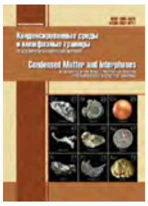

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Liquidus surface of the quasi-ternary system $Cu_2S–In_2S_3–FeS$

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Abstract

A projection of the liquidus surface of the quasi-ternary system Cu_2S-In_2S_3-FeS was constructed as a result of experimental studies of quasi-binary and non-quasi-binary sections and based on the data on binary systems comprising a ternary system. Each section (six quasi-binary and four non-quasi-binary ones) was studied separately using complex methods of physicochemical analysis: differential thermal analysis, X-ray phase analysis, and microstructural analysis.

It was found that the quasi-ternary system Cu_2S-In_2S_3-FeS has six fields of primary crystallisation of separate phases and eleven monovariant equilibrium curves along which two phases are co-crystallised. Non-variant equilibrium points were obtained through the extrapolation of the direction of monovariant equilibrium curves.

The quasi-ternary system Cu_2S-In_2S_3-FeS is characterised by 17 non-variant equilibrium points, where E_1-E_5 are triple eutectic points.

The projection diagram of the liquidus surface is characterised by three crystallisation fields of the initial components (Cu_2S, In_2S_3, FeS), four fields of binary compounds, and one field of a complex compound ($CuFeIn_3S_6$).

Since complete solubility of the initial components in liquid and solid states is observed in the quasi-binary section $CuIn_5S_8$-$FeIn_2S_4$, the fields of primary crystallisation of $CuIn_5S_8$ and $FeIn_2S_4$ are absent; they are replaced by an unlimited solid solution based on these components.

The fields of primary crystallisation of Cu_2S, FeS, and $CuInS_2$ are the most extensive in the ternary system Cu_2S-In_2S_3-FeS.

The reactions occurring at monovariant equilibrium points are presented.

Keywords: system, quasi-ternary, eutectic, liquidus, section

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1. Introduction

The object of the study was the quasi-ternary system Cu_2S-In_2S_3-FeS.

The Cu_2S-In_2S_3-FeS system is formed by congruently melting binary compounds [1–5]. The Cu_2S compound exists in the form of three modifications: a low-temperature modification α-Cu_2S is stable below 376 K, a β-Cu_2S form of hexagonal syngony exists in the 376–708 K temperature range, and above 708 K there is a γ-Cu_2S form with FCC structure which melts at 1402 K [6–8].

The In_2S_3 compound also exists in several structural modifications and belongs to semiconductor materials of type $A_2^{III}B_3^{VI}$. This compound is a wide-band semiconductor. In recent years, it has been of great interest to researchers as the "window" material in thin-film photovoltaic devices with the purpose of substitution of CdS. It is used in optoelectronics to create light-sensitive heterostructures as well as in microelectronics and solar energy as a material with a number of unique properties [9, 10].

Ferric sulphides are usually found in the form of natural compounds. They have been attracting a lot of interest from researches for many years as they possess various crystal structures and phase transformations as well as unusual electric and magnetic properties [11]. Metal-insulator phase transformations, transitions into superconductive state, etc., are observed in these compounds. FeS is used in some technical areas, and another developing application of the compound is the substitution of silicon in solar photovoltaic industry [12].

Therefore, the study of the patterns of physicochemical interaction and phase formation between the specified chalcogenides is of special scientific and practical interest and it allows developing new multi-functional materials based on them.

There is a number of works in scientific literature dedicated to binary chalcogenide compounds Cu_2S, FeS, and In_2S_3 [13–15] that were necessary for the discussion of the obtained results in the present work.

It should be noted that there are no publications on the study of the ternary system. However, there is some literature data on the study of two quasi-binary sections ($CuIn_5S_8$–$FeIn_2S_4$ and $CuInS_2$–FeS [16–18]). We studied the $CuInS_2$–FeS section [21].

The purpose of the work was to construct a projection of the liquidus surface of the Cu_2S-In_2S_3-FeS system: to establish the position of the fields of primary crystallisation of phases in the system, to compose equations of non-variant phase transformations, and to identify the nature of interactions in subordinate triangles.

2. Experimental

For the experimental part of the study of the Cu_2S–In_2S_3–FeS system we used a complex of physicochemical methods: differential thermal analysis (DTA), microstructural analysis (MSA), X-ray diffraction analysis (XRD) as well as microhardness measurement, and density determination [21]. DTA was conducted using a Jupiter STA 449 F3 (NETZSCH, Germany) in synchronous thermal analysis mode. The accuracy of detection of thermal effects was 0.10-0.15 K/deg. XRD was conducted using a "D2 Phaser" X-ray diffractometer (Bruker, Germany). Microhardness of the phases in the alloys was measured on a PMT-3 tester using a well-known method [19]. The load on the diamond pyramid was 0.01-0.02 N. The microstructure was studied on a MIM-8 metallographic microscope. The density was determined at a temperature of 300 K using a pycnometer (with toluene as the filler).

The samples were synthesised from the elements (reduced iron, In – 000 indium, copper with 99.999 % purity, extra pure sulphur 99.9999 %) in evacuated to 1.33 Pa and vacuum-sealed quartz ampoules with the length of 15–18 cm and the diameter of 1.5 cm using direct ampoule method in a single temperature furnace while stirring the samples. Before being put into electrical furnace, the ampoules were heated up to 800 K, then gradually immersed into the furnace together with the samples while the temperature was increased by 50 – 70° C above the melting temperature. The melt was kept at this temperature for 7 hours. The process was repeated several times. After that, the ampoule was hardened in iced water. Then the ingot was subjected to homogenizing annealing. Homogenizing annealing was conducted at a temperature of 900 K for 200 h.

