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Thermodynamic Study of Siver—Tin Selenides by the EMF Method

with Ag4RbI5 Solid Electrolyte

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Abstract—The system Ag-Sn-Se in the region of Ag2Se-SnSe-Se composition is studied by measuring EMF of cells with Ag4RbI5 solid electrolyte in the temperature interval of 300-450 K. Based on the results of EMF measurements, the temperature of Ag8SnSe6 polymorphous transition (355 K) is determined and the partial molar functions of silver in certain phase regions of this system are calculated. Standard thermody­namic functions of formation and standard entropies are estimated for ternary phases AgSnSe2,

Ag0 84Sn116Se2, and two modifications of Ag8SnSe6 and also thermodynamic functions of Ag8SnSe6 poly- morphous transition.

Keywords: silver-tin selenides, phase transition, thermodynamic functions, EMF method, Ag4RbI5 solid electrolyte

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INTRODUCTION

Silver-containing composite chalcogenides pertain to functional materials of high value. Many of them exhibit thermoelectric, photoelectric, optical, mag- netic, etc. properties [1—5]. Furthermore, some of them exhibit ionic conduction with respect to Ag+ cat- ions and can be used as electrochemical sensors, elec- trode materials, components of analog integrators, solid-state fuel cells, supercapacitors, electrochromic visualizers, functional sensors, etc. [6-9].

Silver-tin chalcogenides exhibit mixed ionic-elec- tronic conduction in combination with high thermo­electric [10, 11], photovoltaic [12], and optical [13] characteristics.

The discovery of unipolar superionic conductors with Ag+ conduction opened up the possibility of using them as the solid-state electrolytes in electro­chemical concentration cells. Such electrochemical cells are successfully used in thermodynamic studies of complex systems based on silver [9, 14-28].

It was shown [19-24] that cation-conducting elec­trolytes can be successfully used in thermodynamic investigating silver-containing ternary systems by the EMF (electromotive force) method even when they contain elements less noble than silver. This is explained by the fact that solid electrolytes, in contrast to liquid electrolytes, prevent the appearance of side processes associated with interaction of electrodes

with electrolyte and with one another via the electro- lyte. Thus, the EMF method with solid electrolyte makes it possible to obtain reproducible results for cells irreversible from the classic point of view, which substantially widens the circle of systems for investi- gations.

In the present publication, we show the results of studying the subsystem Ag2Se-SnSe-Se by the EMF method with the Ag4RbI5 solid electrolyte in the tem­perature interval of 290-450 K.

The phase equilibria in the Ag-Sn-Se system were studied in several works [2, 29-31]. According to the complete T-x-y diagram of this system shown in [31], the system is characterized by the formation of two intermediate phases: Ag8SnSe6 and AgSnSe2. The for- mer phase melts congruently at 1015 K and undergoes polymorphous transition at 355 K. The compound AgSnSe2 melts incongruently by a peritectic reaction at 860 K and has a wide homogeneity region (47­58 mol % SnSe) along the “AgSe"-SnSe section [30, 31].

The low-temperature modification of Ag8SnSe6 is crystallized in the orthorhombic lattice (space group Pmn21, a = 0.79168, b = 0.78219, c = 1.10453 nm) [32], whereas the high-temperature modification is crystallized in the cubic lattice (space group F-43m, a = 1.112 nm) [29]. The AgSnSe2 compound has the cubic structure of the NaCl type (a = 0.5627 nm) [33].

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The thermodynamic properties of saturated solid Solutions based in ternary phases of the Ag—Sn—Se system were studied by the EMF method with liquid electrolyte with respect to the tin electrode [2] or with glassy electrolyte with respect to the silver electrode [14, 34].

EXPERIMENTAL

For the thermodynamic study of silver-tin sele- nide, we have assembled the following concentration cells

(-) Ag (s) /Ag4RbIs (s) / (Ag in alloy )(s)(+). (1)

In cells (1), solid superionic conductor Ag4RbI5 with the high ionic conductivity (0.25 S cm-1) even at room temperature served as the electrolyte. Moreover, the level of its electronic conductivity was negligibly low: 10-9 S cm-1 [6].

