%) region of solid solutions based on $AgSbSe_2$ in the $PbSe—AgSbSe_2$ system was confirmed by measuring the emf of the concentration (with respect to the PbSe

Table 5. Relative integral thermodynamic functions of solid solutions $(2PbSe)_{1-x}(AgSbSe_2)_x$ at 298.15 K

Compound	$-\Delta_f G^\circ$(298 K)	$-\Delta_f H^\circ$(298 K)	S°(298 K) /J K^{-1} mol^{-1}
	kJ mol^{-1}		
PbSe	98.6±3.0	100.1±2.1[42,43]	102.5±2.1[42,43]
$AgSbSe_2$[24]	92.5±4.5	91.0±5.0	177.2±6.0
$(2PbSe)_{0.1}(AgSbSe_2)_{0.9}$	103.3±4.8	102.2±5.1	183.0±6.0
$(2PbSe)_{0.2}(AgSbSe_2)_{0.8}$	114.3±5.0	113.6±5.0	185.2±5.5
$(2PbSe)_{0.4}(AgSbSe_2)_{0.6}$	136.8±5.3	136.6±4.8	189.0±4.8
$(2PbSe)_{0.6}(AgSbSe_2)_{0.4}$	158.2±5.6	159.1±4.6	190.9±4.0

electrode) chains. The mutually consistent complex of the data on the standard partial and integral thermodynamic functions of solid solutions $(2PbSe)_x(AgSbSe_2)_{1-x}$ ($x = 0.4$, 0.6, 0.8, and 0.9) was obtained.

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