3. Results and discussion

In order to understand fully the processes occurring in the quasi-ternary system Cu_2S–In_2S_3–FeS, we studied the following quasi-binary and non-quasi-binary sections: $CuInS_2$–$FeIn_2S_4$, $Cu_3In_5S_9$–$FeIn_2S_4$, $Cu_3In_5S_9$–$CuFeIn_3S_6$, $CuFeIn_3S_6$–FeS, $CuInS_2$–FeS were quasi-binary; $FeIn_2S_4$–$(5Cu_2S)_{0.83}(3In_2S_3)_{0.17}$, $(5Cu_2S)_{0.50}(7.5FeS)_{0.50}$–$(5Cu_2S)_{0.16}(3In_2S_3)_{0.84}$, $(5Cu_2S)_{0.16}(3In_2S_3)_{0.84}$–$FeIn_2S_4$, $(5Cu_2S)_{0.350}(3In_2S_3)_{0.650}$–$(7.5\ FeS)_{0.350}(3\ In_2S_3)_{0.650}$ were non-quasi-binary.

Among the studied sections, a complex phase was found only in the $CuInS_2$–$FeIn_2S_4$ section – a compound of the $CuFeIn_3S_6$ composition that participates in the triangulation of the quasi-ternary system Cu_2S–In_2S_3–FeS. Below is a brief description of the studied sections of the quasi-ternary system Cu_2S–In_2S_3–FeS.

The $CuInS_2$–$FeIn_2S_4$ section is a quasi-binary section of the quasi-ternary system Cu_2S–In_2S_3–FeS. A compound of the $CuFeIn_3S_6$ composition which melts congruently at a temperature of 1365 K was found with the component ratio of 1:1. Coordinates of the eutectic point were 31 mol. % and 68 mol. % $FeIn_2S_4$ at temperatures of 1240 and 1290 K respectively.

Based on the initial components and the compound of the $CuFeIn_3S_6$ composition, solubility was observed. The limits of solid solutions were specified and it was established that the resulting solid solutions based on the modifications of the $CuInS_2$ (α, β, γ) compound reached 12 mol. % $FeIn_2S_4$ at 300 K and 20 mol. % FeIn2S4 at 1175 K [20].

The $Cu_3In_5S_9$–$CuFeIn_3S_6$ section is a quasi-binary section of the quasi-ternary system. Its phase diagram is of the simple eutectic type. The eutectic composition corresponds to 55 mol. % $CuFeIn_3S_6$ at a temperature of 1200 K. The solubility based on $Cu_3In_5S_9$ at 900 K is 13 mol. % $CuFeIn_3S_6$ and 20 mol. % $CuFeIn_3S_6$ at 1200 K.

The $CuInS_2$–FeS section is a quasi-binary section [21] of the quasi-ternary system Cu_2S–In_2S_3–FeS. The liquidus of the section consists of the primary crystallisation branches α, β, γ of the modification of the $CuInS_2$ compound. Under the influence of FeS the temperature of the $\gamma CuInS_2 \leftrightarrow \beta CuInS_2$ phase transition decreased and belonged to the eutectoid type. The crystallisation of the alloys ended at 1130 K and 50 mol. % by the reaction liq (e) ↔ α + FeS.

It was found that the solubility reached 12 mol. % FeS at room temperature (300 K) [21].

The $CuIn_5S_8$–$FeIn_2S_4$ section is quasi-binary. Based on the initial components $CuIn_5S_8$ and $FeIn_2S_4$ we observed their complete solubility in liquid and solid states. The liquidus of the section consisted of one curve of primary crystallisation σ-solid solution. A continuous series of the σ-solid solution solidified below the solidus line.

The data that we have obtained corresponds well with the results of the authors who studied the $CuIn_5S_8$–$FeIn_2S_4$ system [16].

The $Cu_3In_5S_9$–$FeIn_2S_4$ section is a quasi-binary section of the eutectic type. Co-crystallisation of the branches of the solid solutions based on the initial components occurred with the composition of 42 mol. % $FeIn_2S_4$ at a temperature of 1150 K. The solubility at room temperature was 3 mol. % $FeIn_2S_4$ based on $Cu_3In_5S_9$ and 5 mol. % based on $FeIn_2S_4$.

The $CuFeIn_3S_6$–FeS section is a quasi-binary section of the quasi-ternary system of the simple eutectic type. Co-crystallisation of the initial components finished at a temperature of 1100 K and had the composition of 30 mol. % FeS. There was solubility based on both components.

The $(5Cu_2S)_{0,50}(7.5FeS)_{0.50}$–$(5Cu_2S)_{0.16}(3In_2S_3)_{0.84}$ (e6–e2) section is a non-quasi-binary section (Fig. 1). This section of the ternary system crossed the fields of subordinate ternary systems Cu_2S–$CuInS_2$–FeS, $CuInS_2$–$CuFeIn_3S_6$–FeS, $CuInS_2$–$Cu_3In_5S_9$–$CuFeIn_3S_6$; $Cu_3In_5S_9$–$CuFeIn_3S_6$–$FeIn_2S_4$, and $CuInS_2$–$FeIn_2S_4$–$CuIn_5S_8$. Therefore, its phase diagram consisted of five independent parts. The liquidus of the section had the form of four branches of primary separation of α, γ, σ, δ-phases. A part of the section went through the subordinate ternary system Cu_2S–$CuInS_2$–FeS in the range of the concentration 0–61 mol. % $(5Cu_2S)_{0.50}(7.5FeS)_{0.50}$. There was one ternary eutectic (E_5) equilibrium at 990 K in this part of the section. The second part of the section crossed the secondary ternary system $CuInS_2$– $CuFeIn_3S_6$–FeS in the range of 61–79 mol. % $(5Cu_2S)_{0.16}(3In_2S_3)_{0.84}$, where a non-variant eutectic reaction was formed:

$$liq \leftrightarrow \gamma(CuInS_2) + \gamma_1(FeS) + \delta(CuFeIn_3S_6).$$

The crystallisation of the alloys in the third part of the section ended with the solidification of the triple eutectic at E_2 at a temperature of 1100 K (Fig. 2).

