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THERMODYNAMIC STUDY OF THE $CuAsSe_2$ COMPOUND by EMF METHOD WITH SOLID ELECTROLYTE

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Abstract. By using the measurements of electromotive forces (EMF) of the concentration cells of the type(-) Cu (s.) | solid electrolyte $Cu_4RbCl_3I_2$ | (Cu-As-Se) (s.) (+) in the temperature range 300–450 K, the thermodynamic properties of the $CuAsSe_2$ compound have been studied. From the EMF measurements data for equilibrium three-phase alloys Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3, a linear equation of the temperature dependence of the EMF is obtained, from which the partial thermodynamic functions of copper in the alloys are calculated. Based on these data and the diagram of solid-phase equilibria of the Cu-As-Se system using the corresponding thermodynamic functions of As_2Se_3 and Cu_3AsSe_4, the standard Gibbs free energy of formation and enthalpy of formation, as well as the standard entropy of the $CuAsSe_2$ compound were calculated.

Keywords: *copper-arsenic selenide, EMF method, thermodynamic properties, solid electrolyte.*

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1. Introduction

Three-component copper chalcogenides are among the promising functional materials of modern technology. Due to their diverse functional properties, they are considered very promising for use in cross-cut energy conversion, energy storage, sensors, and medical devices (Babanly *et al.* 1993; Coughlan *et al.*, 2017; Zeng *et al.*, 2021; Xia *et al*,. 2018; Jacyna-Onyszkiewicz *et al.*, 2003; Liu *et al.*, 2020; Embden *et al.*, 2020). Some of them are superionic conductors with high conductivity for Cu^+ cations and are considered promising for use as ion-selective electrodes, solid electrolytes, etc. (Lin *et al.*, 2015; Sunandana, 2015).

The Cu-As-Se system is of increased interest due to the fact that both crystalline and glassy phases possess practically important functional properties (Babanly *et al.* 1993; Popesku, 2001; Xin *et al*., 2008).

The results of studies on phase equilibria in the Cu-As-Se system and the properties of its intermediate ternary phases, carried out before the early 90s of the last century, are summarized in Babanly et al. (1993); Tedenac, (1994). A somewhat later published work Cohen et al. (1995) presents new data on phase equilibria in this system, which differs from those previously published. In particular, of the ternary compounds Cu_3AsSe_4, $CuAsSe_2$, Cu_3AsSe_3, $Cu_6As_4Se_9$, described in the literature, only the first two are reflected in the phase diagram constructed by the authors Cohen et al. (1995). Unfortunately, in Cohen et al (1995) there are no references to previously works and, therefore, there is no comparative analysis of previously published data. A comparison of the available literature data shows that, despite the knowledge of a number of

polythermal sections, a reliable picture of phase equilibria in the Cu-As-Se system has not yet been obtained.

Considering the above, we have undertaken a new detailed study of phase equilibria in the Cu-As-Se system and the thermodynamic properties of copper-arsenic selenides. In Mashadieva et al (2017), the data on phase equilibria in the Cu-Cu_2Se-As subsystem are presented, while in Mashadieva et al (2017), the phase diagram of the Cu_2Se-Cu_3AsSe_4-Se subsystem and the thermodynamic functions of the Cu_3AsSe_4 compound.

The purpose of this work is a thermodynamic study of the $CuAsSe_2$ compound by the EMF method with a solid electrolyte.

Various modifications of the EMF method with liquid (Morachevsky *et al.*, 2003; Babanly *et al*., 2019; Imamaliyeva *et al.,* 2020; Imamaliyeva, 2021; Vasiliev *et al.*, 2019), solid (Morachevsky *et al.,* 2003; Moroz *et al.,* 2018; Mammadli *et al.,* 2021; Alverdiev *et al.,* 2018) and ionic liquid (Aliev *et al.,* 2018; İmamaliyeva *et al.,* 2019) are widely used for the thermodynamic study of semiconductor chalcogenides.