Solid electrolyte Ag4RbI5 was synthesized by the procedure described in [9, 19]. The synthesis was car- ried out by alloying chemically pure RbI and AgI in a quartz ampoule in vacuum (~10-2 Pa) which was fol- lowed by rapid cooling of the melt to room tempera- ture. In the process, the melt was crystallized into a fine-grain, microhomogeneous body. Additional annealing at 400 K for 200 h led to complete homoge- nization of Ag4RbI5. The results of differential thermal analysis (DTA) and X-ray diffraction analysis (XRD) confirmed the monophase nature of synthesized Ag4RbI5 [19]: melts with decomposition by a peritectic reaction at 505 K and crystallizes in cubic lattice (space group P4132, a = 1.1238 nm, z = 4), which agrees with reference data [6]. From the thus prepared cylindrical ingot with the diameter of ~1 cm, pellets with the thickness of 4-6 mm were cut, which were used as the solid electrolyte in cells (1). The samples of Ag4RbI5 solid electrolyte prepared by this procedure were successfully used earlier in thermodynamic stud- ies by the EMF method [19-27].

Metal silver served as the reference electrode, the electrodes on the right represented alloys from the fol- lowing phase regions: Ag2Se-Ag8SnSe6-Se, Ag2Se- Ag8SnSe6-SnSe, Ag8SnSe6-SnSe2-Se, AgSnSe2-

SnSe2, and Ago.^SnugSe^SnSe^SnSe (Ag0.84Sn116Se2 is the composition of the y phase saturated with SnSe), which were chosen according to the Ag-Sn-Se phase diagram [31]. The alloys were prepared from prelimi- narily synthesized and identified compounds Ag2Se, SnSe, SnSe2, and Ag8SnSe6, and also from elemental selenium of the high degree of pureness by alloying them in evacuated (~ 10-2 Pa) quartz ampoules at tem- peratures exceeding the liquidus temperature by 30- 50°C. Taking into account that the state of electrode- alloys should be maximally close to the equilibrium state, the casted nonhomogenized samples were sub- jected to long-term step-wise thermal annealing at

600 K (500 h) and 450 K (200 h). The phase composi­tion of annealed alloys was controlled by the XRD method (powder diffractometer D8 ADVANCE (Bruker), CuXa1) [31]. Then, the annealed alloys were grinded to powder, pressed to pellets with the mass of 0.5-1 g, and used as the anodes in cells (1).

The electrochemical cell assembled as in [9, 27] was evacuated, filled with argon, and placed in a spe- cially made resistance tube furnace where it was ther- mally controlled at ~380 K for 40-50 h. The cell tem­perature was measured by chromel-alumel thermo- couples and mercury thermometers with the accuracy ±0.5°C.

The EMF was measured by means of a high-resis- tance digital voltmeter V7-34A in the temperature interval of 300-450 K. The EMF of alloys from the Ag8SnSe6-SnSe2-Se phase region was measured first in the temperature range of the existence of the high- temperature modification of Ag8SnSe6, and then in the region of its low-temperature modification [31]. The first equilibrium values were obtained after the cell was thermally controlled under the aforemen- tioned conditions, the subsequent values were obtained every 3 h after the establishment of a certain temperature. The EMF values which, in the repeated experiments at a given temperature, differed from one another by no more 0.5 mV irrespective of the direc- tion of temperature variation were assumed to be equi- librium.

RESULTS AND DISCUSSION

The measurements have shown that the concentra­tion dependence of EMF cells (1) well corresponds to the diagram of solid-state equilibria in the Ag2Se- SnSe-Se system (Fig. 1) [31]. At the constant tem­perature, within each three-phase region, the EMF values remained constant irrespective of the gross composition of the alloy-anode, and changed step- wise with the transition from one region to another. According to the conditions of thermodynamic equi- librium, the EMF values of cells (1) cannot decrease when the amount of silver decreases along the radial lines from Ag in the vertex of the concentration trian- gle [28]. Our experimental data fulfill this require- ment. Furthermore, the EMF values in three-phase regions Ag2Se-Ag8SnSe6-Se and Ag2Se-Ag8SnSe6- SnSe coincided to ±3 mV with thermodynamic data [35, 36] for compound Ag2Se.

For thermodynamic properties of compounds Ag8SnSe6, AgSnSe2, and the y phase with the limiting composition Ag0 84Sn116Se2, we used the results of EMF measurements for alloys from phase regions Ag8SnSe6-SnSe2-Se, AgSnSe2-SnSe2, and

Ag0.84Sn1.16Se2-SnSe-SnSe2.