The $(5Cu_2S)_{0.350}(3In_2S_3)_{0.650}$–$(7.5FeS)_{0.350}(3In_2S_3)_{0.650}$ (c–d) section. To study the processes occurring in compound triangles Cu_2S–$CuInS_2$–FeS, $CuInS_2$–$CuFeIn_3S_6$–FeS, and

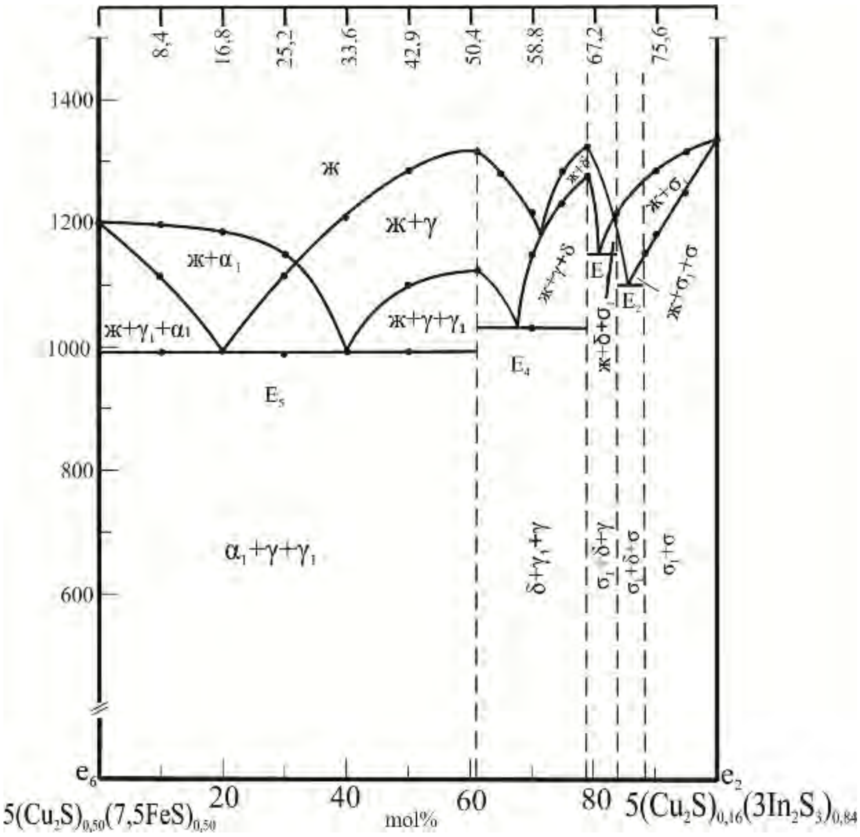

Fig. 1. Phase diagram of the $5(Cu_2S)_{0.50}7.5(FeS)_{0.50}$–$5(Cu_2S)_{0.16}3(In_2S_3)_{0.84}$ system

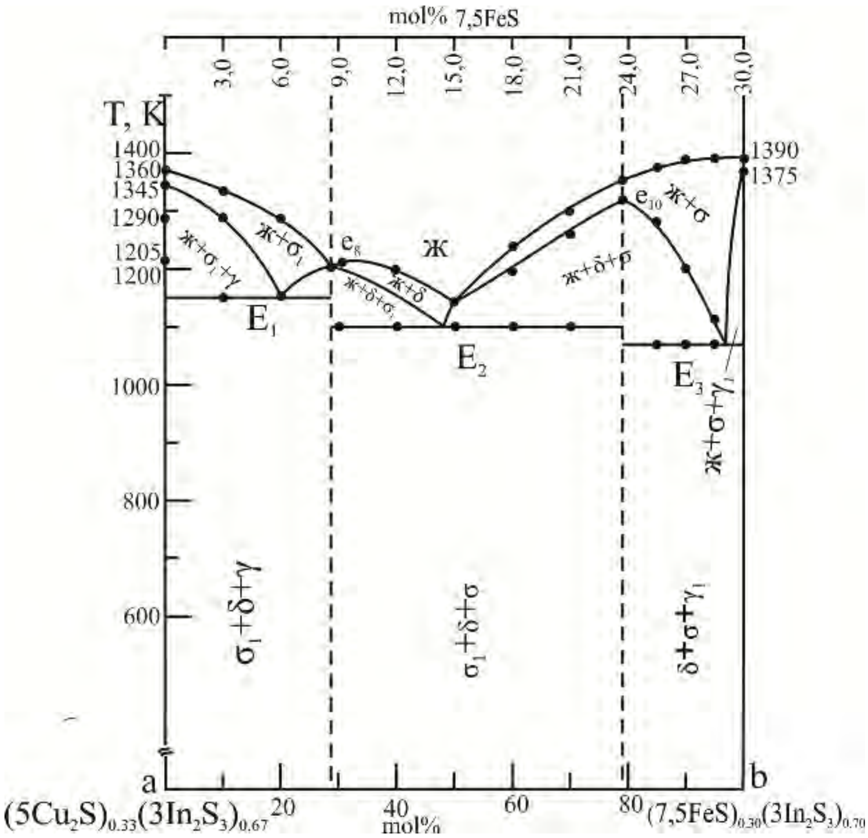

Fig. 2. Phase diagram of the $5(Cu_2S)_{0.33}3(In_2S_3)_{0.67}$–$5(FeS)_{0.30}3(In_2S_3)_{0.70}$ system

