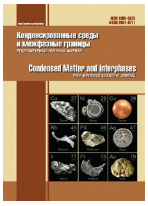

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The quasi-binary $Cu_3In_5S_9$ – $FeIn_2S_4$ section

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Abstract

The $Cu_3In_5S_9$–$FeIn_2S_4$ section was studied by methods of physicochemical analysis; differential thermal (DTA), X-ray phase (XRD), microstructural (MSA) and microhardness measurement. Based on the results of the obtained data, a phase diagram of the $Cu_3In_5S_9$–$FeIn_2S_4$ section of the Cu_2S–In_2S_3–FeS ternary system was constructed. It was established that the $Cu_3In_5S_9$–$FeIn_2S_4$ section is a quasi-binary section of the ternary Cu_2S–In_2S_3–FeS systems and is eutectic by type with limited solubility based on both initial components. The liquidus of the system consists of two branches of primary crystallization of σ_1 (solid solution based on $Cu_3In_5S_9$) and σ (solid solution based on $FeIn_2S_4$) phases. The eutectic point has coordinates: 1150 K temperature and composition 42 mol% $FeIn_2S_4$. The boundaries of the solid solutions were also determined. The region of solid solutions based on $Cu_3In_5S_9$ extends to 3 mol. % $FeIn_2S_4$, the region of solid solutions based on $FeIn_2S_4$ extends to 5 mol. % $Cu_3In_5S_9$ at room temperature.

Keywords: Microhardness, Phase diagram, System, section, Quasi-binary, Eutectic, Solid solution

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1. Introduction

The study of systems based on heavy metal chalcogenides is of interest due to the relevance of the development of new semiconductor materials with different functional properties. These include systems based on compounds of groups I, III and VI (where I is Cu, Ag; III is AI, Ga, In; VI is S, Te) [1–8]. Ternary compound $FeIn_2S_4$ is a dilute magnetic semiconductor. This group of semiconductors attract attention due to the potential for their use in spintronics [9–12] for the production of Schottky diodes, switches, and lasers controlled by a magnetic field, light modulators, and other devices [13–16].

This study is a continuation of our research on the ternary Cu_2S-In_2S_3-FeS system along the $Cu_3In_5S_9$–$FeIn_2S_4$ section. The study was carried out in order to clarify the nature of the chemical interaction in the ternary Cu_2S–In_2S_3–FeS system in regions with a high content of In_2S_3 and the determination of the phase formation in $Cu_3In_5S_9$–In_2S_3–$FeIn_2S_4$ and $CuFeIn_3S_6$–$Cu_3In_5S_9$–$FeIn_2S_4$ systems [17].

The initial components of the $Cu_3In_5S_9$ and $FeIn_2S_4$ section are formed in the corresponding binary Cu_2S–In_2S_3 and In_2S_3–FeS systems which are quasi-binary sections of the ternary Cu_2S–In_2S_3–FeS system [18-20].

The compound with the composition of $Cu_3In_5S_9$ melts congruently at a temperature of 1085 °C and crystallizes in a monoclinic system with lattice parameters: a = 0.660 nm, b = 0.691 nm, c = 0.812 nm, β = 89°, Z = 1 [17, 18, 21]. The compound with the composition of $FeIn_2S_4$ melts congruently at a temperature of 1125 °C and crystallizes in a cubic lattice with parameters: a = 1.053 nm [20, 24, 25].

The purpose of this study was the investigation of the nature of the chemical interaction between the $Cu_3In_5S_9$ and $FeIn_2S_4$ compounds.

2. Experimental

Samples for the study were synthesized from preliminarily obtained Cu_2S, In_2S_3, and FeS in evacuated quartz ampoules (1.33 Pa) with a length of 15–18 cm, a diameter of 15 cm, at temperatures of 1370÷1400 K. After completion of the reaction the ampoules were kept under the regime for 1.5–2 h. After that, the ampoules were cooled to 900 K and long-term homogenizing annealing was carried out at the same temperature.

The alloys were studied by methods of physicochemical analysis: differential thermal DTA, microstructural MSA, X-ray phase XRD analyses; microhardness measurement. DTA was carried using a Jupiter STA 449 F3 thermal analyser (NETZSCH, Germany) at a heating rate of 10 deg/min using a Pt-Pt/Rh thermocouple. The device was operated under control of the Proteus software.

XRD of the samples was carried using a D2 Phaser X-ray diffractometer (Bruker, Germany) using Cu*K*α-radiation (Ni-filter). The microhardness of the alloys was measured using a PMT-3 microhardness tester under loads of 0.1 and 0.2 N. The MSA of the alloys of the system was studied using an MIM-8 metallographic microscope on pre-etched sections polished with paste. An etchant of the composition NH_4NO_3 (3–8 wt %) + $K_2Cr_2O_7$ (0.02–0.5 wt %) + concentrated H_2SO_4 during the study of the microstructure of the alloys with the etching time of 20 s.

