Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 3159-0040
Vol. 2 Issue 3, March - 2015

Phase Equilibra and Some Electrophycal Properties in the $CuCr_2S_4$-In System

Chingiz Abilov
Department of Radio Engineering and Telecommunication Azerbaijan Technical University
Baku/AZERBAIJAN
cabilov@yahoo.com

Adalet Kuliyev
Azerbaijan State Pedagogical University Baku/AZERBAIJAN
adalet-guliyev@rambler.ru

Mehriban Hasanova
Department of Radio Engineering and Telecommunication Azerbaijan Technical University
Baku/AZERBAIJAN
mhsh28@mail.ru

***Abstract*—The $CuCr_2S_4$-In system has been investigated by the complex methods of physic-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 dissolubility on the basis of $CuCr_2S_4$, a boundary of which reaches 70 moll% $CuCr_2S_4$ at 300 K. The equations for calculation of enthalpy and free energy of the formation of $CuCr_2S_4$ and $Cu_{1-x}In_xCr_2S_4$ have been worked onto Examination o temperature dependence of electric conductivity of solid solutions of $Cu_{1-x}In_xCrS_4$ showed that with increasing indium in composition the character of conductivity changes from polymetallic to semiconducting one, and in composition of $Cu_{0,7}In_{0,3}Cr_2S_4$ 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 $Cu_{1-x}In_xCr_2S_4$, however, up to present diagram of state of the $CuCr_2S_4$-In system has not been studied yet. Therefore, there exist the contradictory data on maximum of dissolubility boundaries of indium in the compound $CuCr_2S_4$. Consequently, plotting a state diagram of the $CuCr_2S_4$-In system is actual. One of the initial components of this system – the compound $CuCr_2S_4$ is thoroughly examined magnetic semi-conductor crystallized in a structure of spinel [4, 5]. In [6] to investigate conditions of formation of $CuCr_2S_4$ the process of synthesis carried out from binary compounds CuS and Cr_2S_4 was registered. It appeared that on curves of heating $CuCr_2S_4$, 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 $CuCr_2S_4$ from the initial compounds CuS and Cr_2S_4 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 $CuCr_2S_4$ from an elementary copper, sulfur and Cr_2S_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 $CuCr_2S_4$ from the elements entering composition o this compound. To receive $CuCr_2S_4$ the authors [7] use the hydrothermal method by means of crystallization of CuS and Cr_2S_3 from aqueous solutions.

II. EXPERIMENTAL PART

The character of physic-chemical interaction in the $CuCr_2S_4$-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 TERMSKAN-2 and BDTA-8M, MUM-8, D2, FHASER (CuKa radiation with Ni-filter respectively). Mikrosolidity was determined on the metallographic 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 – electrolytic, 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 thermo grams 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 $CuCr_2S_4$ till composition $Cu_{0,7}In_{0,3}Cr_2S_4$ the spinel structures of solid solutions of subtraction form what is indicated by decrease in the values of micro hardness from ~2350 MP for $CuCr_2S_4$ to ~200 MP for solid solutions $Cu_{0,7}In_{0,4}Cr_2S_4$. Psychometric densities change within the bounds 5.44 g/cm^3÷5.68

g+cm^3 at transit from $CuCr_2S_4$ to composition of $Cu_{0,7}In_{0,3}Cr_2S_4$. The results of DTA and HDA showed that all the fixed effects on the curves of heating and cooling are reversible. Three series of effects at 426 K, 973 K and 1033 K characterize three isothermal processes of occurring in the $CuCr_2S_4$-In system. It has been also established that at interaction of the initial components a wide field of a – solid solutions on the basis of $CuCr_2S_4$ forms. In Fig. 1 the plotted diagram of a state of the $CuCr_2S_4$ system is cited. As is seen, the system is non-quasibinary, a field of solid solutions discovered in it, has a boundary of ~70 moll% $CuCr_2S_4$. It is supposed that at interaction of $CuCr_2S_4$ with In two reactions may proceed: $CuCr_2S_4+In \rightarrow CuInS_2 + InS + CrS$ and $CuCr_2S_4 + In \rightarrow CuInS_2 + 2CrS$.

In both cases the display of the compound $CuInS_2$ in this system becomes probable.