$CuFeIn_3S_6$–$FeIn_2S_4$–FeS, as well as to determine the composition and temperature of triple non-variant points, we studied the interaction in the $(5Cu_2S)_{0.350}(3In_2S_3)_{0.650}$–$(7.5FeS)_{0.350}(3In_2S_3)_{0.650}$ section. This section is non-quasi-binary and it crossed two extensive areas of primary crystallisation. Its liquidus is shown as two curves of primary crystallisation of the components $(5Cu_2S)_{0.350}(3In_2S_3)_{0.650}$ and $(7.5FeS)_{0.350}(3In_2S_3)_{0.650}$. A part of the section went through the ternary system Cu_2S–$CuInS_2$–FeS in the range of concentration of 0–68 mol. % $(7.5FeS)_{0.350}(3In_2S_3)_{0.650.}$ There was one ternary eutectic equilibrium E_5 at 990 K in this part of the section. The second part of the section went through the ternary system $CuInS_2$–$CuFeIn_3S_6$–FeS in the range of concentration of 68–84 mol. % $(7.5FeS)_{0.350}(3In_2S_3)_{0.650}$ where the equilibrium ended at a temperature of 1030 K in the triple eutectic E_4. The third part of the section crossed the ternary system $FeIn_2S_4$–$CuFeIn_3S_6$–FeS in the range of concentration of 84-0 mol. % $(7.5FeS)_{0.350}(3In_2S_3)_{0.650}$. There was also one triple eutectic equilibrium E_3 here.

Depending on the concentration below the solidus line, the section is represented as a mechanical mix of the three phases.

The $(5Cu_2S)_{0.33}(3In_2S_3)_{0.67}$–$(7.5FeS)_{0.30}(3In_2S_3)_{0.70}$ (a–b) section is a non-quasi-binary section of the quasi-ternary system Cu_2S–In_2S_3–FeS which crossed three secondary triangles (Fig. 2).

The phase diagram consisted of three parts. The liquidus of the system which went through the subordinate system $CuInS_2$–$Cu_3In_5S_9$–$CuFeIn_3S_6$ consisted of the primary crystallisation of the high-temperature modification of $\sigma_1(Cu_3In_5S_9)$. In this part the crystallisation ended at the temperature of triple eutectic E_1 (1150 K). The liquidus of the system which went through the subordinate system $Cu_3In_5S_9$–$CuFeIn_3S_6$–$FeIn_2S_4$ consisted of two branches: primary crystallisation δ-modification of the $CuFeIn_3S_6$ compound and σ-solid solution based on $FeIn_2S_4$.

Final crystallisation occurred at 1100 K, the temperature of triple eutectic (E_2).

The third part of the section crossed the $CuFeIn_3S_6$–$FeIn_2S_4$–FeS phase triangle. There was one triple eutectic point E_3 here. The liquidus of this part consisted of the branches of primary crystallisation of the solid solution $\sigma(FeIn_2S_4)_{1-x}(CuIn_5S_8)_x$.

The $(7.5FeS)_{286}(3In_2S_3)_{0.714}$–$(5Cu_2S)_{0.83}(3In_2S_3)_{0.17}$ (D_4–e_4) section is a non-

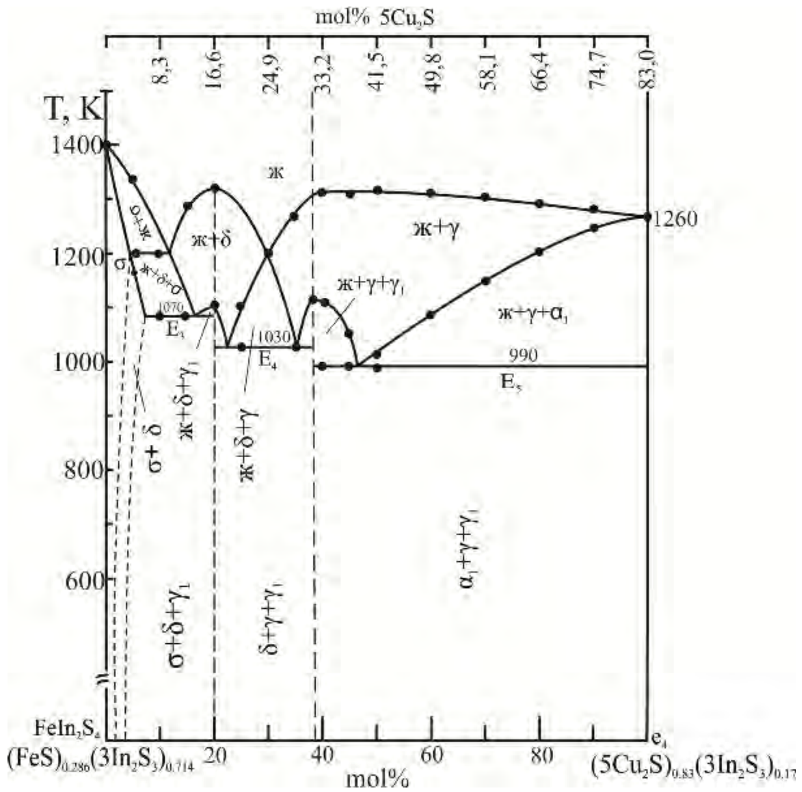

Fig. 3. Phase diagram of the $(FeS)_{0.286}3(In_2S_3)_{0.714}$–$5(Cu_2S)_{0.83}3(In_2S_3)_{0.17}$ system

quasi-binary section of the ternary system. Its phase diagram consisted of three parts (Fig. 3).

