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PHASE DIAGRAMS OF THE $FeGa_2S_4$- $FeIn_2S_4$ AND FeS- $FeGaInS_4$ SYSTEMS

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The phase equilibriums in the $FeGa_2S_4$- $FeIn_2S_4$ and FeS- $FeIn_2S_4$ systems were experimentally investigated by means of differential thermal and X-ray diffraction analyses. It found that they are quasi-binary and characterized by limited mutual solubility of starting compounds. The phase with composition $FeGaInS_4$ crystallizes in the $FeGa_2S_4$-type structure, melts at 1375 K without decomposition, and can be characterized as a congruently melting compound by its behavior in the phase diagram.

Keywords: *$FeGa_2S_4$, $FeIn_2S_4$, $FeGaInS_4$, phase diagram, solid solutions*
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INTRODUCTION

Of special interest are valuable functional materials with complex metal chalcogenidesand-based phases characterized by thermoelectric, photoelectric, optical, magnetic, topological insulator and other properties [1-6] and AB_2X_4 magnetic compounds (A-Mn, Fe, Co, Ni, B-p^1-p^3 elements, X-chalcogen). They are promising materials for the production of wide-gap converters of optical radiations, light modulators, photo-detectors, as well as spintronic and other magnetic-field-controllable functional devices [7-11].

The development and optimization of processes for the preparation of new complex phases are based on phase equilibriums data and thermodynamic characteristics of the corresponding system [12, 13]. At the same time, systems formed by structural or formuleanaloges are of particular interest, since it can expect the formation of wide areas of solid solutions in them [14, 15].

This work is part of a complex physicochemical study of the FeS-Ga_2S_3-In_2S_3 quasi-ternary system and is devoted to the investigation of phase relations in the $FeGa_2S_4$- $FeIn_2S_4$ and 2FeS-$FeGaInS_4$polythermal sections.

The initial compounds of these systems are studied in detail.

FeS melts congruently at 1461 K and undergoes polymorphic transitions at 411 and 588 K [16]. The high-temperature modification of FeS crystallizes in the tetragonal structure (Sp.gr.P4/nmm) with lattice parameters a = 0.3768 nm, c = 0.5039 nm [17] or a = 0.36735 nm, c = 0.50328 nm [18], while low-temperature modification has hexagonal structure: a = 0.34436(1) nm, c = 0.57262(2) nm [19].

The $FeGa_2S_4$ and $FeIn_2S_4$ternary compounds melt congruently at 1418 [20] K and 1398 K [21] respectively. According to [22], $FeGa_2S_4$ is formed by the peritectic reaction at 1343 K and undergoes a polymorphic transformation at 1283 K.

$FeGa_2S_4$crystallizes in the rhombic structure of the $ZnAl_2S_4$ type and with lattice parameters a=1.289 nm; b=0.751; c=0.609 nm [23]. According to [24] this compound has two crystalline modifications: low-temperature has trigonal [Sp.gr. $P\bar{3}ml$;a=0.3654(2) nm;

c=1.2056 nm], and high-temperature – rhombic (*a*=1.289; *b*=0.751; *c*=0.609 nm) structure. The $FeIn_2S_4$ compound crystallizes in a spinel structure (Sp.gr.Fd-3m) with a lattice period *a*=1.0598 [23] or *a*=1.053 nm [21].

The $FeGaInS_4$ compound has a trigonal structure of the $ZnAl_2S_4$ (Sp.gr.P-3*m*1) type with parameters: *a*=0.37765, *c*=1.22257 nm [25, 26].

EXPERIMENTAL PART

2.1. Materials and syntheses

FeS, $FeGa_2S_4$, $FeIn_2S_4$, and $FeGaInS_4$ were synthesized through the use of high purity iron (99.995%), indium (99.999%), gallium (99.999%), and sulfur (99.99%) purchased from Alfa Aesaras starting materials. Stoichiometric mixtures of elements were sealed in an evacuated quartz tube (15 cm in length and 1.5 cm in diameter) with a residual pressure of ~10^{-2} Pa. The sealed tubes were then placed in a two-zone furnace for 2/3 of their length. The lower "hot zone" was slowly heated at a room temperature to ~ 30-50 K above the melting point of the synthesized compounds and outside part of the ampoule was quenched with water ("cold zone"). The interaction of components occurs in the "hot zone" and in the cold zone the chalcogen condenses and returns to the interaction zone. As a result of the reaction in the cold zone the mass of the chalcogen decreases and within 1-2 hours it is spent almost. Thereafter, the ampoule completely placed in a furnace and kept at the pointed temperature for 1-2 hours. The obtained samples were subjected to heat treatment at 800 K for 100 h. in order to increase the degree of crystallinity.