2. Experimental part

Despite the fact that a reliable picture of phase equilibria in the Cu-As-Se system has not yet been obtained, the data on phase equilibria in the region of compositions rich in selenium are beyond doubt. According to these data, the sections Cu_3AsSe_4-$CuAsSe_2$(As_2Se_3) and $CuAsSe_2$-As_2Se_3 are quasi-binary and belong to the eutectic type. This means that the system contains an elementary triangle Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3. For the thermodynamic study of the $CuAsSe_2$ compound, we used equilibrium alloys from the indicated three-phase region.

Samples from the Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3 phase region were prepared by fusing high-purity elementary components (copper, CAS №7440-50-8; arsenic №7440-38-2; selenium, № 7782-49-2) in evacuated quartz ampoules. Two samples weighing 1 g with several compositions were synthesized. Taking into account the tendency of alloys to glass formation (Popesku, 2001), after alloying, they were subjected to prolonged (up to 1500 h) thermal annealing at 450 K.

The phase compositions of the annealed alloys were determined by XRD (diffractometer Bruker D8 ADVANCE, CuKα- radiation). Fig. 1 shows a powder diffractogram of the samples from investigated area. As can be seen, this alloy consists of a three-phase mixture Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3 and its crystallinity degree is quite high.

For thermodynamic studies, concentration cells of the

$$(-)\ Cu\ (s.)\ |\ Cu_4RbCl_3I_2\ (s.)\ |\ (Cu\text{-}As\text{-}Se)\ (s.)\ (+) \qquad (1)$$

type were assembled.

The compound $Cu_4RbCl_3I_2$, used as a solid electrolyte in the cells of type (1), was synthesized by melting of stoichiometric amounts of chemically pure, anhydrous CuCl (CAS № 7758-89-6), CuI (CAS №7681-65-4), and RbCl (CAS №7791-11-9) in an evacuated (~10^{-2} Pa) quartz ampoule at 900 K followed by cooling to 450 K and homogenizing annealing at this temperature for 100 h (Babanly *et al.,* 2011). From the obtained cylindrical ingot with a diameter of ~6 mm, tablets with a thickness of 3-4 mm were cut out, which were used in the cells of type (1) as a solid electrolyte.

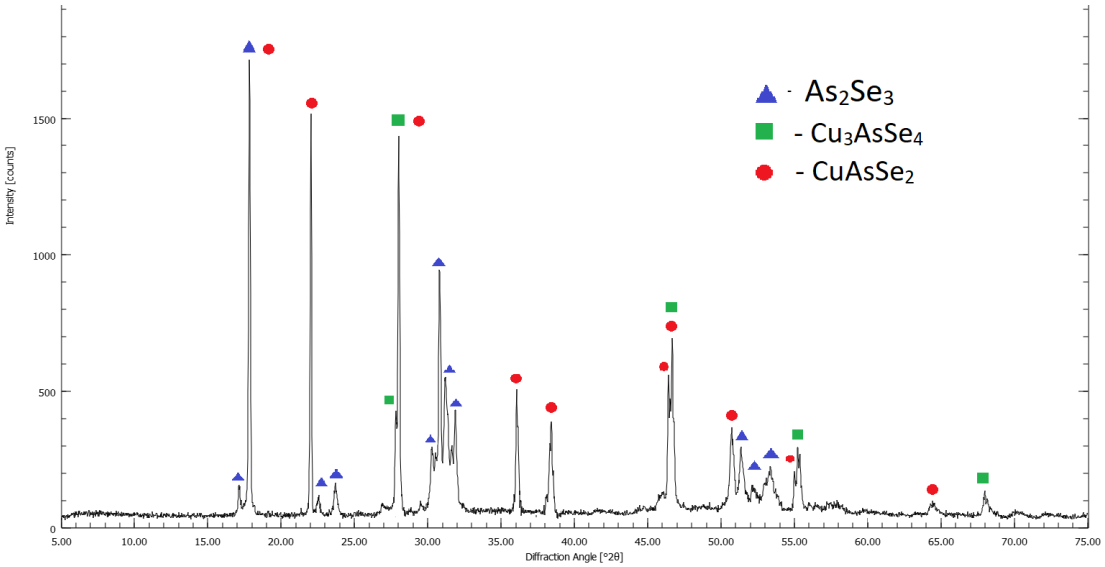

Figure 1. The powder diffractogram of the samples from the Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3 three-phase area

The pre-synthesized and annealed equilibrium alloys from the Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3 phase region, were used as the right electrodes of type (1) cells. The right electrodes were prepared by pressing of powdered alloys in the cylindrical tablets of ~6 mm in diameter and 3-4 mm in thickness.

