ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2017, Vol. 91, No. 9, pp. 1642–1646. © Pleiades Publishing, Ltd., 2017.
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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Thermodynamic Study of Solid Solutions in the SnTe–$AgSbTe_2$ System by Means of EMF with Solid Electrolyte Ag_4RbI_5

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Received August 30, 2016

Abstract—The results from studying the SnTe–$AgSbTe_2$ system by means of EMF with the solid electrolyte Ag_4RbI_5 in the temperature range of 300–430 K are presented. The formation of a wide (≥80 mol % of $AgSbTe_2$) region of solid solutions based on SnTe is confirmed. Partial thermodynamic functions $\Delta\overline{G}$, $\Delta\overline{H}$, and $\Delta\overline{S}$ of silver in alloys are calculated from the equations for the EMF temperature dependences. Based on the literature data regarding solid-phase equilibria in the Ag_2Te–SnTe–Sb_2Te_3–Te system, potential-determining reactions are identified that allow us to calculate the standard thermodynamic formation functions and standard entropies of solid solutions $(2SnTe)_x(AgSbTe_2)_{1-x}$ ($x = 0.2$, 0.4, 0.6, 0.8, and 0.9).

Keywords: SnTe–$AgSbTe_2$ system, thermodynamic properties, EMF method, solid electrolyte Ag_4RbI_5, solid solutions, silver–tin–antimony tellurides

DOI: 10.1134/S0036024417090187

INTRODUCTION

Complex heavy metal chalcogenides are considered promising functional materials. Quasi-ternary systems $Ag_2Te–A^{IV}Te–B^V_2Te_3$ (A^{IV} = Ge, Sn, Pb; B^V= Sb, Bi) are of particular interest because of the importance of finding and developing new thermoelectric materials, since their binary and ternary compounds are considered good matrix phases for this purpose [1–4]. In addition, tetradymite-like binary (Bi_2Te_3, Sb_2Te_3) and ternary compounds (e.g., $A^{IV}B^V_2Te_4$, $A^{IV}B^V_4Te_7$, and $A^{IV}B^V_6Te_{10}$) are topological insulators and can be used in spintronics and quantum computers [5–7]. Some complex silver chalcogenides have ionic conductivity over Ag^+ cations and can be used as, e.g., solid electrolytes and ion-selective electrodes [8, 9].

To study and develop physicochemical bases for the production of new multicomponent phases and materials in $Ag_2Te–A^{IV}Te–B^V_2Te_3$ systems, we must study the phase equilibria in them and the thermodynamic properties of their intermediate phases.

Comprehensive studies of the phase equilibria and thermodynamic properties of $Ag_2Se–PbSe–Bi_2Se_3$ [10, 11] and $Ag_2Te–PbTe–Bi_2Te_3$ [12, 13] systems have been performed in a number of works [10–13] where wide regions of solid solutions were found along the $PbX–AgBiX_2$ sections. The phase diagram of the SnTe–$AgSbTe_2$ system was constructed in [14], where it was found that it is also characterized by the formation of a large region (~90 mol %) of solid solutions based on SnTe.

In this work, we present the results from a thermodynamic study of solid solutions in the SnTe–$AgSbTe_2$ system by means of EMF with solid Ag^+ conducting electrolyte Ag_4RbI_5.

EXPERIMENTAL

Tin telluride, which melts congruently at 1079 K, crystallizes directly from a melt of stoichiometric composition [4]. It was therefore synthesized by fusing elemental components of high purity in evacuated (~10^{-2} Pa) quartz ampule at a temperature of 1150 K with subsequent slow cooling. The synthesized SnTe was identified via DTA and X-ray powder diffraction.

The presence of $AgSbTe_2$ compound with NaCl-type cubic structure, reported in [15, 16], was not confirmed in a repeated study of phase equilibria in the $Ag_2Te–Sb_2Te_3$ system [17]. According to [17], the ternary compound with a cubic structure has a different composition ($Ag_{19}Sb_{29}Te_{52}$) in this system and melts incongruently at 847 K. According to the data in [18], this compound decomposes upon cooling by the

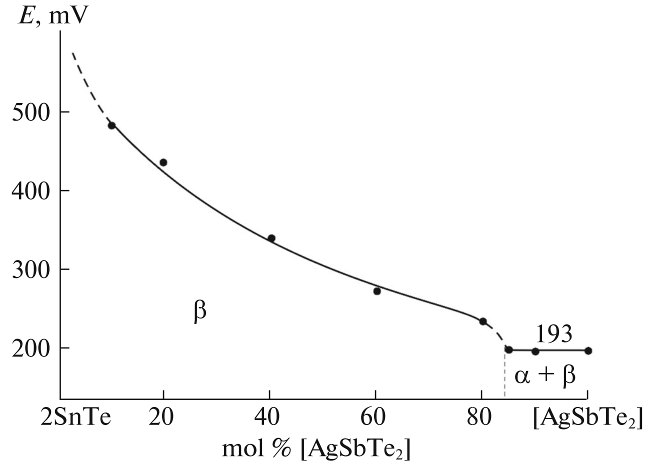

Fig. 1. Dependence of the EMF of a concentration circuit of type (1) on composition at 300 K.