Figure 2 shows the temperature dependences of EMF of concentration cells (1) for alloys from the

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Se

Fig. 1. Diagram of solid-phase equilibria in the Ag—Sn—Se system [31]. Triangles show the composition of samples under study, dashed line AgSnSe2—SnSe2 means conode. Numbers in certain three-phase regions are the EMF values (mV) of concentration cell (1) at 300 K.

aforementioned phase regions. It is evident that all these dependences are linear. For the three-phase region Ag8SnSe6—SnSe2—Se, the dependence is a straight line with a break at 355 K which corresponds to the temperature of polymorphous transition of Ag8SnSe6 [2, 31].

Comparison of our results with the data of [14] obtained by the EMF method employing a glassy Ag+- conducting electrolyte demonstrates (Fig. 2) that they virtually coincide for the three-phase region Ag8SnSe6—SnSe2—Se (lines I and IV) but considerably differ (~25—30 mV) for the region AgSnSe2—SnSe2 (lines III and V). In is probable that this difference is associated with the deviation from the stoichiometric AgSnSe2 composition in the temperature interval con- sidered in [14].

For thermodynamic calculations, we processed the results of EMF measurements by the least-square technique and obtained the linear equations as in [28, 37]

E = a + bT ± t

SE + sE(t - t)2 12

n £ (T - T)2 \_

(2)

where n is the number of E and T pairs; SE is the dis-

persion of an individual EMF result; T is the average absolute temperature; t is the Student criterion. For 95% confidence level and the number of experimental points n > 20, the Student criterion t < 2. As an exam- ple, Table 1 shows the experimental pairs of E and T values and also the results of calculations for the AgSnSe2—SnSe2 phase region.

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E, mV

300 340 380 420 460 500 540 T, K

Fig. 2. Temperature dependences of EMF in certain phase regions of the Ag—Sn—Se system. (I—III) data of this study for regions (I) Ag8SnSe6—SnSe2—Se, (II) Ag0 84SnU6Se2—SnSe—SnSe2, (III) AgSnSe2—SnSe2. Lines IV and V are the data of [14] for regions of Ag8SnSe6—SnSe2—Se and AgSnSe2—SnSe2, respectively.

Based on the derived equations for the EMF tem­perature dependence (Table 2) and the relationships [37]

*AGas* = -zFE, (3)

A^g = -z

E - T (dE

\_ \ƏT/pj

= -zFa,

(4)

aS«=zF (i )p=zFi- (5)

we calculated the relative partial molar functions of silver in alloys (Table 3).

According to the diagram of solid-phase equilibria (Fig. 1), the partial molar functions of silver in equilib- rium alloys in the three-phase regions under consider- ation (Table 2, 3, regions 1—3) pertain to the following potential-determining reactions (all substances are in the crystalline state):

Ag + 0.125SnSe2 + 0.5Se = 0.125 Ag8SnSe6, (6)

Ag + SnSe2 = AgSnSe2, (7)

Ag + 0.38SnSe + SnSe2 = 1.19Ag0 84Sn116Se2. (8)

According to reaction (6), the free Gibbs energy and the enthalpy of formation of compound Ag8SnSe6 can be estimated by the relationship

A fZ (Ag8SnSe6) = 8AZAg + AfZ(SnSe2), (9)

where Z = G, H, and the entropy can be calculated by the relationship

S °(Ag8SnSe6) = 8 [aS^ + S 0(Ag)] (10)

+ 4S 0(Se) + S 0(SnSe2).

The standard integral thermodynamic functions for AgSnSe2 and Ag0 84Sn116Se2 were calculated in the similar way. Table 4 shows the results of calculations. The errors were estimated by the rounding-off method.

In calculations, we used the standard entropies for silver and selenium (S°(Ag) = 42.55 ± 0.50 J mol-1 K-1; S°(Se) = 42.44 ± 0.50 J mol-1 K-1) [38] and also the standard thermodynamic functions of SnSe and SnSe2 (Table 4) found by the EMF method [39]. The enthal- pies of formation of both compounds found in this study well agree with the reference calorimetric data [38, 40, 41]. Moreover, the values of free Gibbs energy of the formation of these compounds calculated from the values of enthalpy of formation and standard entropy recommended in these reference books virtu- ally coincide with the results of [39]. This demon- strates reliability of thermodynamic data for SnSe and SnSe2 used in our calculations.

Table 4 shows also the values of standard integral thermodynamic functions for P-Ag8SnSe6 and AgSnSe2, taken from [2, 14, 34]. The analysis of data in Table 4 demonstrated good agreement between the existing data including those obtained here. It is only for the enthalpy of formation of AgSnSe2 that the larg- est deviation (14%) was observed between our results and those of [14].