The electrochemical cell described (Aliev *et al.*, 2018) was assembled, vacuumized, filled with argon, and placed in a cylindrical furnace. All contacts and leads of the cell were kept at the same temperature. The first equilibrium EMF values were obtained after holding the electrochemical cell at ~350 K for ~60 h, and the subsequent ones every 3–4 h after reaching the desired temperature. The system was considered to be in equilibrium if measured EMF values were constant or their variations were not significant (<0.5 mV) regardless of the direction of the temperature change at repeated measurements at a given temperature.

3. Results and its discussion

EMF measurements of the cells of type (1) for samples from the Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3 three-phase region showed a linear character of the EMF dependence on temperature (Fig. 2). This makes it possible to use the indicated data for thermodynamic calculations (Babanly *et al.*, 2011). Taking this into account, the EMF data were processed by the least-squares method using the Microsoft Office Excel 2003 computer program. The initial experimental data and the steps of calculations are presented in Table. A linear equation is obtained, which is presented in the form

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

Here, *a* and *b* are coefficients, *n* is the number of pairs of values E (mV) and T (K); $\overline{T}$ - average temperature (K), t is Student's test, and δ_E^2 and δ_b^2 are the variances of

individual EMF values and the constant *b*. Due to number of experimental points *n* = 30, and the confidence level equal to 95%, the Student's test is t ≤ 2.

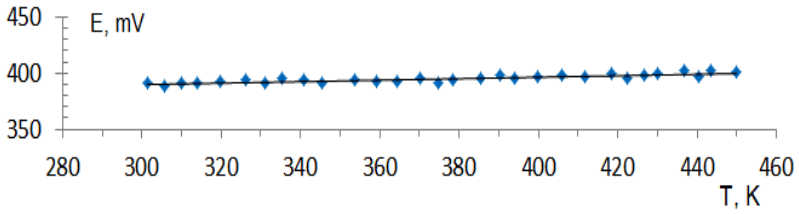

Figure 2. The EMF dependence on temperature for the alloys from the Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3 three-phase area

From the equation obtained

$$E, mV = 370.73 + 0{,}0652T \pm 2\left[\frac{2.43}{30} + 3.9 \cdot 10^{-5}(T - 376.2)^2\right]^{1/2} \quad (3)$$

using the relations (Morachevsky *et al*., 2003; Babanly *et al*., 2011)

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

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

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

the relative partial thermodynamic functions of copper in the Cu_3AsSe_4+$CuAsSe_2$+As_2Se_3 three-phase alloys were calculated:

$\Delta\bar{G}_{Cu}$= -37.65±0.05 кJ·mol^{-1};

$\Delta\overline{H}_{Cu}$= -35.77±0.23 кJ·mol^{-1};

$\Delta\overline{S}_{Cu}$= 6.29±0.61 J·K^{-1}·mol^{-1}.

According to the phase composition of the right electrodes of the cells of type (1), the partial molar values of copper are the thermodynamic characteristics of the following potential-formation reaction (the state of all substances is crystalline):

$$Cu + 0{,}5Cu_3AsSe_4 + As_2Se_3 = 2{,}5\ CuAsSe_2 \quad (7)$$

In accordance with relation (7), the standard thermodynamic functions of formation and the standard entropy of the Cu_3AsSe_4 compound were calculated from the relations

$$\Delta_f Z^0(CuAsSe_2) = 0{,}4\Delta\overline{Z}_{Cu} + 0.4\Delta_f Z^0(As_2Se_3) + 0.2\Delta_f Z^0(Cu_3AsSe_4) \quad (8)$$

$$S^0(CuAsSe_2) = 0.4\Delta\overline{S}_{Cu} + 0.4S^0(Cu) + 0.4S^0(As_2Se_3) + 0.2S^0(Cu_3AsSe_4) \quad (9)$$

(Z = G, H)

and the following data were received:

Δ_fG^0(298 K) = -66.6±0.4 кJ·mol^{-1};

Δ_fH^0(298 K) = -67.3±2.0 кДж·моль$^{-1}$;

S^0(298 K)=150.9±6.2 J·K^{-1}·mol^{-1}.