3. Results and discussion

The interaction between $Cu_3In_5S_9$ and $FeIn_2S_4$ was studied using 15 samples, the compositions of which are presented in the Table. Based on the DTA data, it can be assumed that the nature of the interaction between these compounds is simple, since the samples have two effects on the thermograms.

Table 1. Composition and DTA results of alloys of the $Cu_3In_5S_9$–$FeIn_2S_4$ system

Composition mol. %		Thermal effects T, K
$Cu_3In_5S_9$	$FeIn_2S_4$	
100	–	1360
95	5	1350, 1275
90	10	1340, 1215
80	20	1300, 1150
70	30	1240, 1150
60	40	1148, 1170
50	50	1150, 1200
40	60	1150, 1250
30	70	1300, 1155
20	80	1350, 1150
10	90	1370, 1150
5	95	1390, 1150
–	100	1400

MSA studies, carried out on ground polished surfaces of alloys, showed that samples up to 5 mol % $FeIn_2S_4$ and 7 mol % $Cu_3In_5S_9$ were homogeneous, and with an increase in the content of the second component, two-phase mechanical mixtures consisting of solid solutions based on the initial components ($\sigma_1+\sigma$) were formed.

Microhardness was measured under a load of 0.1 N. When measuring the microhardness, the values for $Cu_3In_5S_9$ of 2900 MPa and for $FeIn_2S_4$ of 3300 Mpa were stably obtained (Fig. 1.) As can be seen from the Figure, the microhardness values of alloys rich in $Cu_3In_5S_9$ and $FeIn_2S_4$, increased significantly from 2700 to 2900 MPa and from 3150 to 3300 MPa with the formation of solid solutions.

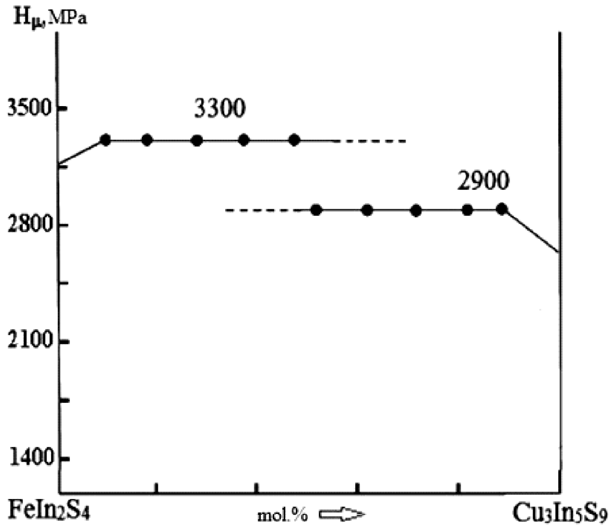

Fig. 1. Hμ-x diagrams of the $Cu_3In_5S_9$ - $FeIn_2S_4$ system

Samples containing 0, 30, 50, 70, and 100 mol % $FeIn_2S_4$ were studied by the XRD method.

Samples of 30, 50, 70 mol % $FeIn_2S_4$ turned out to be two-phase (Fig. 2).

The results of DTA are presented in the Table 1.

Based on the obtained results, the phase diagram of the $Cu_3In_5S_9$–$FeIn_2S_4$ section was constructed. The phase diagram provides an idea about the nature of the chemical interaction between the initial components (Fig. 3)

The section is a quasi-binary section of the ternary Cu_2S-In_2S_3-FeS system.

The liquidus of the system consists of two branches of primary crystallization of the σ_1 (solid solution based on $Cu_3In_5S_9$) and σ_2 (solid solution based on $FeIn_2S_4$) phases.

The co-crystallization of σ_1 and σ_2 phases occurs at a composition of 42 mol % $FeIn_2S_4$ and a temperature of 1150 K:

$$Liq \leftrightarrow \sigma_1 + \sigma.$$

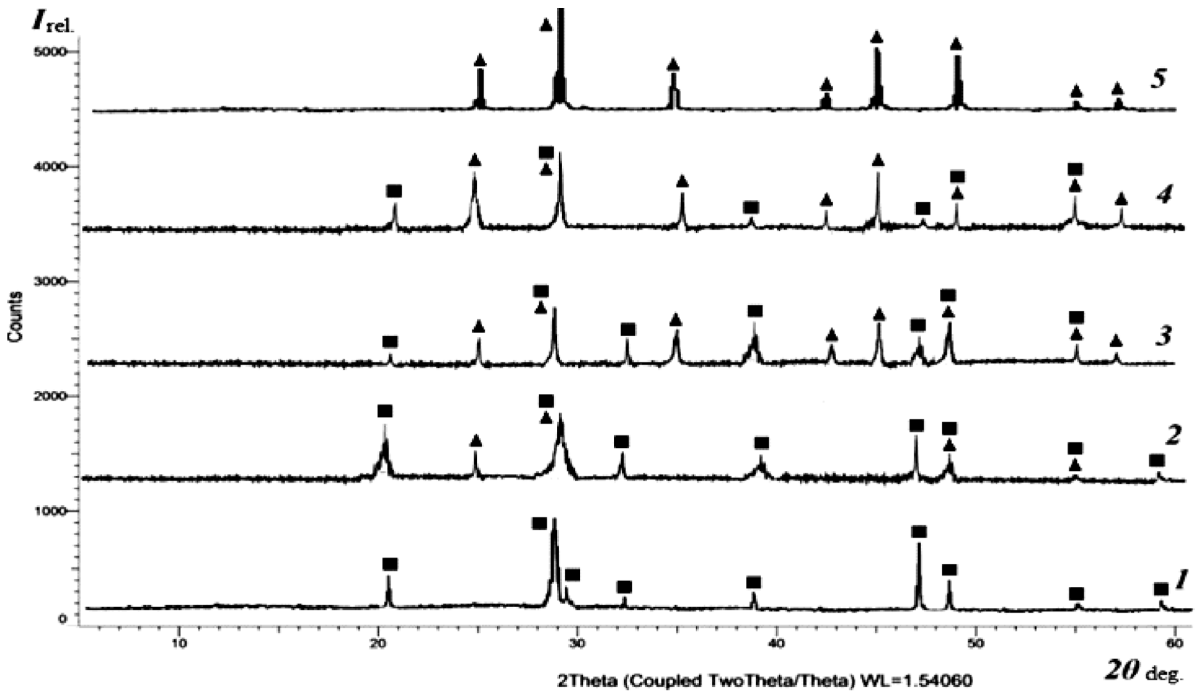

Fig. 2. Powder X-ray diffraction patterns of alloys of the $Cu_3In_5S_9$ – $FeIn_2S_4$ system: *1* – $Cu_3In_5S_9$; *2* – 30 mol % $FeIn_2S_4$; *3* – 50 mol % $FeIn_2S_4$; *4* – 70 mol % $FeIn_2S_4$; *5* – $FeIn_2S_4$ (▲ – $FeIn_2S_4$; ■ – $Cu_3In_5S_9$)

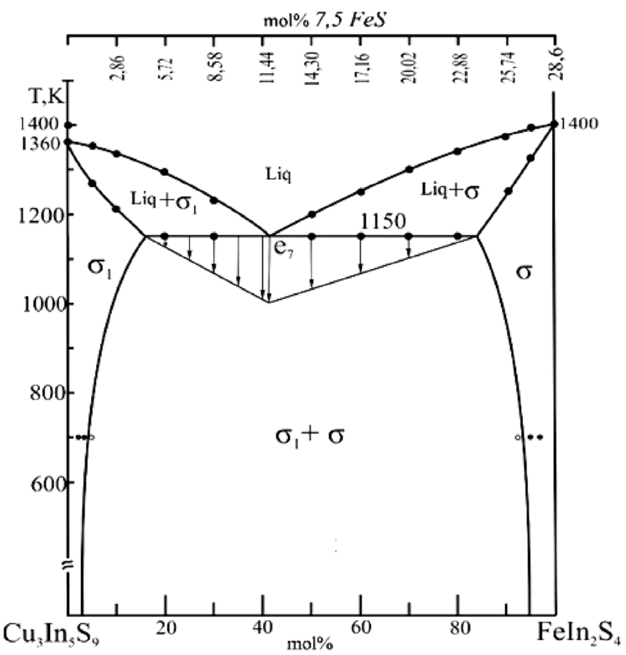

Fig. 3. Phase diagram of the $Cu_3In_5S_9$–$FeIn_2S_4$ system

The composition of the eutectic was also confirmed by the plotting of the Tamman's triangle using a graphical method. As can be seen from the Figure, there are solid solution areas on the bases of the components.

To determine the limits of the regions of the solid solutions, alloys with the following compositions were additionally synthesized: 2.0; 3.0; 5.0 mol % $FeIn_2S_4$ and 3.0; 5.0; 8.0; mol % $Cu_3In_5S_9$. The samples were annealed at 700 K for 150 h and then quenched in iced water. After heat treatment, the microstructures of these samples were carefully studied. It was established that at a temperature of 700 K the mutual solubility of the components reached 5 mol % based on $Cu_3In_5S_9$ and 7 mol % based on $FeIn_2S_4$. At room temperature the mutual solubility was 3 mol % based on $Cu_3In_5S_9$ and 5 mol % based on $FeIn_2S_4$.

4. Conclusion

The phase diagram of the $Cu_3In_5S_9$–$FeIn_2S_4$ system was constructed. It has been established that the section is a quasi-binary section of the ternary Cu_2S–In_2S_3–FeS system and is eutectic. The mutual solubility of the components at a temperature of 700 K reaches 5 mol % based on $Cu_3In_5S_9$ and 7 mol % based on $FeIn_2S_4$.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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