The liquidus of the section consisted of the curves of primary crystallisation σ-, δ- and γ-phases of solid solutions based on the compound $Cu_3In_5S_9$, $FeIn_2S_4$ and solid solution of γ-phase transition $CuInS_2$ respectively. There were three triple eutectic transformations E_3, E_4, and E_5 in the section. We present the reactions occurring in these non-variant eutectic points as follows:

liq ↔ δ($CuFeIn_3S_6$) + σ($FeIn_2S_4$) + γ_1(FeS) E_3

liq ↔ γ($CuInS_2$) + γ_1(FeS) + δ($CuFeIn_3S_6$) E_4

liq ↔ α_1(Cu_2S) + γ($CuInS_2$) + γ_1(FeS) E_5

3.1. Projection of the liquidus surface

Through the quasi-binary sections (there are 6 of them), which are triangulating section lines, the quasi-ternary system Cu_2S–In_2S_3–FeS was triangulated into six subordinate triangles:

1. $Cu_3In_5S_9$– In_2S_3–$FeIn_2S_4$
2. $CuInS_2$–$Cu_3In_5S_9$ –$CuFeIn_3S_6$
3. $CuFeIn_3S_6$ –$Cu_3In_5S_9$–$FeIn_2S_4$
4. Cu_2S–$CuInS_2$–FeS
5. $CuInS_2$–$CuFeIn_3S_6$ –FeS
6. $CuFeIn_3S_6$–$FeIn_2S_4$–FeS

Each of them can be represented separately as an independent ternary system.

Below we provide the nature of the chemical interaction for individual secondary ternary systems.

The $Cu_3In_5S_9$–In_2S_3–$FeIn_2S_4$ system

A quasi-binary section D_1($CuIn_5S_8$)–D_4($FeIn_2S_4$), where a continuous series of solid solution was formed, did not participate in the triangulation of the ternary system. Therefore, crystallisation in the $Cu_3In_5S_9$–In_2S_3–$FeIn_2S_4$ system ended in curves e_1p_1 and e_2e_7 in a double non-variant point instead of a triple non-variant point. A monovariant curve e_1p_1 characterises the equilibrium:

liq ↔ β(In_2S_3) + σ[$(CuIn_5S_8)_{1-x}(FeIn_2S_4)_x$],

while curve e_2e_7 characterises the following one:

liq ↔ σ[$(CuIn_5S_8)_{1-x}(FeIn_2S_4)_x$] + σ_1($Cu_3In_5S_9$)

$CuInS_2$–$Cu_3In_5S_9$–$CuFeIn_3S_6$

One eutectic transformation occurred in this compound triangle, therefore this system is characterised by the presence of one non-variant point E_1 where the reaction occurs:

liq ↔ σ_1($Cu_3In_5S_9$) + δ($CuFeIn_3S_6$) + γ($CuInS_2$).

The crystallisation field of this system is mainly represented by fields $CuInS_2$ (5), $Cu_3In_5S_9$ (3), and $CuFeIn_3S_6$ (4).

Three monovariant equilibrium curves e_3E_1, e_8E_1, and e_9E_1 converge in a non-variant point E_1 at a temperature of 1150 K.

The $CuFeIn_3S_6$–$Cu_3In_5S_9$–$FeIn_2S_4$ system

The liquidus of this system is represented by the fields $Cu_3In_5S_9$, $CuFeIn_3S_6$, σ$(FeIn_2S_4)_{1-x}(CuIn_5S_8)_x$ separated by monovariant equilibrium curves e_8E_2, e_7E_2, and $e_{10}E_2$.

The system is characterised by one non-variant point E_2 where these monovariant equilibrium curves converge, and the chemical reaction occurred here at a temperature of 1150 K:

liq ↔ σ_1 ($Cu_3In_5S_9$) + σ($CuFeIn_3S_6$) +
+ σ[$(FeIn_2S_4)_{1-x}(CuIn_5S_8)_x$] ($E_2$).

The Cu_2S –$CuInS_2$–FeS system

The crystallisation surface of this secondary system was occupied by the fields Cu_2S, $CuInS_2$, and FeS. One eutectic transformation E_5 occurred in this compound triangle, and the following chemical reaction occurred here:

liq ↔ α_1(Cu_2S) + γ($CuInS_2$) + γ_1(FeS)

Three monovariant equilibrium curves e_4E_5; e_6E_5, and E_5e_{12} converged at this point separating the fields Cu_2S, $CuInS_2$, and FeS.

The $CuInS_2$–$CuFeIn_3S_6$–FeS system

Only one eutectic transformation E_4 occurred in this secondary ternary system. Monovariant curves e_9E_4, $e_{12}E_4$, and $e_{11}E_4$ converged at this point. Three phases $CuInS_2$, $CuFeIn_3S_6$, and FeS were co-crystallised in a non-variant point E_4 at a temperature of 1030 K.

