Phase Equilibria and Some Electrophysical Properties in the CuCr$_2$S$_4$-In System

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Abstract—The CuCr$_2$S$_4$-In system has been investigated by the complex methods of physico-chemical analysis and its state diagram has been plotted. It is established that the system is non-quasibinary. There has been exposed a wide field of solubility on the basis of CuCr$_2$S$_4$, a boundary of which reaches 70 mol% CuCr$_2$S$_4$ at 300 K. The equations for calculation of enthalpy and free energy of the formation of CuCr$_2$S$_4$ and Cu$_{1-x}$In$_x$CrS$_3$ have been worked onto Examination of temperature dependence of electric conductivity of solid solutions of Cu$_{1-x}$In$_x$CrS$_3$ showed that with increasing indium in composition the character of conductivity changes from polymetallic to semiconducting one, and in composition of Cu$_{0,4}$In$_{0,3}$CrS$_3$ mechanism of jumping conductivity is revealed.

Keywords—magnetic semiconductor; faze diagram; thermodynamically functions; jumping conductivity.

I. INTRODUCTION

The numerous works [1-3] are dedicated to investigation of solid solutions of Cu$_{1-x}$In$_x$CrS$_3$, however, up to present diagram of state of the CuCr$_2$S$_4$-In system has not been studied yet. Therefore, there exist the contradictory data on maximum of solubility boundaries of indium in the compound CuCr$_2$S$_4$. Consequently, plotting a state diagram of the CuCr$_2$S$_4$-In system is actual. One of the initial components of this system – the compound CuCr$_2$S$_4$ is thoroughly examined magnetic semiconductor crystallized in a structure of spinel [4, 5]. In [6] to investigate conditions of formation of CuCr$_2$S$_4$ the process of synthesis carried out from binary compounds CuS and Cr$_2$S$_3$ was registered. It appeared that on curves of heating CuCr$_2$S$_4$, preliminarily synthesized and undergone to annealing, there is observed one endothermic effect at 1433 K, corresponding to the temperature of decay for this compound. as well the authors showed that at synthesis of CuCr$_2$S$_4$ from the initial compounds CuS and Cr$_2$S$_3$ don’t give the positive results, though prolonged thermal annealing increases maintenance of a spinel structure. The unfavorable results are also obtained at synthesis of the compound CuCr$_2$S$_4$ from an elementary copper, sulfur and Cr$_2$S$_3$. Therefore, on the basis of the numerous and of many days tests the conclusion has been drawn that it is expedient to carry out synthesis of CuCr$_2$S$_4$ from the elements entering composition of this compound. To receive CuCr$_2$S$_4$ the authors [7] use the hydrothermal method by means of crystallization of CuS and Cr$_2$S$_3$ from aqueous solutions.

II. EXPERIMENTAL PART

The character of physico-chemical interaction in the CuCr$_2$S$_4$-In system was studied by the differential and thermal analysis (DTA), including also high temperature (HDTA), microstructural (MSA) and X-ray phase (RPA) analyses on the devices THERMSKAN-2 and BDTA-8M, MUM-8, D2, FHASER(CuKa radiation with Ni-filter respectively). Mikrosolidity was determined on the metallurgical microscope PMT-3, and density was measured by means of pycnometer with toluene liquid. The synthesis of the alloys was carried out from the elements: Cu – electrolyt, Cr of Erkh mark, sulfur «OSCh» and indium In-000. Technological mode of obtaining alloys of the studied system was similar to the methods cited in [6], with a slight difference of synthesis temperature (±303-323 K) and homogenization annealing. At interaction of copper, indium, chrome and sulfur some sharply expressed heat effects were observed on the thermograms what testifies to intensive proceeding of reaction between these elements with isolation of a great volume of heat. Homogenizing annealing was carried out at ~1073 K within 300 h. Afterwards such thermal treatment the samples were brought to a powdery state and compressed, then endured within 10 days at temperature of 873 K. Consequently, the process of thermal treatment of samples had two-stage character. The electro-physical properties were measured by the compensating method [8] on the compressed samples of the parallelepiped form in the 80-703 K range.

III. THE RESULTS OF THE EXPERIMENT AND THEIR DISCUSSION

At substitution of copper atoms for indium atoms in structure of CuCr$_2$S$_4$ till composition Cu$_{0,7}$In$_{0,3}$Cr$_2$S$_4$ the spinel structures of solid solutions of subtraction form what is indicated by decrease in the values of micro hardness from ~2350 MP for CuCr$_2$S$_4$ to ~200 MP for solid solutions Cu$_{0,7}$In$_{0.3}$Cr$_2$S$_4$. Psychometric densities change within the bounds 5.44 g/cm$^3$-5.68
CuCr$_2$S$_4$ and solid solutions Cu$_{1-x}$In$_x$CuCr$_2$S$_4$ have been calculated. By Kelly’s method, the standard entropy of the compound is a sum of the partial pies of ions increments of composition:

$$S^0_{298}(\text{CuCr}_2\text{S}_4) = S^0_{298}(\text{Cu}^{2+}) + 2S^0_{298}(\text{Cr}^{3+}) + 4S^0_{298}(\text{S}^{2-}) = 211 \text{ J mol}^{-1} \text{K}^{-1}.$$