Table. Experimentally obtained data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the Cu_3AsSe_4-$CuAsSe_2$-As_2Se_3 three-phase region

T_i, K	E_i, мВ	$T_i - \bar{T}$	$E_i(T_i - \bar{T})$	$(T_i - \bar{T})^2$	$\tilde{E}$	$E_i - \tilde{E}$	$(E_i - \tilde{E})^2$
301,3	391,15	-74,90	-29298,44	5610,51	390,37	0,78	0,61
305,8	388,92	-70,40	-27381,26	4956,63	390,66	-1,74	3,03
310,1	391,83	-66,10	-25901,27	4369,65	390,94	0,89	0,79
314	390,67	-62,20	-24300,98	3869,25	391,20	-0,53	0,28
319,9	393,12	-56,30	-22133,97	3170,07	391,58	1,54	2,37
326,2	394,45	-50,00	-19723,81	2500,33	391,99	2,46	6,04
331,1	390,91	-45,10	-17631,34	2034,31	392,31	-1,40	1,96
335,3	395,28	-40,90	-16168,27	1673,08	392,58	2,70	7,27
340,8	393,36	-35,40	-13926,26	1253,40	392,94	0,42	0,17
345,4	391,72	-30,80	-12066,28	948,85	393,24	-1,52	2,32
353,6	394,19	-22,60	-8910,01	510,91	393,78	0,41	0,17
359,2	392,7	-17,00	-6677,21	289,11	394,14	-1,44	2,08
364,5	392,35	-11,70	-4591,80	136,97	394,49	-2,14	4,57
370,2	395,97	-6,00	-2377,14	36,04	394,86	1,11	1,23
374,7	391,84	-1,50	-589,07	2,26	395,15	-3,31	10,97
378,3	394,42	2,10	826,97	4,40	395,39	-0,97	0,94
385,5	395,91	9,30	3680,64	86,43	395,86	0,05	0,00
390,2	397,83	14,00	5568,29	195,91	396,16	1,67	2,78
394,1	395,25	17,90	7073,66	320,29	396,42	-1,17	1,36
399,8	397,46	23,60	9378,73	556,80	396,79	0,67	0,45
406	397,82	29,80	11853,71	887,84	397,19	0,63	0,39
411,7	396,7	35,50	14081,53	1260,01	397,56	-0,86	0,75
418,4	398,96	42,20	16834,78	1780,56	398,00	0,96	0,92
422,5	395,83	46,30	18325,61	2143,38	398,27	-2,44	5,94
426,7	398,24	50,50	20109,79	2549,91	398,54	-0,30	0,09
430,2	398,91	54,00	21539,81	2915,64	398,77	0,14	0,02
436,9	401,73	60,70	24383,67	3684,09	399,21	2,52	6,37
440,3	397,44	64,10	25474,58	4108,38	399,43	-1,99	3,95
443,6	401,78	67,40	27078,63	4542,31	399,64	2,14	4,57
449,8	400,77	73,60	29495,34	5416,47	400,05	0,72	0,52
$\bar{T}$ =376,2	$\bar{E}$ =395,3						

In the calculations, in addition to our experimental results, we used the values of the standard entropy of copper (33.15±0.08 $J \cdot K^{-1} \cdot mol^{-1}$) [Thermal constants of substances: Database], as well as the standard integral thermodynamic functions of As_2Se_3 (Babanly *et al.*, 2017) and Cu_3AsSe_4 (Mashadieva *et al.*, 2018) obtained by the EMF method.

4. Conclusion

Using the EMF method with a Cu^+ -conducting solid electrolyte, a new set of consistent thermodynamic data for the $CuAsSe_2$ compound was obtained, including the partial molar Gibbs free energy of formation, the enthalpy and entropy of copper in the Cu_3AsSe_4+$CuAsSe_2$+As_2Se_3 alloys, and the corresponding standard thermodynamic formation and standard entropy.

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