The $CuFeIn_3S_6$–$FeIn_2S_4$–FeS system

The field of this secondary system is mainly occupied by the area FeS as well as by the fields $CuFeIn_3S_6$ and $(FeIn_2S_4)_{1-x}(CuIn_5S_8)_x$. Only eutectic transformations occur on the three sides of this triangle. This triangle has one non-variant eutectic point E_3 at a temperature of 1070 K where three monovariant equilibrium curves $e_{10}E_3$, $e_{11}E_3$, and e_5E_3 converge.

The following chemical reaction occurred in this compound triangle:

liq ↔ δ($CuFeIn_3S_6$+σ[$(FeIn_2S_4)_{1-x}(CuIn_5S_8)_x$] +
+ γ_1(FeS) (E_3)

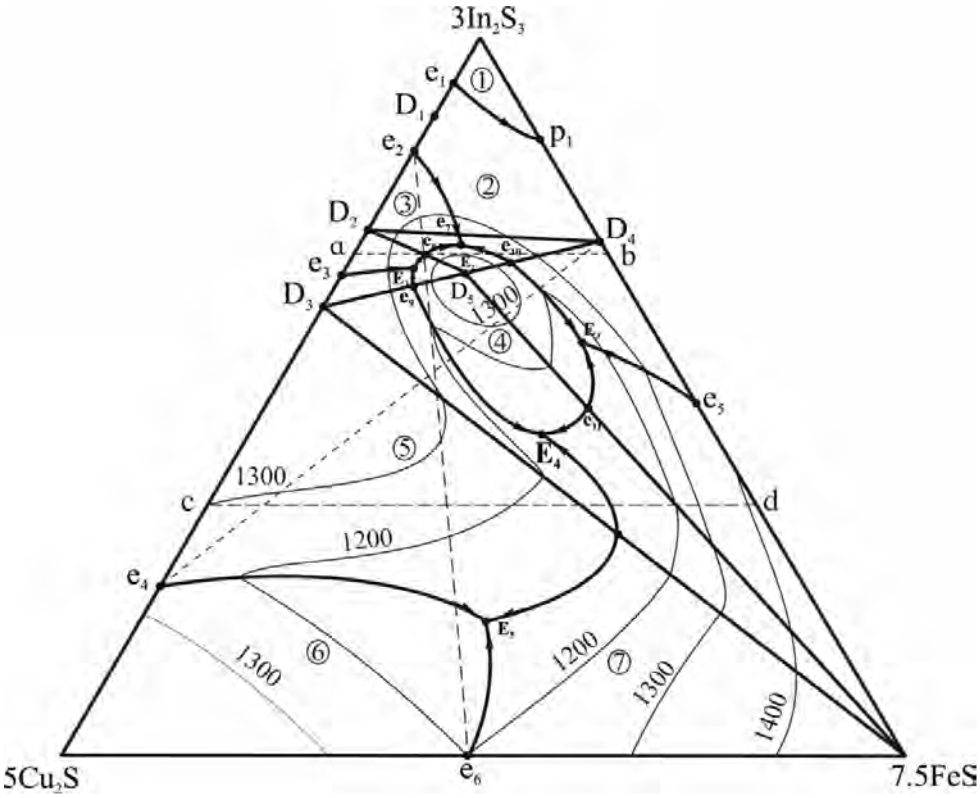

Fig. 4. Liquidus surface of the Cu_2S-In2S_3-FeS system

The projection of the liquidus surface of the ternary quasi-ternary system Cu_2S– In_2S_3–FeS (Fig. 4) was constructed based on the data on phase equilibriums in double systems comprising a ternary system and on a number of experimentally studied internal sections which were briefly characterised above.

The diagram of the projection of the liquidus surface is characterised by three fields of crystallisation of the initial components (Fig. 2) (Cu_2S, In_2S_3, FeS), four fields of double compounds, and one field of a complex compound ($CuFeIn_3S_6$).

Since complete solubility of the initial components in liquid and solid states was observed in the quasi-binary section $CuIn_5S_8$–$FeIn_2S_4$, primary crystallisation fields $CuIn_5S_8$ and $FeIn_2S_4$ are absent; they are replaced by an unlimited solid solution based on these components.

The solid solution area found in the $CuIn_5S_8$–$FeIn_2S_4$ section occupied a part of the crystallisation field of the secondary ternary systems $CuIn_5S_8$–$FeIn_2S_4$–$Cu_3In_5S_9$ and In_2S_3–$CuIn_5S_8$–$FeIn_2S_4$. There are 7 fields of primary crystallisation of separate phases in the ternary system. The most extensive fields in the ternary system Cu_2S–In_2S_3–FeS are primary crystallisation fields Cu_2S (6), FeS (7), and $CuInS_2$ (5).

The separating primary crystallisation fields of the line of monovariant equilibriums intersect at ternary non-variant points (Tables 1 and 2).

4. Conclusions

There are 5 non-variant equilibrium points in the system, which are triple eutectic points, and there are nine monovariant equilibrium curves. The temperatures and compositions of the discovered non-variant points were compared to the data obtained during the study of non-quasi-binary sections as well as to the thermograms of alloys near the alleged points.

Therefore, for the first time, we constructed the projection of the liquidus surface of the quasi-ternary system Cu_2S–In_2S_3–FeS. We also determined the areas of primary crystallisation of the phases and the coordinates of all non-variant and monovariant equilibriums.

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.