All investigated samples were prepared from pre-synthesized compounds in evacuated quartz tubes. The samples were annealed first at 1000 K (200 h), and then at 700 K (300 h) in order to reach the state closest to equilibrium. Some alloys after annealing were quenched in cold water.

2.2. Analysis

Differential thermal analysis (DTA) and X-ray powder diffraction (XRD) were used to analyze the samples. DTA was carried out using a NETZSCH 404 F1 Pegasus system at a room temperature and ~1450 K depending on the composition of the alloys at a heating rate of 10 K· min^{-1}. Temperatures of thermal effects were taken mainly from the heating curves. The accuracy of the temperature measurements was ±2 K.

Powder X-ray diffraction (PXRD) data were collected on a Bruker D2 Phaser diffractometer using Cu $K\alpha_1$ (λ=1.54056 Å) radiation at a room temperature. The unit cell parameters of initial compounds and intermediate alloys were calculated by indexing of powder patterns using Topas V3.0 software.

According to DTA, synthesized compounds melt at 1460 K (FeS), 1420 K ($FeGa_2S_4$),and 1415 K ($FeIn_2S_4$).First two data are consistent with literature data [16,20], and the last isslightly higher (17 K) than indicated in [21].

The XRD powder patterns of synthesized compounds indicated the formation of single-phase materials. The calculated lattice constants of hexagonal FeS (*a* = 0.34440 nm and *c* = 0.57260 nm), trigonal$FeGa_2S_4$ (*a*=0.36543; *c*=1.20558nm) and cubic $FeIn_2S_4$ (*a* = 1.0607 nm) were in good agreement with the literature data [19, 22, 23].

RESULTS AND DISCUSSION

$FeGa_2S_4$- $FeIn_2S_4$section (Table 1, Fig.1) is quasi-binary to pertain to the eutectic type with the formation of wide areas of solid solutions based on the initial ternary compounds. The eutectic has a composition of 70 mol% $FeIn_2S_4$ and crystallizes at 1340 K.

Table 1. *Experimental data of the DTA for the $FeGa_2S_4$- $FeIn_2S_4$ and FeS- $FeGaInS_4$ systems*

System	Composition	Thermal effects, K
	mol% $FeIn_2S_4$	
$FeGa_2S_4$-$FeIn_2S_4$	0 ($FeGa_2S_4$)	1327; 1420
	5	1415
	10	1415
	20	1390-1410
	30	1383-1400
	40	1385
	45	1380
	50	1375
	55	1355-1370
	60	1340-1363
	65	1338-1350
	70	1340
	80	1355-1380
	90	1390-1400
	95	1410
	100	1415
2FeS-$FeGaInS_4$	mol% $FeGaInS_4$	
	0 (FeS)	1460
	10	1370-1435
	20	1308-1412
	40	1310-1378
	50	1312-1355
	60	1310
	70	1310-1328
	80	1312-1348
	90	1308-1360
	100	1375

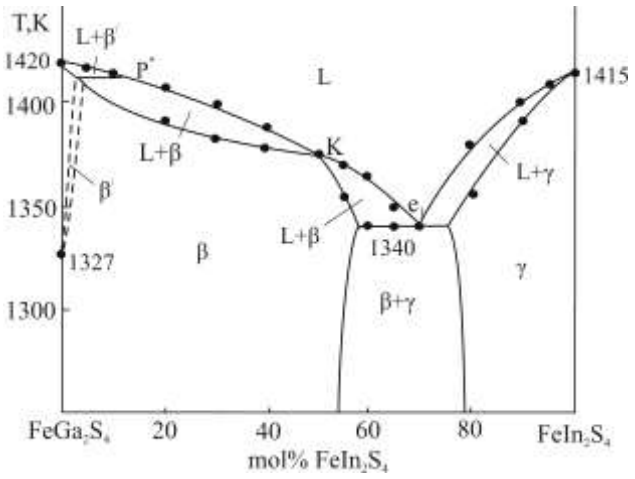

Fig.1. Phase diagram of the $FeGa_2S_4$- $FeIn_2S_4$ system

The thermal effect at 1327 K relating to the polymorphic transformation of $FeGa_2S_4$ was not found in the alloys of this section. Taking into account the X-ray data on the crystal structure of the $FeGa_2S_4$-based β -solid solutions, we assume that the formation of the β-phase leads to a sharp increase in the temperature of this phase transition and the establishment of peritectoid equilibrium (point p*).

