THERMODYNAMIC STUDY OF Cu_2SnSe_3 BY EMF METHOD WITH SOLID ELECTROLYTE $Cu_4RbCl_3I_2$

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By measuring the EMF of the concentration cells with solid Cu^+ conductive electrolyte $Cu_4RbCl_3I_2$, the thermodynamic properties of the Cu_2SnSe_3 compound, which is of great interest as a potential environmentally friendly thermoelectric, were studied. The partial molar functions of copper in the alloys, as well as the standard thermodynamic formation functions and the standard entropy of this compound, are calculated from the EMF measurements.

Keywords: EMF method, solid electrolyte, Cu_2SnSe_3, thermodynamic functions.
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1. INTRODUCTION

Copper -containing complex chalcogenides refer to high-value functional materials. Many of them exhibit thermoelectric, photoelectric, optical, magnetic, etc. properties [1– 5]. Furthermore, some of them exhibit ionic conduction with respect to Cu^+ cations and can be used as electrochemical sensors, materials of electrodes, solid-state fuel cells, supercapacitors, electrochromic visualizers, etc. [6–10].

In recent years, the Cu_2SnSe_3 compound, as well as phases and composites based on it, have been intensively studied as potential environmentally friendly thermoelectric and photoelectric materials [11-17]. The thermodynamic properties of this compound have hardly been studied. The work [18] presents the results obtained by measuring the EMF of concentration relative to tin chains with liquid electrolyte.

This paper presents the results of a study of the thermodynamic properties of this compound by EMF with solid Cu^+ conductive electrolyte $Cu_4RbCl_3I_2$. This modification of the EMF method is successfully used for the thermodynamic study of complex copper-based chalcogenides [19–26]. It was shown [23, 24] that cation-conducting electrolytes can be successfully used in thermodynamic investigating copper-containing ternary systems by the EMF method even when they contain elements less noble than copper.

2. EXPERIMENTAL PART

For experiments, we composed concentration cells of the type

(–) Cu (sol.) $Cu_4RbCl_3I_2$ (sol.) (Cu in alloy) (sol.) (+) (1)

The right electrodes were equilibrium alloys from the phase region Cu_2SnSe_3-$SnSe_2$-Se. The synthesis was carried out by fusing the elementary components with a purity of at least 99.999% in stoichiometric ratios in quartz tubes evacuated to ~10^{-2} Pa and sealed. Then based on phase diagram data [5], they were subjected to stepwise homogenizing annealing at 800 K (500 h) and 450 K (300 h) followed by slow cooling to room temperature in order to reach the equilibrium state.

The right electrodes were prepared by pressing the powdered annealed alloys into pellets with a diameter of ~0.8 cm and a thickness of 0.5 cm. A high-purity copper plate with a diameter of ~1 cm and a thickness of 0.1 cm was used as the left electrode.

The $Cu_4RbCl_3I_2$ solid electrolyte was synthesized by the procedure described in [19] by fusing stoichiometric amounts of chemically pure anhydrous CuCl, CuI and RbCl in an evacuated (~10^{-2} Pa) quartz tube at 900 K followed by cooling to 450 K and homogenizing annealing at this temperature for 100 h. Pellets with a thickness of ~0.4 cm were cut from the obtained cylindrical ingot with a diameter of ~0.8 cm, which were used as a solid electrolyte in cells (1).

The design of the electrochemical cell and the method of its assembly were described in [18, 19]. The EMF was measured with a high-resistance B7-34A digital voltmeter in the temperature range 300–450 K. In this temperature range, the alloys under study were in a solid-state, and the compositions of the equilibrium phases were almost independent of temperature [5]. The first equilibrium EMF values were obtained after the electrochemical cell was kept at~400K for 40h, and subsequent values were obtained every 3 or 4 h after a certain temperature was reached. In repeated measurements at a given temperature, the EMF values differed from each other by no more than 0.5 mV irrespective of the direction of temperature variation. During the measurements, all the necessary measures were taken [18, 27] to ensure reversibility of cells (1).