Table 1. Non-variant reactions in the quasi-ternary system $Cu_2S–In_2S_3–FeS$

Symbols	Equilibriums	Compositions, %			*T*, K
		$5Cu_2S$	$3In_2S_3$	7.5FeS	
e_1	liq ↔ $\beta(In_2S_3) + \sigma(D_1)(CuIn_5S_8)$	7.00	93.00	–	1340
e_2	liq ↔ $\sigma(D_1)(CuIn_5S_8) + \sigma_1(D_2)(Cu_3In_5S_9)$	16.00	84.00	–	1330
e_3	liq ↔ $\sigma_1(D_2)(Cu_3In_5S_9) + \gamma(D_3)(CuInS_2)$	33.00	67.00	–	1345
e_4	liq ↔ $\alpha_1(Cu_2S) + \gamma(D_3)(CuInS_2)$	77.00	23.00	–	1260
e_5	liq ↔ $\sigma(D_4)(FeInS_4) + \gamma_1(FeS)$	–	51.00	49.00	1375
e_6	liq ↔ $\alpha_1(Cu_2S) + \gamma_1(FeS)$	52.00	–	48.00	1200
e_7	liq ↔ $\sigma_1(D_2)(Cu_3In_5S_9) + \sigma(D_4)(FeInS_4)$	15.50	72.50	12.00	1150
e_8	liq ↔ $\sigma_1(D_2)(Cu_3In_5S_9) + \delta(D_5)(CuFeIn_3S_6)$	22.00	70.00	8.00	1200
e_9	liq ↔ $\gamma(D_3)(CuInS_2) + \delta(D_5)(CuFeIn_3S_6)$	25.50	66.00	8.500	1285
e_{10}	liq ↔ $\delta(D_5)(CuFeIn_3S_6) + \sigma(D_4)(FeInS_4)$	12.00	69.00	19.00	1290
e_{11}	liq ↔ $\delta(D_5)(CuFeIn_3S_6) + \gamma_1(FeS)$	12.50	46.50	41.00	1100
e_{12}	liq ↔ $\gamma(D_3)(CuInS_2) + \gamma_1(FeS)$	18.50	31.50	50.00	1130
E_1	liq ↔ $\sigma_1(D_2)(Cu_3In_5S_9) + \delta(D_5)(CuFeIn_3S_6) + \gamma(D_3)(CuInS_2)$	24.00	68.00	8.00	1150
E_2	liq ↔ $\sigma_1(D_2)(Cu_3In_5S_9) + \delta(D_5)(CuFeIn_3S_6) + \sigma((D_4)_{1-x}(D_1)_x$	16.00	71.50	12.50	1100
E_3	liq ↔ $\delta(D_5)(CuFeIn_3S_6) + \sigma((D_4)_{1-x}(D_1)_x + \gamma_1(FeS)$	7.00	58.00	35.00	1070
E_4	liq ↔ $\gamma(D_3)(CuInS_2) + \gamma_1(FeS) + \delta(D_5)(CuFeIn_3S_6)$	17.50	45.00	37.50	1030
E_5	liq ↔ $\alpha_1(Cu_2S) + \gamma(D_3)(CuInS_2) + \gamma_1(FeS)$	38.50	18.50	43.00	1090

Table 2. Monovariant reactions in the quasi-ternary system $Cu_2S–In_2S_3–FeS$

Symbols	Equilibriums	*T*, K
$e_2\ e_7\ E_2$	liq ↔ $\sigma(CuIn_5S_8)_{1-x}(FeIn_2S_4)_x + \sigma_1(Cu_3In_5S_9)$	1330–1150–1100
$e_3\ E_1$	liq ↔ $\sigma_1(Cu_3In_5S_9) + \gamma(CuInS_2)$	1345–1150
$E_1\ e_8\ E_2$	liq ↔ $\sigma_1(Cu_3In_5S_9) + \delta(CuFeIn_3S_6)$	1150–1200–1100
$E_1\ e_9\ E_4$	liq ↔ $\delta(CuFeIn_3S_6) + \gamma(CuInS_2)$	1150–1285–1030
$E_4\ e_{12}\ E_5$	liq ↔ $\gamma(CuInS_2) + \gamma_1(FeS)$	1030–1130–1090
$e_4\ E_5$	liq ↔ $\gamma(CuInS_2) + \alpha_1(Cu_2S)$	1260–1090
$e_6\ E_5$	liq ↔ $\alpha_1(Cu_2S) + \gamma_1(FeS)$	1200–1090
$E_4\ e_{11}\ E_3$	liq ↔ $\delta(CuFeIn_3S_6) + \gamma_1(FeS)$	1030–1100–1070
$e_5\ E_3$	liq ↔ $\sigma(CuIn_5S_8)_{1-x}(FeIn_2S_4)_x + \gamma_1(FeS)$	1375–1070
$E_2\ e_{10}\ E_3$	liq ↔ $\sigma(CuIn_5S_8)_{1-x}(FeIn_2S_4)_x + \delta(CuFeIn_3S_6)$	1100–1315–1070
$e_1\ p_1$	liq ↔ $\beta(In_2S_3)+ \sigma(CuIn_5S_8)_{1-x}(FeIn_2S_4)_x$	1340–1305
e_2e_7	liq ↔ $\sigma(CuIn_5S_8)_{1-x}(FeIn_2S_4)_{x+} + \sigma_1(Cu_3In_5S_9)$	1330–1150

References

1. Tomashik V. Cu–In–S (Copper – Indium - Sulfur). *Non-Ferrous Metal Systems*. 2006;V11C1(1): 1–19. https://doi.org/10.1007/10915981_24

2. Binsma J. J. M., Giling L. J., Bloem J. Phase relations in the system $Cu_2S—In_2S_3$. *Journal of Crystal Growth*. 1980;50(2): 429–436. https://doi.org/10.1016/0022-0248(80)90090-1

3. Rustamov P. Q., Babaeva P. K., Allazov M. R. State diagram of the section $FeS-In_2S_3$. *Russian Journal of Inorganic Chemistry*. 1979;24(8): 2208–2211. (In Russ.)