Revealing or reveling of the existence of indium monosulfides and chrome in this system is clarified in the results of RFA (Fig.2). Comparison of x-ray grams of some structures of the $CuCr_2S_4$-In system showed that they consist in the intensities of lines $CuInS_2$ and CrS only. Therefore, the probable reaction proceeding in the $CuCr_2S_4$-In system is above-stated second reaction.

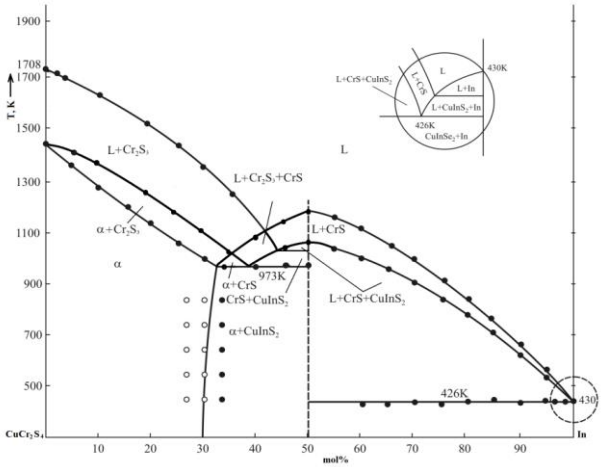

Fig.1. *Diagram of $CuCr_2S_4$-In system status*

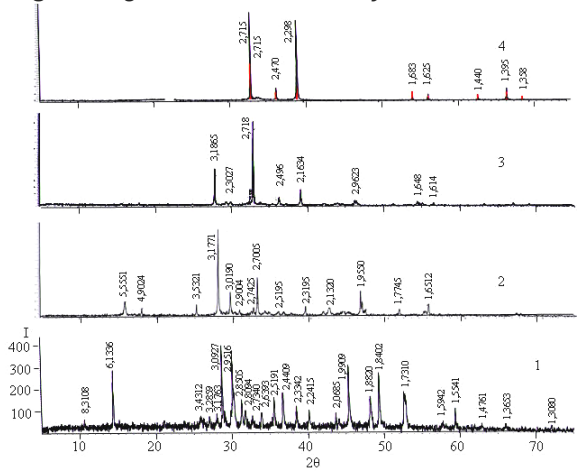

Fig.2. *Diffraction patterns of the original components and some alloys of system $CuCr_2S_4$-In system*

$CuCr_2S_4$ and solid solutions $Cu_{1-x}In_xCr_2S_4$ 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:

$$S^0_{298}(CuCr_2S_4) = S^0_{298}(Cu^{2+}) + 2S^0_{198}(Cr^{3+}) + 4S^0_{298}(S^{2-}) = 211\frac{J}{molk}.$$

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

$$S^0_{298}(CuCr_2S_4) = m\left[3R\ln(\frac{M/m}{\rho^{2/3}T} + 52,33\right] = 179\frac{J}{molK},$$

where m=7 is a number of atoms in a molecule, M=296, molar mass of a compound, T=1473, ρ =5,44 g/sm^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. $S^6_{298}(CuCr_2S_4) = 195\frac{J}{molK}$. Entropy of compound formation mab be written as follows:

$$\Delta S^0_{298}(CuCr_2S_4) = S^0_{298}(CuCr_2C_4) - \left[S^0_{298}(Cu) + 2S^0_{298}(Cr_2) + 4S^0_{298}(S)\right] = -15,4\frac{J}{molK}.$$

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

$$\Delta H^0_{298}(CuCr_2S_4) = \Delta H^0_{298}(CuS) + \Delta H^0_{298}(Cr_2S_3) - m\cdot A,$$

where A is a deviation index from addictiveness and for supplied compounds $A = 10\frac{kJ}{mol\cdot atom}$. Free energy of compound $CuCr_2S_4$ is calculated by Gibbs – Hellhole's equation: The calculated value of thermodynamic functions of compound $CuCr_2S_4$ are equal to: $-\Delta H^0_{298} = 577,0\frac{kJ}{mol}$ and $\Delta G^0_{298} = 572,4\frac{kJ}{mol}$. At x_{In}=0-0,3 for curve line of liquids of the system $CuCr_2S_4$-In it is possible to write that T, K =1473-2500 x_{In}. To estimate thermodynamic stability of solid solutions Cu_{1-x} In_x Cr_2S_4 there were approximated their integral thermodynamic function of formation with the use of the values above determined of entropy, enthalpy and free energy