3. RESULTS AND DISCUSSION

An analysis of the temperature dependences of EMF (fig.) showed that they were almost linear for all the samples under study. Therefore, the results of the EMF measurements were processed by using Microsoft Excel computer program in an approximation of their linear temperature dependence by the least-squares method, and linear equation of the following type was obtained [27]:

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

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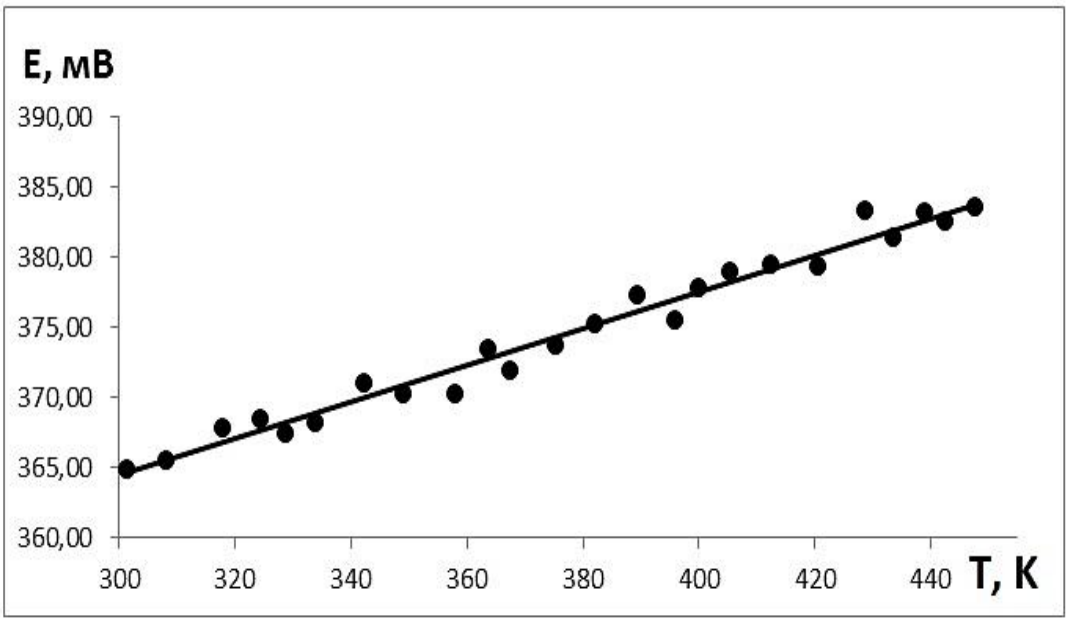

Fig. Temperature dependences of EMF for the alloys from three-phase area Cu_2SnSe_3-$SnSe_2$-Se at 300-450 K.

where n is the number of pairs of the E and T values; S_E and S_b - are the dispersions of the individual measurements of EMF and b coefficient, respectively; is the average absolute temperature, and t is the Student criterion. At a confidence level of 95% and the number of experimental points $n \geq 20$, the Student criterion is $t \leq 2$.

The experimental data of T_i and E_i and steps of calculation are presented in table 1. Follow equation is received

$$E, \text{мВ} = 325{,}34 + 0{,}1305\text{T} \pm 2\left[\frac{0{,}86}{24} + 1{,}81\cdot10^{-5}(\text{T}-377{,}7)^2\right]^{1/2} \quad (3)$$

The relative partial thermodynamic functions of copper at 298 K in Cu_2SnSe_3-$SnSe_2$-Se phase area were calculated from the obtained equation (3) of the temperature dependences of EMF by the equations

$$\Delta\overline{G}_{Cu} = -zFE \quad (4)$$

$$\Delta\overline{H}_{Cu} = -zF\left[E + T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa \quad (5)$$

$$\Delta\overline{S}_{Cu} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb \quad (6)$$

where z is the charge on the current-forming Cu^+ cation, F is the Faraday number, and a and b are the constants in the equation $E = a + bT$.

And the following values are received

$\Delta\overline{G}_{Cu}$ = -35,15±0,07 kJ·mol^{-1}
$\Delta\overline{H}_{Cu}$ = -31,39±0,31 kJ·mol^{-1}
$\Delta\overline{S}_{Cu}$ = 12,59±0,82 J·mol^{-1}·K^{-1}

According to the diagram of solid-phase equilibria, these partial molar functions of copper are thermodynamic functions of the following potential-forming reaction:

$$2Cu + SnSe_2 + Se = Cu_2SnSe_3$$

From this equation it follows that the Gibbs integral free energy of the formation of the compound Cu_2SnSe_3 can be calculated by the relation:

$$\Delta_f G°(Cu_2SnSe_3) = 2\Delta\overline{G}_{Cu} + \Delta_f G°(SnSe_2) \quad (7)$$

The enthalpy of formation was calculated in a similar way. The standard entropy can be calculated by the equation:

$$S°(Cu_2SnSe_3) = 2\Delta\overline{S}_{Cu} + 2S°(Cu) + S°(SnSe_2) + S°(Se) \quad (8)$$

In calculations (7) and (8), we used the standard entropies for copper and selenium S°(Cu)= 33.15±0.08 J·mol^{-1}·K^{-1}), S°(Se)= 42.13±0.21 J·mol^{-1}·K^{-1} [28] and also the standard thermodynamic functions of $SnSe_2$ found by the EMF method [29]:

Δ_fG°= -119.2±2.5 kJ·mol^{-1}
Δ_fH°= -124.7±4.2 kJ·mol^{-1}
S°= 118.0±3.0 J·mol^{-1}·K^{-1}

The enthalpies of formation of $SnSe_2$ compound obtained [29] well agree with the calorimetric data [28, 30]. Moreover, the values of free Gibbs energy of the formation calculated from the values of enthalpy of formation and standard entropy recommended in these reference books virtually coincide with the results of [29]. This demonstrates the reliability of thermodynamic data for $SnSe_2$ used in our calculations.

Our results and the literature data are given in Table 2.

Table 1.

Results of computer processing of EMF measurements of concentration chains (1)

T_i, K	E_i, mV	$T_i - \overline{T}$	$E_i(T_i - \overline{T})$	$(T_i - \overline{T})^2$	$\tilde{E}$	$E_i - \tilde{E}$	$(E_i - \tilde{E})^2$
301,3	364,9	-76,45	-27895,08	5843,97	364,66	0,24	0,06
308,1	365,6	-69,65	-25462,52	4850,54	365,54	0,06	0,00
317,9	367,9	-59,85	-22017,28	3581,52	366,82	1,08	1,16
324,2	368,5	-53,55	-19731,64	2867,16	367,65	0,85	0,73
328,6	367,5	-49,15	-18061,09	2415,31	368,22	-0,72	0,52
333,9	368,3	-43,85	-16148,42	1922,46	368,91	-0,61	0,37
342,2	371,1	-35,55	-13191,06	1263,51	369,99	1,11	1,22
349,1	370,3	-28,65	-10607,55	820,58	370,90	-0,60	0,35
358	370,3	-19,75	-7311,88	389,90	372,06	-1,76	3,09
363,7	373,5	-14,05	-5246,12	197,29	372,80	0,70	0,49
367,5	371,9	-10,25	-3810,43	104,98	373,30	-1,40	1,95
375,3	373,7	-2,45	-914,01	5,98	374,31	-0,61	0,38
382,1	375,3	4,35	1634,12	18,96	375,20	0,10	0,01
389,4	377,3	11,65	4397,12	135,82	376,15	1,15	1,31
395,7	375,5	17,95	6741,79	322,35	376,98	-1,48	2,18
400	377,8	22,25	8407,62	495,25	377,54	0,26	0,07
405,2	379	27,45	10405,13	753,73	378,22	0,78	0,61
412,3	379,5	34,55	13113,31	1193,99	379,14	0,36	0,13
420,6	379,3	42,85	16254,59	1836,48	380,23	-0,93	0,86
428,5	383,3	50,75	19454,07	2575,99	381,26	2,04	4,18
433,4	381,4	55,65	21226,50	3097,39	381,90	-0,50	0,25
438,8	383,2	61,05	23395,96	3727,61	382,60	0,60	0,36
442,5	382,5	64,75	24768,47	4193,10	383,08	-0,58	0,34
447,6	383,6	69,85	26796,06	4879,60	383,75	-0,15	0,02
$\overline{T}$ =377,7	$\overline{E}$ =374,6						

Table 2.

Standard integral thermodynamic functions of the Cu_2SnSe_3

$-\Delta_fG°$	$-\Delta_fH°$	S^0	Notes
kJ·mol^{-1}		J·mol^{-1}·K^{-1}	
189.5±2.6	187.5±4.8	251.6±5.0	The present work. EMF method with solid electrolyte
198.4±0.6	198.5±2.9	237±5	[18], EMF method with liquid electrolyte
-	180.5	-	[31], calorimetry method

From Table 2, it follows that the data obtained by us on the standard Gibbs energy of formation and enthalpy of formation are somewhat (5%) lower than the data obtained by the EMF method with liquid electrolyte, where metal tin served as the left electrode [18].

It should also be noted that our data on the standard enthalpy of formation of the Cu_2SnSe_3 compound are in better agreement (4% discrepancy) with calorimetric data [31] than the results of [18] (9% discrepancy).

4. CONCLUSION

Using the EMF technique with solid electrolyte $Cu_4RbCl_3I_2$, new complexes of mutually-agreed thermodynamic data ($\Delta_fG°$, $\Delta_fH°$, S^0) for Cu_2SnSe_3 compound are obtained. A comparative analysis of the obtained and published data is carried out. The results of this work confirm the possibility of use of the EMF method with a cation-conducting solid electrolyte to systems containing a more active metal (in our case, tin) than copper.

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