4. Raghavan V. Fe-In-S (Iron – Indium - Sulfur). *Journal of Phase Equilibria*. 1998;19(3): 270. https://doi.org/10.1361/105497198770342337

5. Manual G. J., Patino F., Salinas E. Medición del contenido calórico de la mata de cobre (Cu_2S-FeS) usando un calorímetro de gota. *Revista de la Sociedad Quimica de Mexico*. 2001;45(1): 13–16. Available at: https://www.researchgate.net/publication/26465784_Medicion_del_contenido_calorico_de_la_mata_de_cobre_Cu2S-FeS_usando_un_calorimetro_de_gota

6. Patil M., Sharma D., Dive A., Mahajan S., Sharma R. Synthesis and characterization of Cu_2S thin film deposited by chemical bath deposition method. *Procedia Manufacturing*.2018:20: 505–508. https://doi.org/10.1016/j.promfg.2018.02.075

7. Li S., Wang H., Xu W., Si H., Tao X., Lou S., et al. Synthesis and assembly of monodisperse spherical Cu_2S nanocrystals. *Journal of Colloid and Interface Science*. 2009;330(2): 483–487. https://doi.org/10.1016/j.jcis.2008.10.062

8. Kozer V. R., Parasyuk O. V. Phase equilibria in the quasi-ternary system Cu_2S-In_2S_3-CdS. *Chemistry of Metals and Alloys*. 2009;2(1/2): 102–107. https://doi.org/10.30970/cma2.0087

9. Gorai S., Guha P., Ganguli D., Chaudhuri S. Chemical synthesis of β-In_2S_3 powder and its optical characterization. *Materials Chemistry and Physics*. 2003;82(320): 974–979. https://doi.org/10.1016/j.matchemphys.2003.08.013

10. Bodnar I. V., Polubok V. A., Rud V. Yu., Rud Yu. V. Photosensitive structures based on In_2S_3 crystals. *Semiconductors*. 2003; 37(11): 1308–1310. https://doi.org/10.1134/1.1626214

11. Mitsui H., Sasaki T., Oikawa K., Ishida K. Phase equilibria in FeS–XS and MnS–XS (X = Ti, Nb and V) systems. *ISIJ International*. 2009;49(7): 936–941. https://doi.org/10.2355/isijinternational.49.936

12. Terranova U., de Leeuw N. H. Phase stability and thermodynamic properties of FeS polymorphs. *Journal of Physics and Chemistry of Solids*. 2017;111: 317–323. https://doi.org/10.1016/j.jpcs.2017.07.033

13. Thomere A., Guillot-Deudon C., Caldes M. T., Bodeux R., Barreau N., Jobic S., Lafond A. Chemical crystallographic investigation on Cu_2S-In_2S_3-Ga_2S_3 ternary system. *Thin Solid Films*. 2018;665: 46–50. https://doi.org/10.1016/j.tsf.2018.09.003

14. Hurman Eric R. Activities in CuS-FeS-SnS melts at 1200. *Metallurgical Transactions B*.1993;24(2):301–308. https://doi.org/10.1007/bf02659132

15. Womes M., Olivier-Fourcade J., Jumas J.-C., Aubertin F., Gonser U. Characterization of the single phase region with spinel structure in the ternary system In_2S_3–FeS–FeS_2. *Journal of Solid State Chemistry*. 1992;97(2): 249–256. https://doi.org/10.1016/0022-4596(92)90032-q

16. Olekseyuk I. D., Parasyuk O. V., Kozer V. R. Research of systems of type Cu (Ag) In_5S_8 - $FeIn_2S_4$. *Naukovii visnik Volins'kogo natsional'nogo universitetu* im. *Lesi Ukraïnki: Khimichni nauki*. 2009;24: 3-8. (In Ukrainian)

17. Mirzoeva R. J., Shikhalibeyli S. Sh., Allazov M. R. Investigation of the $CuInS_2$-FeS semiconductor system. In: *Physico-chemical processes in condensed matter and interphase bondaries: Proc. 7th All-Russian Conf., 10–13 November 2015*. Voronezh: Nauchnaya Kniga Publ.; 2015. p. 371. (In Russ.)

18. Trukhanov S. V., Bodnar I. V., Zhafar M. A. Magnetic and electrical properties of $(FeIn_2S_4)_{1-x}(CuIn_5S_8)_x$ solid solutions. *Journal of Magnetism and Magnetic Materials*. 2015;379: 22–27. https://doi.org/10.1016/j.jmmm.2014.10.120

19. Glazov V. M., Vigodorovich V. K. *Microtverdost metallov i poluprovodnikov* [Microhardness of metals and semiconductors]. Moscow: Metallurgy; 1969. 248 p. (In Russ.)

20. Abdullayeva Sh. S., Mammadov F. M., Bakhtiyarly İ. B. Quasi-binary section $CuInS_2$–$FeIn_2S_4$. *Russian Journal of Inorganic Chemistry*. 2020;65(1); 100–105. https://doi.org/10.1134/s0036023619110020

21. Bakhtiyarly I. B., Abdullayeva Sh. S., Gurbanova R. J., Mammadova F. M. Guseynova Sh. B. Study of interactions in the $CuInS_2$–FeS system. *Russian Journal of General Chemistry*. 2019;89(8):1281–1284. https://doi.org/10.1134/s1070363219080188

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