On the other hand, according to Eastman’s method the standard entropy of compound formed by paratactic reaction is calculated as follows:

$$S_{298}^n(\text{CuCr}_2\text{S}_4) = m \left[3R \ln \left( \frac{M}{m} \rho^2 \right) + 52.33 \right] = 179 \text{ J mol}^{-1} \text{K}^{-1},$$

where $m=7$ is a number of atoms in a molecule, $M=296$, molar mass of a compound, $T=1473$, $\rho=5.44 \text{ g cm}^{-3}$. If the values of standart entropy, calculated by the different methods are distinctive, it is expedient to assume as a basis their average values, i.e.

$$S_{298}^n(\text{CuCr}_2\text{S}_4) = 195 \text{ J mol}^{-1}.$$

Entropy of compound formation mab be written as follows:

$$\Delta S^o_{298}(\text{CuCr}_2\text{S}_4) = S_{298}^o(\text{CuCr}_2\text{S}_4) - S_{298}^o(\text{In}) = -15.4 \text{ J mol}^{-1} \text{K}^{-1}.$$

Enthalpy of formation of three – component compound with account for addictiveness, is formed from enthalpy of formation of the corresponding two-component compounds:

$$\Delta H^o_{298}(\text{CuCr}_2\text{S}_4) = \Delta H^o_{298}(\text{CuS}) + \Delta H^o_{298}(\text{CrS}) - m \cdot A,$$

where $A$ is a deviation index from addictiveness and for supplied compounds $A=10 \text{ kJ mol}^{-1} \text{atom}^{-1}$. Free energy of compound CuCr$_2$S$_4$ is calculated by Gibbs – Hellhole’s equation: The calculated value of thermodynamic functions of compound CuCr$_2$S$_4$ are equal to:

$$-\Delta G^o_{298} = 577.0 \text{ kJ mol}^{-1}$$

and

$$\Delta G^o_{298} = 572.4 \text{ kJ mol}^{-1}.$$
partial thermodynamic stability of the studied composition.

The results of investigation of temperature dependence of electric conductivity of pure compound CuCr$_2$S$_4$ and solid solutions Cu$_{1-x}$In$_x$Cr$_2$S$_4$ are cited in Fig. 3.

It is seen that at transition from a matrix compound to solid solutions the character of conductivity changes polymetallic to semiconducting one. All the compositions of the examined samples possess a field of own conductivity at high temperatures. According to the tangent of incline angle of the curves of dependence $\ln \sigma ~ f(10^3/T, K)$ the values of thermal width of inhibited zone have been calculated. In addition to Fig. 3 the dependence of width values of inhibited zone on composition of solid solutions Cu$_{1, x}$In$_x$Cr$_2$S$_4$ is cited. With increasing the quantity of indium in composition of alloys the growth of a value of $\Delta E$ is observed. Temperature dependence of electric conductivity of solutions Cu$_{0.8}$In$_{0.2}$Cr$_2$S$_4$ and Cu$_{0.7}$In$_{0.3}$Cr$_2$S$_4$ may be conditionally divided into several fields which are differed by the diverse mechanisms of charge transfer. In composition of Cu$_{0.8}$In$_{0.2}$Cr$_2$S$_4$ a temperature range of ~250°C K a curve of course $\ln \sigma ~ f(10^3/T, K)$ is of exponential character with diminishing energy of activation of charge carriers. Like temperature dependence of conductivity is characteristic for non-regulated crystals in which conductivity is performed through jumping mechanism over localized states with a variable length of jumping near Fermi level. At low temperatures for composition Cu$_{0.8}$In$_{0.2}$Cr$_2$S$_4$ weak temperature dependence of electric conductivity is observed and it is typical of weakly actin voted jumping conductivity. A course of curve plotted in Mott’s coordinates [9] in low temperature field (Fig. 4) testifies in favor for the stated. As is seen, dependence $\ln \sigma ~ f(T^{4/25}, K)$ for composition of Cu$_{0.7}$In$_{0.3}$Cr$_2$S$_4$ is seen a rectilinear what testifies to that conductivity is carried out through jumps of charge carriers over the localized states concentrated in a narrow strip of energies near Fermi level.

Fig.3. The temperature dependence of conductivity CuCr$_2$S$_4$ and solid solutions Cu$_{1, x}$In$_x$Cr$_2$S$_4$ (on the console of dependence of the prohibited zone values on the composition of the solid solutions Cu$_{1, x}$In$_x$Cr$_2$S$_4$)

IV. RESULTS AND CONCLUSIONS

The plotted state diagram indicated to non-quasibility of the CuCr$_2$S$_4$-In system and exposed existence of the homogeneous field based on CuCr$_2$S$_4$, determined a boundary of this field which at 300 K reaches ~70 moli% CuCr$_2$S$_4$.

Determination of thermodynamic functions of the obtained materials pointed to the partial thermodynamic stability of solid solutions Cu$_{1, x}$In$_x$Cr$_2$S$_4$.

Investigation of temperature dependence of electric conductivity of CuCr$_2$S$_4$ and solid solutions Cu$_{1, x}$In$_x$Cr$_2$S$_4$ showed change of the character of current transfer from polymetallic (for connecting CuCr$_2$S$_4$ and homogeneous compositions Cu$_{0.6}$In$_{0.4}$Cr$_2$S$_4$, Cu$_{0.4}$In$_{0.6}$Cr$_2$S$_4$) to semiconducting one with jumping mechanism of conductivity (for solid solutions Cu$_{0.7}$In$_{0.3}$Cr$_2$S$_4$).

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