$$S^0_{298} = xS^0_{298}(CuCr_2S_4) + (1-x)S^0_{298}(In) - R\left[x\ln f(y) + (1-x)\ln f_2(y)\right] =$$
$$= 195x + 57,8(1-x) - 8,31\cdot T_l\left[x\ln f_1(y) + (1-x)\ln f_2(y)\right],$$

$$\Delta S^0_{298} = -15,4_x - 8,31T_l\left[x\ln f_1(y) + (1-x)\ln f_2(y)\right],$$

$$\Delta G^0_{298} = -577x - 8,31T_l\left[x\ln f_1(y) + (1-x)\ln f_2(y)\right].$$

The results of calculations show that the values of free energy of solid solutions $Cu_{1-x}In_xCr_2S_4$ are negative in the range of temperatures and concentrations of their existence, what testifies to

partial thermodynamic stability of the studied composition.

The results of investigation of temperature dependence of electric conductivity of pure compound $CuCr_2S_4$ and solid solutions $Cu_{1-x}In_xCr_2S_4$ are cited in Fig. 3.

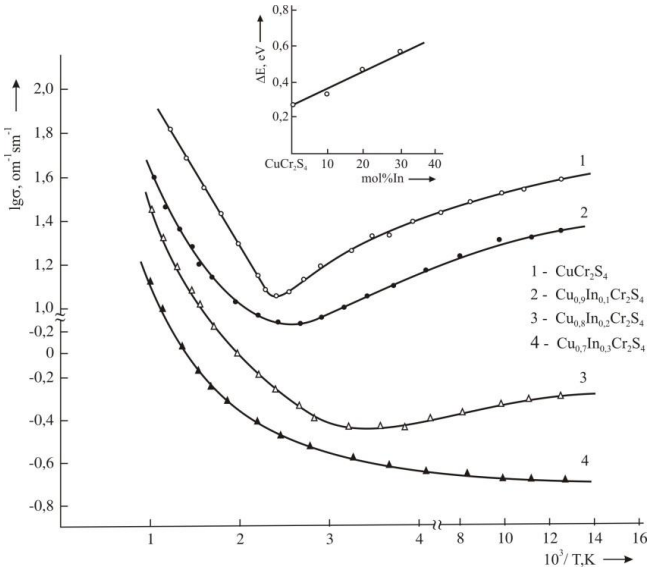

Fig.3. *The temperature dependence of conductivity $CuCr_2S_4$ and solid solutions $Cu_{1-x}In_xCr_2S_4$ (on the console of dependence of the prohibited zone values on the composition of the solid solutions $Cu_{1-x}In_xCr_2S_4$)*

It is seen that at transition from a matrix compound to soled 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 $lg\sigma \sim f(10^3/T, K)$ 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 of $Cu_{1-x}In_xCr_2S_4$ is cited. With increasing the quantity of indium in composition of alloys the growth of a value of ΔE is observed. Temperature dependence of electric conductivity of solutions $Cu_{0,8}In_{0,2}Cr_2S_4$ and $Cu_{0,7}In_{0,3}CrS_4$ may be conditionally divided into several fields which are differed by the diverse mechanisms of charge transfer. In composition of $Cu_{0,7}In_{0,3}Cr_2S_4$ in a temperature range of ~250 ÷250 K a course of curve $lg\sigma \sim f(10^3/T, K)$ 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 $Cu_{0,7}In_{0,3}Cr_2S_4$ weal 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 [9j in low temperature field (Fig. 4) testifies in favor for the stated. As is seen, dependence $ln\sigma \sim f(T^{-0,25}, K)$ for composition of $Cu_{0,7}In_{0,3}Cr_2S_4$: s 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.