Based on the thermodynamic data obtained for two modifications of Ag8SnSe6, we calculated the thermo­dynamic functions for polymorphous transition of this compound. Insofar as in the temperature interval of

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Table 1. Calculation of constants a and b and also of errors, based on EMF data for the phase region AgSnSe2-SnSe2

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| T, K | Ei, mV | T - T | Eİ(Tİ - T) | (Ti - t )2 | E | E i - E | (Ei - E)2 |
| 302.1 | 219.5 | -79.56 | -17463.97 | 6330.19 | 218.52 | 0.98 | 0.96 |
| 307.5 | 219.8 | -74.16 | -16300.92 | 5500.08 | 219.21 | 0.59 | 0.35 |
| 313.7 | 220.9 | -67.96 | -15012.92 | 4618.90 | 219.99 | 0.91 | 0.82 |
| 321.8 | 221.9 | -59.86 | -13283.49 | 3583.52 | 221.02 | 0.88 | 0.77 |
| 338.4 | 222.8 | -43.26 | -9638.89 | 1871.64 | 223.13 | -0.33 | 0.11 |
| 343.7 | 221.7 | -37.96 | -8416.29 | 1441.15 | 223.81 | -2.11 | 4.43 |
| 347.3 | 224.1 | -34.36 | -7700.64 | 1180.78 | 224.26 | -0.16 | 0.03 |
| 356.2 | 225 | -25.46 | -5729.06 | 648.34 | 225.39 | -0.39 | 0.15 |
| 361.5 | 226.7 | -20.16 | -4570.84 | 406.53 | 226.07 | 0.63 | 0.40 |
| 367.3 | 226.3 | -14.36 | -3250.23 | 206.28 | 226.80 | -0.50 | 0.25 |
| 373.2 | 228 | -8.46 | -1929.45 | 71.61 | 227.55 | 0.45 | 0.20 |
| 379.9 | 227.8 | -1.76 | -401.50 | 3.11 | 228.41 | -0.61 | 0.37 |
| 388.6 | 226.6 | 6.94 | 1572.04 | 48.13 | 229.51 | -2.91 | 8.47 |
| 395.1 | 230 | 13.44 | 3090.63 | 180.57 | 230.34 | -0.34 | 0.11 |
| 400.5 | 230.5 | 18.84 | 4342.04 | 354.85 | 231.02 | -0.52 | 0.27 |
| 406.7 | 231.2 | 25.04 | 5788.67 | 626.88 | 231.81 | -0.61 | 0.37 |
| 410.1 | 233.5 | 28.44 | 6640.16 | 808.69 | 232.24 | 1.26 | 1.58 |
| 417.4 | 233.7 | 35.74 | 8351.85 | 1277.17 | 233.17 | 0.53 | 0.28 |
| 424.2 | 233.5 | 42.54 | 9932.51 | 1809.44 | 234.03 | -0.53 | 0.29 |
| 432.3 | 237.1 | 50.64 | 12006.15 | 2564.16 | 235.06 | 2.04 | 4.15 |
| 436.5 | 235.5 | 54.84 | 12914.23 | 3007.15 | 235.60 | -0.10 | 0.01 |
| 441.8 | 236.8 | 60.14 | 14240.56 | 3616.52 | 236.27 | 0.53 | 0.28 |
| 445.7 | 236.2 | 64.04 | 15125.66 | 4100.80 | 236.77 | -0.57 | 0.32 |
| 448.4 | 238 | 66.74 | 15883.53 | 4453.89 | 237.11 | 0.89 | 0.79 |
| T = 381.66 | E = 228.63 |  | X E (T- - T) = 6189.84 | X (T- - T)2 =48710.38 |  |  | X (Ei - E)2 = 25.78 |

Table 2. Dependences of EMF of concentration cells of type (1) for compounds Ag8SnSe6

Phase region

Temperature interval, K

E,mV = a + bT ± tSE(T)

a-Ag8SnSe6-SnSe2-Se 300-350

P-Ag8SnSe6-SnSe2-Se 360-450

AgSnSe2-SnSe2 300-450

Ag0.84Sn116Se2-SnSe2-SnSe 300-450

1. + 0.089T ± 2.2
2. + 0.145T ± 2 210.1 + 0.127T ± 2 209.8 + 0.168T ± 2

— + 1.1 x 10-5(T - 328.2)2

L 15

* + 1.3 x 10-5(T - 397.5)2L 24
* + 2.2 x 10-5(T - 381.7)2

L 24

089 + 1.8 x 10-5(T - 377.2)224

-1/2

-1/2

-1/2

-.1/2

EMF measurements, the heat of Ag8SnSe6 formation is virtually constant, we can write