solid-phase reaction $Ag_{19}Sb_{29}Te_{52} \rightarrow Ag_2Te + Sb_2Te_3$, and does not exist below 523 K. In light of this, alloys of the $2SnTe$–$AgSbTe_2$ system with compositions of 10, 20, 40, 60, and 80 mol % $AgSbTe_2$ were prepared from pre-synthesized SnTe and elemental Ag, Sb, and Te via fusion under vacuum conditions.

To eliminate the inhomogeneity of solid solutions in the composition and achieve a state as close as possible to equilibrium, cast nonhomogenized alloys obtained through the slow cooling of melts were ground into powder, thoroughly mixed, pressed into pellets with masses of 0.8–1 g, and annealed at 770 K (for 500 h) and 400 K (for 200 h).

To conduct our EMF experiments, we built a concentration circuit of the type

$$(-)\ \mathrm{Ag\ (solid)}|\mathrm{Ag_4RbI_5\ (solid)}|\mathrm{(Ag\ in\ alloy)\ (solid)}\ (+). \quad (1)$$

Solid Ag_4RbI_5 electrolyte was synthesized from chemically pure RbI and AgI using the procedure described in [19]. A stoichiometric mixture of the initial iodides was melted in vacuum (~10^{-2} Pa) inside a quartz ampoule and rapidly cooled to room temperature. When cooled, the melt crystallized into a fine-grained and microscopically homogeneous body. Subsequent annealing at 400 K for 200 h resulted in complete homogenization of the Ag_4RbI_5. Pellets 4–6 mm thick were cut out from the resulting cylindrical ingot with a diameter of ~1 cm and were used as the solid electrolyte in chains of type (1).

The annealed alloys were powdered and pressed into the form of pellets weighing 0.5–1 g to prepare the right electrodes. An electrochemical cell of the type described in [20] was constructed, evacuated, filled with argon, and placed in a specially prepared tubular resistance furnace, where it was thermostatted at a temperature of ~380 K for 40–50 h. The cell temperature was measured using chromel–alumel thermocouples and mercury thermometers with an accuracy of ±0.5°C.

EMF was measured via compensation using a V7-34A digital voltmeter. Measurements were made every 3 h after a certain temperature was established. Equilibrium values were the EMF readings that differed by no more than 0.5 mV for repeated measurements at a given temperature, irrespective of the direction in which the temperature was varied. To prevent thermo-EMFs, the contacts of all of the current collectors with copper wire had the same temperature.

RESULTS AND DISCUSSION

The results from measuring the EMF of chains of type (1) showed that in the ≤80 mol % region of compositions of $AgSbTe_2$, the EMF values were a continuous function of composition at a given temperature. They remained constant for compositions of 85 and 90 mol % $AgSbTe_2$, regardless of the total composition of the alloys (Fig. 1), confirming the data in [14]. It should be noted that the EMF values for alloys with compositions 85 and 90 mol % of $AgSbTe_2$ practically coincided with the value for pure Ag_2Te [21, 22]. This indicates they contained the Ag_2Te phase, which agrees with the data in [17, 18].

Analysis of the EMF measurement data showed that the temperature dependences of the EMF for all our samples were virtually linear. For our thermodynamic calculations, the results from our EMF measurements were therefore processed using the least squares method and are presented in Table 1 as linear equations of the type

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

recommended in [23], where n is the number of pairs of values of E and T; S_E and S_b are the dispersions of the individual EMF measurements and coefficient b, respectively; $\bar{T}$ is the mean absolute temperature; and t is Student's test. At a confidence level of 95% and $n \geq 20$ experimental points, Student's test yields $t \leq 2$.

From the data of Table 1, partial molar functions $\Delta\bar{G}$, $\Delta\bar{H}$, and $\Delta\bar{S}$ of silver in alloys at 298 K (Table 2) were calculated using the familiar thermodynamic equations in [19, 23].