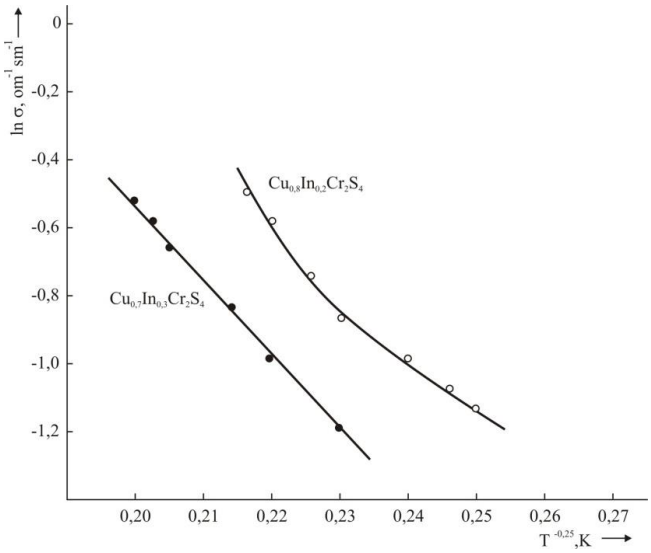

Fig.4. *The temperature dependence of solid solutions conductivity $Cu_{0,8}In_{0,2}Cr_2S_4$ and $Cu_{0,7}In_{0,3}Cr_2S_4$ in Mott coordinates (237K<T<623K)*

IV.RESULTS AND CONCLUSIONS

The plotted state diagram indicated to non-quasibinary of the $CuCr_2S_4$-In system and exposed existence of the homogeneous field based on $CuCr_2S_4$, determined a boundary of this field which at 300 K reaches ~70 moll% $CuCr_2S_4$.

Determination of thermodynamic functions of the obtained materials pointed to the partial thermodynamic stability of solid solutions $Cu_{1-x}In_xCr_2S_4$.

Investigation of temperature dependence of electric conductivity of $CuCr_2S_4$ and solid solutions $Cu_{1-x}In_xCr_2S_4$ showed change of the character of current transfer from polymetallic (for connecting $CuCr_2S_4$ and homogeneous compositions $Cu_{0,9}In_{0,1}Cr_2S_4$, $Cu_{0,6}In_{0,2}Cr_2S_4$) to semiconducting one with jumping mechanism of conductivity (for solid solutions $Cu_{0,7}In_{0,3}Cr_2S_4$).

REFERENCES

[1] R. Plumier, M. Sougi. Magnetic ordering normal spine $Cu_{0,5}In_{0,5}Cr_2S_4$// Sol. State Commun. 1989, vol. 69, №4, pp. 341-345.

[2] L.I. Koroleva. Magnetic semiconductors. M., 2003, Print-house, MSU, 312 p.

[3] K.P. Belov, L.I. Koroleva, N.A. Tsvetkova. The features of magnetic and transport properties of the system of solid solutions x $CuCr_2S_4$–(1–x) $Cu_{0,5}In_{0,5}Cr_2S_4$ // Physic of solid, 1981, V. 23, №2, pp. 372-378.

[4] S.G. Ovchinnikov. Variable valence in chalcogenide chromium spinals // Physics of solid, 1979, v. 21, №10, pp. 994-3002.

[5] T. Saha-Dasgupta, M. De Raychaudhury, D.D. Sarema. Ferromagnetism in metallic chalcospinels $CuCr_2S_4$ and $CuCr_2Se_4$// Phys. Rev. B, 2007, vol. 76, №5, pp. 71-75.

[6] G.G. Shabunina, T.G. Aminov. Investigation of interaction in the Cu-Cr-S // Journal of inorganic chemistry, 1994, v. 39, №3, pp. 1575-1579.

[7] El-H.M. Difellah, A.Y. Ovoid, A.A. Samarkandy, M.M. Abel Bodei, A.A. El-Bellihit. Formation of copper-chromium sulfide spinal and thermal decomposition reactions in CuS-Cr_2S_3 crystalline mixtures // J. of Solid State Chemistry, 1995, vol. 117, №2, pp 122-126.

[8] M.A. Kretova, P.S. Avilov, V.C. Zemskov. Introduction into methods of experiment, results and their discussions. M., 2004, Nauka, 196 p.

[9] S.N. Mott. Electrons in glass // Rev. Mod. Phys. 1978, vol. 50, №2, p. 203-208.