From the DTA data (Table 1), it follows that the melting of the β-phase with a composition of 50 mol% $FeIn_2S_4$ is an isothermal process (point K) while solid solutions with other compositions melt in the temperature range. This allows us to characterize the alloy $FeGaInS_4$ as a chemical compound with congruent melting.

The evtectic horizontal is extended from ~ 58 to 75mol% $FeIn_2S_4$. Thus, at an eutectic temperature (1340 K) the $FeGa_2S_4$-based solubility is ~ 58mol% $FeIn_2S_4$(β-phase), and $FeIn_2S_4$ is ~ 25 mol% (γ-phase).

The XRD results of the powdered samples of the system (Fig.2) are in accordance with the phase diagram. According to Fig.2, the diffraction patterns of the alloys in the 0-50 mol% $FeIn_2S_4$ range of compositions are qualitatively similar to those of pure $FeGa_2S_4$with a slight reflection lines shift which is typical for substitutional solid solutions. The powder X-ray diffraction pattern of the alloy with 80 mol% $FeIn_2S_4$ compositions is identical to pure $FeIn_2S_4$ while the 60 mol% $FeIn_2S_4$ alloy contains and βandγ-phase reflections.

Table 2 presents the types and parameters of the crystal lattices of solid solutions of the $FeGa_2S_4$-$FeIn_2S_4$ system.The accuracy of the crystal lattice parameters is shown in parentheses.

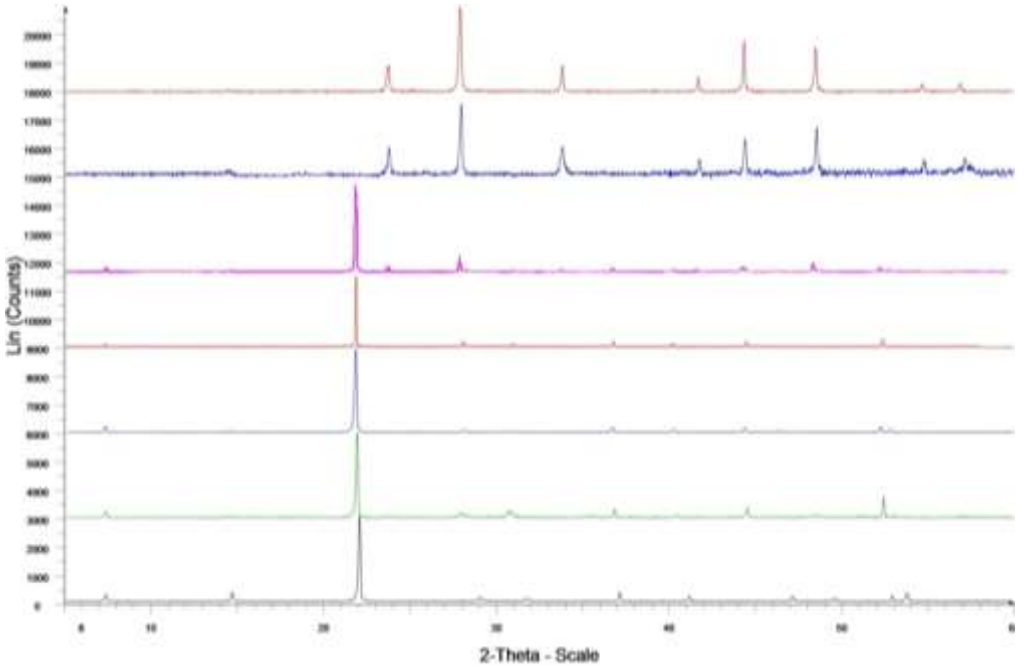

Fig.2. XRD powder patterns of some alloys of the $FeGa_2S_4$- $FeIn_2S_4$ system

The mutual solubility of the components at a room temperature was determined by us from the graph of the concentration dependence of the lattice parameters of the β- and γ- solid solutions and is 52 and 20mol%, respectively.

2FeS-$FeGaInS_4$ section (Fig.3) has a phase diagram of the eutectic type with limited

mutual solubility of the components in the solid state. The compositions of three phases in eutectic equilibrium L↔α+βat 1310 K are determined by the construction of the Tamman triangle. The eutectic point has a composition of ~ 63 mol% $FeGaInS_4$, and two ends of the eutectic horizontal corresponding to the mutually saturated compositions of the α- and β-phases have the compositions 13 and 91 mol% $FeGaInS_4$, respectively.