The curves of the concentration dependences of these functions at 298 K (Fig. 2) have the form characteristic of systems with the formation of solid substitutional solutions. Within the homogeneity range of β-solid solutions based on SnTe, the partial silver molar functions are monotonic composition func-

Table 1. Temperature dependences of the EMF (E, mV = $a + bT \pm 2S_E(T)$, $S_E(T) = [a_1/24 + b_1 \times 10^{-5}(T - c)^2]^{1/2}$) of a concentration circuit of type (1) for alloys 2SnTe–$AgSbTe_2$

$AgSbTe_2$, mol %	a	b	a^1	b^1	c
10	403.7	0.294	0.91	2.2	365.6
20	342.6	0.271	0.73	1.8	364.6
40	274.5	0.186	0.49	1.2	364.9
60	239.8	0.112	0.68	1.7	365.7
80	215.3	0.073	0.26	6.2	364.2

Table 2. Relative partial thermodynamic functions of silver in 2SnTe–$AgSbTe_2$ alloys at 298.15 K

$AgSbTe_2$, mol %	$-\Delta\overline{G}_{Ag}$	$-\Delta\overline{H}_{Ag}$	$\Delta\overline{S}_{Ag}$, J/(K mol)
	kJ/mol		
10	47.41 ± 0.07	38.95 ± 0.32	28.37 ± 0.91
20	40.852 ± 0.06	33.06 ± 0.30	26.15 ± 0.82
40	31.84 ± 0.05	26.49 ± 0.24	17.95 ± 0.67
60	26.36 ± 0.06	23.14 ± 0.29	10.81 ± 0.80
80	22.87 ± 0.04	20.77 ± 0.17	7.04 ± 0.48

tions; in the heterogeneous region, α + β (α-solid solutions based on Ag_2Te) [14] have constant values, since the compositions of the coexisting phases are virtually constant.

Upon reducing the concentration of silver in solid solutions, there is a drop in $\Delta\overline{G}_{Ag}$ and $\Delta\overline{H}_{Ag}$ and an increase in $\Delta\overline{S}_{Ag}$; this corresponds to the positions of the thermodynamics of solutions [19].

Analysis of the Ag–Sn–Sb–Te concentration tetrahedron (Fig. 3) allows us to determine the potential-determining reactions for individual compositions of solid solutions by the means described in [20]. It is clear from Fig. 3 that the lines radiating from the Ag apex of this tetrahedron and passing through the SnTe–$AgSbTe_2$ section reach the lateral ternary system Sn–Sb–Te in the three-phase region SnTe + $SnSb_2Te_4$ + Te. The phases of this three-phase region and elementary silver should thus interact in the equilibrium potential-determining reaction for solid solutions $(2SnTe)_x(AgSbTe_2)_{1-x}$. For a solid solution with, e.g., the composition $(2SnTe)_{0.9}(AgSbTe_2)_{0.1}$, the reaction equation has the form

$$\mathrm{Ag} + 17.5\mathrm{SnTe} + 0.5\mathrm{SnSb_2Te_4} + 0.5\mathrm{Te} = 10[(2\mathrm{SnTe})_{0.9}(\mathrm{AgSbTe_2})_{0.1}].$$

According to this equation, the thermodynamic functions of the formation of the phase $(2SnTe)_{0.9}(AgSbTe_2)_{0.1}$ can be calculated using the equation

$$\Delta_f Z^0 = 0.1\Delta\overline{Z}_{Ag} + 1.75\Delta_f Z^0(\mathrm{SnTe}) + 0.05\Delta_f Z^0(\mathrm{SnSb_2Te_4}),$$

where $\Delta Z \equiv \Delta G$ or ΔH, and the entropy can be calculated according to the equation

$$S^0 = 0.1\Delta\overline{S}_{Ag} + 0.1S^0(\mathrm{Ag}) + 1.75S^0(\mathrm{SnTe}) + 0.05S^0(\mathrm{SnSb_2Te_4}) + 0.05S^0(\mathrm{Te}).$$

The standard functions thermodynamic formation and standard entropies of solid solutions of other compositions were calculated in a similar way. The results are shown in Table 3.

For calculations in accordance with the equations of potential-determining reactions, we used the

Table 3. Standard partial thermodynamic functions of silver in solid alloys $(2SnTe)_{1-x}(AgSbTe_2)_x$

Compound	$-\Delta_f G^0$(298 K)	$-\Delta_f H^0$(298 K)	S^0(298 K), J/(K mol)
	kJ/mol		
SnTe [22]	61.1 ± 1.0	61.1 ± 1.0	101.3 ± 4.2
$SnSb_2Te_4$ [24]	144.0 ± 2.0	140.8 ± 1.8	357.0 ± 7.3
$(2SnTe)_{0.9}(AgSbTe_2)_{0.1}$	118.9 ± 1.9	117.9 ± 1.9	204.7 ± 7.9
$(2SnTe)_{0.8}(AgSbTe_2)_{0.2}$	114.2 ± 1.7	112.3 ± 1.8	206.3 ± 7.3
$(2SnTe)_{0.6}(AgSbTe_2)_{0.4}$	102.6 ± 1.4	99.9 ± 1.5	206.8 ± 6.2
$(2SnTe)_{0.4}(AgSbTe_2)_{0.6}$	87.8 ± 1.1	86.7 ± 1.2	204.7 ± 5.1
$(2SnTe)_{0.2}(AgSbTe_2)_{0.8}$	75.9 ± 0.8	72.9 ± 0.9	202.3 ± 3.8