A^p, = AfH0(P) - AfH0(a), (11)

where AHpt is the heat of polymorphous transition of

compound Ag8SnSe6, A fH 0(P) and A fH 0(a) are the heats of formation of two modifications. On the other

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hand, it follows from Eq. (6) that the contribution of SnSe2 into the latter two functions is the same. Hence, AHp.t was calculated based on the relationship

AHp, = 8[AHAg(P) - AHAg(a)], (12)

which does not include the error in the heat of forma­tion of SnSe2.

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Table 3. Partial molar thermodynamic functions of silver in Ag8SnSe6 and AgSnSe2

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Phase region | T, K | 4?IG<11 | -AHAg | ASAg, J K 1 mol 1 |
| kJ mol 1 |
| a-Ag8SnSe6-SnSe2-Se | 298 | 27.01 ± 0.05 | 24.46 ± 0.24 | 8.57 ± 0.70 |
| p-Ag8SnSe6-SnSe2-Se | 400 | 28.14 ± 0.08 | 22.54 ± 0.30 | 13.99 ± 0.71 |
| AgSnSe2-SnSe2 | 298 | 23.93 ± 0.09 | 20.27 ± 0.35 | 12.25 ± 9.91 |
| Ag084Sn116Se2-SnSe2-SnSe | 298 | 25.08 ± 0.07 | 20.24 ± 0.31 | 16.21 ± 0.82 |

Table 4. Standard integral thermodynamic functions of silver-tin selenides

|  |  |  |  |
| --- | --- | --- | --- |
| Phase | A fG 0 | A fH 0 | S0, J K-1 mol-1 |
| kJ mol 1 |
| SnSe2 | 119.2 ± 2.5 [39] | 124.7 ± 4.2 [39] | 118.0 ± 3.0 [39] |
| SnSe | 96.3 ± 0.4 [39] | 94.6 ± 2.1 [39] | 106.8 ± 8.4 [39] |
| a-Ag8SnSe6 | 335.3 ± 2.9 | 320.4 ± 6.4 | 695.5 ± 10.5 |
| P-Ag8SnSe6 | 342.4 ± 3.2\* | 305.0 ± 6.8 | 738.8 ± 10.6 |
|  | 350.3 ± 1.8 [2] | 320.4 ± 8.1 [2] | 736.6 ± 23.8 [2] |
|  | 352.5 ± 1.9 [14] | 323.1 ± 1.6 [14] | - |
|  | 347.6 ± 27.2 [34] | 336.2 ± 19.2 [34] | - |
| AgSnSe2 | 144.1 ± 2.6 | 145.0 ± 4.8 | 172.8 ± 4.1 |
|  | 146.4 ± 0.5 [2] | 148.0 ± 3.0 [2] | - |
|  | 133.9 ± 1.6 [14] | 124.9 ± 1.3 [14] | - |
| Ag0.84Sn1.16Se2 | 152.0 ± 2.3 | 152.0 ± 4.7 | 182.7 ± 6.0 |

This result corresponds to 400 K.

The entropy of polymorphous transition was calcu- lated based on the relationship

ASP, = AHp,/Tp,.

We obtained the following values for the thermody­namic function of phase transition of Ag8SnSe6:

AHp t = 15.4 ± 4.3 kJ mol-1.

ASp.t = 43.4 ± 12.1 J mol-1 K-1.

The relatively high errors in our data are associated with the fact that in the EMF method, the partial enthalpy and partial entropy are calculated indirectly from the coefficient of temperature dependence [28, 37].

CONCLUSIONS

Using the EMF technique with solid electrolyte Ag4RbI5, new complexes of interconsistent thermody- namic data are obtained for ternary phases of AgSnSe2, Ag0 84Sn116Se, and two modifications of Ag8SnSe6. The results of this study supplement and refine the thermodynamic data for AgSnSe2 and high-

temperature modification of Ag8SnSe6. The thermo­dynamic data for the Ag0 84Sn116Se2 phase and the low-temperature modification Ag8SnSe6 and its poly­morphous transition were obtained for the first time.

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