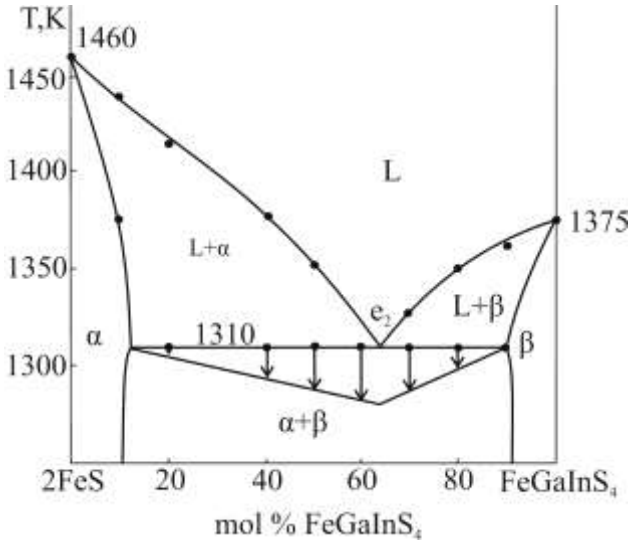

Fig.3. Phase diagram of the 2FeS-$FeGaInS_4$ section

Table 2. Phase compositions and crystallographic parameters of the phases in the $FeGa_2S_4$-$FeIn_2S_4$ system

Composition, mol % $FeIn_2S_4$	Phase	Type and parameters of the crystal lattice, nm
$FeGa_2S_4$	β	Trigonal, P-*3m*1, *a*=0.36543(3); *c*=1.20558(8)
20	β	"-", *a*=0,369503(3); *c*=1.211243(7)
40	β	"-", *a*=0,379503(2); *c*=1.216903(6)
50	β	Trigonal, P-*3m*1, *a*=0.37765(1), *c*=1.22257(3)
80	γ	Cubic, *a* = 1.05152(8)
100	γ	Cubic, Fd-3m,*a* = 1.0607(7)

CONCLUSION

The character of phase equilibriums in the $FeGa_2S_4$- $FeIn_2S_4$ and FeS- $FeGaInS_4$ sections of the FeS-Ga_2S_3-In_2S_3 quasi-ternary system was revealed. They are quasi-binary and characterized by wide areas of solid solutions based on starting compounds. The alloy with composition $FeGaInS_4$ can be characterized as a congruently melting compound.

Experimental results obtained can be used to select the composition of solution - melt in the growth of high-quality crystals of intermediate phases which are of interest as magnetic semiconductors.

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$FeGa_2S_4$-$FeIn_2S_4$ və FeS-$FeGaInS_4$ SİSTEMLƏRİNİN FAZA DİAQRAMLARI

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$FeGa_2S4$-$FeIn_2S_4$ və FeS-$FeGaInS_4$ sistemlərində faza tarazlıqları differensial termiki analiz və rentgenfaza analizi üsulları ilə tədqiq edilmişdir. Müəyyən edilmişdir ki, hər iki sistem kvazibinardır və başlanğıc komponentlər əsasında məhdud bərk məhlul sahələri əmələ gəlməsi ilə səciyyələnir. $FeGaInS_4$ tərkibli nümunə $FeGa_2S_4$ quruluş tipində kristallaşır, parçalanmadan 1375 K-də əriyir və konqruent əriyən birləşmə hesab edilə bilər.

Açar sözlər: *$FeGa_2S_4$, $FeIn_2S_4$, $FeGaInS_4$, fazadiaqramı, bərk məhlullar*

ФАЗОВЫЕ ДИАГРАММЫ СИСТЕМ $FeGa_2S_4$-$FeIn_2S_4$ И FeS-$FeGaInS_4$

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Фазовые равновесия в системах $FeGa_2S_4$-$FeIn_2S_4$ и FeS-$FeGaInS_4$ экспериментально исследованы методами дифференциального термического и рентгенофазового анализов. Установлено, что они являются квазибинарными и характеризуются ограниченной взаимной растворимостью исходных соединений. Фаза состава $FeGaInS_4$ кристаллизуется в структуре типа $FeGa_2S_4$, плавится при 1375 K без разложения и по его поведению на фазовой диаграмме может характеризоваться как конгруэнтно плавящееся соединение.

Ключевые слова: *$FeGa_2S_4$, $FeIn_2S_4$, $FeGaInS_4$, фазовая диаграмма, твердые растворы*