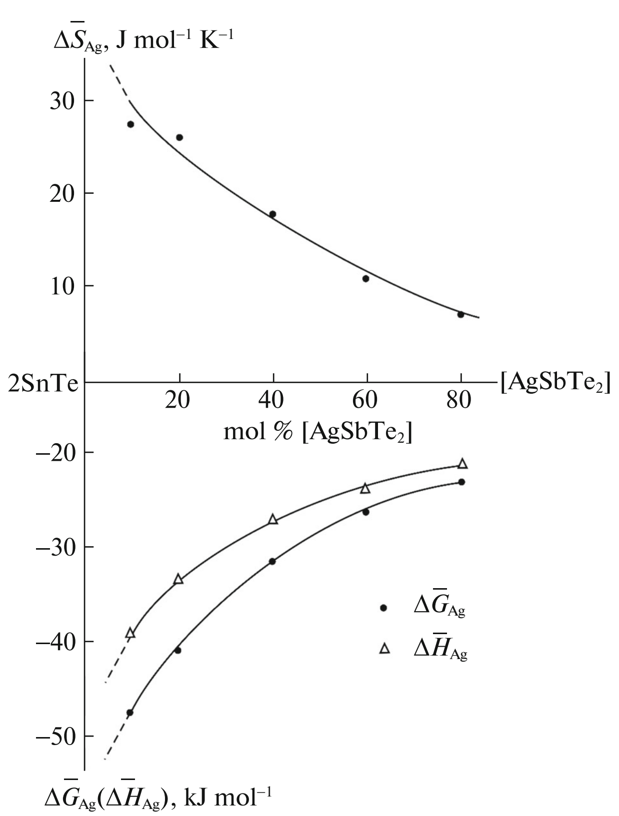

Fig. 2. Concentration dependences of the partial thermodynamic functions of silver in solid solutions $(2SnTe)_{1-x}(AgSbTe_2)_x$ at 298.15 K.

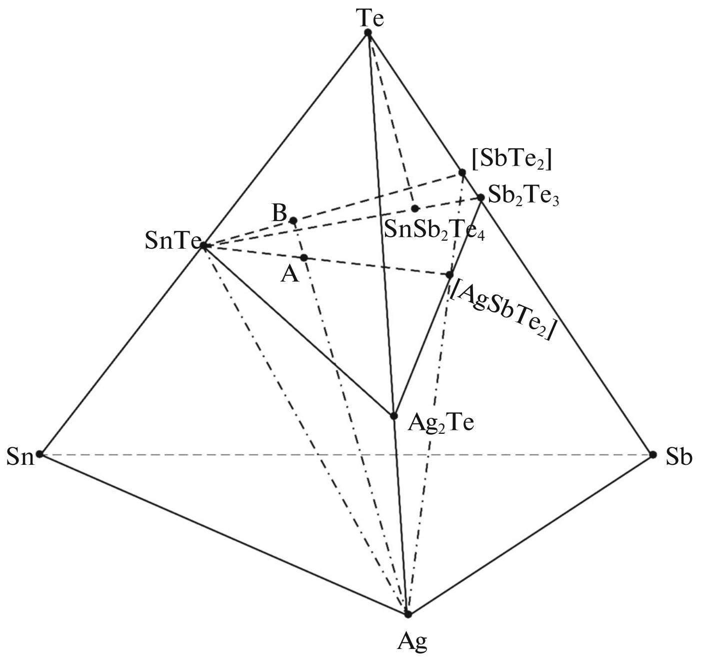

Fig. 3. Concentration tetrahedron Ag–Sn–Sb–Te: A is the alloy on the SnTe–AgSbTe$_2$ section; B is the three-phase SnTe + SnSb$_2$Te$_4$ + Te alloy in the side system of Sn–Sb–Te. The dotted-and-dashed lines radiate from Ag.

reported data on the corresponding standard integral thermodynamic functions for compounds SnTe [22] and $SnSb_2Te_4$ [24] (Table 3) and the standard entropies of elemental silver (42.6 ± 0.5 J K^{-1} mol^{-1}) and tellurium (49.5 ± 0.2 J K^{-1} mol^{-1}) recommended in [25]. Errors were identified as they accumulated.

ACKNOWLEDGMENTS

This work was supported by the Science Foundation of the State Oil Company of the Republic of Azerbaijan as part of the project Preparing and Studying New Functional Materials Based on Multicomponent Metal Chalcogenides for Alternative Sources of Energy and Electronic Engineering, 2014.

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Translated by V. Avdeeva