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PHASE DIAGRAM OF THE FeSe–In₂Se₃ SYSTEM

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The quasi-binary system FeSe–In₂Se₃ was re-examined by the methods of DTA and XRD and its T – x phase diagram was constructed. It was established that the diagram is somewhat different from the earlier one given by us in the literature. FeIn₂Se₄ compound, which congruently melts at 1195 K, was found in the system. This compound forms eutectics with both the initial binary compounds. The crystal structure of FeIn₂Se₄ is refined by using the powder diffraction data by the Rietveld method.

Keywords: FeSe–In₂Se₃ system, phase diagram, FeIn₂Se₄ compound, eutectic, Rietveld method, crystal structure.

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Introduction

Complex chalcogenides and phases based on them have long attracted attention due to a number of promising functional properties [1–4]. Recent studies have shown that some of them are topological insulators and extremely promising for use in spintronics in quantum computing [5–7].

Materials which include AB₂X₄ compounds (A – Mn, Fe, Co, Ni; B – p^1 – p^3 elements, X – chalcogen) are the group known for their anisotropic physical properties that find potential applications in the fields of photodetectors, switches, and photovoltaic as well as many semiconducting and magnetic applications [8–17].

Design and development of novel methods for the directed synthesis of new complex phases and materials require the study of phase equilibria in the corresponding systems [18–20].

The studies of the phase equilibria in systems MX–Ga₂X₃–In₂X₃ (M – Mn, Fe; X – S, Se, Te) were undertaken by us in order to search and develop the physicochemical basis for obtaining new magnetic semiconductors. The preliminary results obtained [21, 22] showed the formation of wide regions of solid solutions along the MGa₂X₄–MIn₂X₄ sections of these systems. However, an analysis of the literature data showed that the phase diagrams of some of the boundary quasi-binary components of these quasi-ternary systems require clarification. In [23], new refined data on phase

equilibria in the systems FeSe–Ga₂Se₃ и Ga₂Se₃–In₂Se₃ were presented.

This paper presents the results of repeated studies of the system FeSe–In₂Se₃.

Experimental part**Synthesis**

FeSe and In₂Se₃ used in research were synthesized using high purity iron (99.995%), indium (99.999%), and selenium (99.99%) purchased from Evochem. The calculated amounts of elements were sealed in a vacuum quartz tube with a residual pressure of $\sim 10^{-2}$ Pa. Then the ampoules were placed in two-zone furnace. The hot zone was maintained at 1300 K (FeSe) or 1200 K (In₂Se₃), and the temperature of the cold zone was about 900 K, which is slightly below the boiling point of selenium (958 K) [24].

Intermediate samples of the FeSe–In₂Se₃ system were prepared from pre-synthesized compounds in evacuated quartz ampoules at 1250 K followed thermal annealing at 1000 K (200 h), and then at 700 K (300 h). Some alloys after annealing were quenched in cold water in order to investigate by XRD method.

Analysis

In order to analyze the samples, the differential thermal analysis (DTA) and X-ray powder diffraction (XRD) were used. DTA was carried out using a NETZSCH 404 F1 Pegasus system in the range within room temperature (~ 1400) K at a heating rate of 10 K min^{–1}.

The crystal structures of the initial compounds and intermediate samples were investigated by powder X-ray diffraction analysis on a Bruker D2 Phaser powder diffractometer (CuK α -radiation) in the 2 θ range of 10–75°. The lattice parameters were indexed using the TOPAS-4.2 software.

Two thermal effects were present on the FeSe thermogram; they corresponded to the peritectoid reaction of formation of β -FeSe (730 K) and melting (1345 K). According to DTA data, synthesized In₂Se₃ melts at 1160 K. Obtained data are in accordance with the data of [25, 26].

The powder patterns of FeSe and In₂Se₃ showed the formation of single-phase materials. The calculated lattice constants of tetragonal FeSe (Sp.gr. *P4-nm*, $a=0.37743(4)$, $c=0.55301(7)$ nm), and hexagonal In₂Se₃ (Sp.gr. *R3m*, $a=0.405(2)$, $c=2.877(4)$, $z=3$) nm were consistent with the literature data [27, 28].

Results and discussion

Phase diagram of the FeSe–In₂Se₃ system

The phase diagram constructed (Figure 1) refers to the dystectic type. The intermediate γ -phase with the stoichiometric composition of FeIn₂Se₄ melts congruently at 1195 K. This compound forms eutectics with both the initial compounds of the system, which have the com-

positions 40 (e_1) and 70 (e_2) mol% In₂Se₃ and crystallize at 1170 and 1070 K, respectively. At the eutectic temperature e_1 , the area of homogeneity of solid solutions on the basis of a high-temperature modification of iron selenide is about 3 mol%, and the γ -phase is about 5 mol% (48–53 mol% In₂Se₃). At the eutectic temperature e_2 , the homogeneity region of the β_4 -phase on the basis high-temperature modification of In₂Se₃ reaches 9 mol%, and the γ -phase is about 7 mol% (48–55 mol% In₂Se₃). The system is characterized by a series of solid-phase reactions associated with the polymorphism of FeSe and In₂Se₃. Eutectoid equilibrium

occurs at 727 K.

Horizontal lines at 980, 915 and 483 K correspond to eutectoid

and peritectoid

equilibria; herein β_1 , β_2 , β_3 , and β_4 – solid solutions based on various crystalline modifications of In₂Se₃.

The ternary compound of composition Fe₂In₂Se₅, described in [29], was not found by us. XRD data showed that the alloy of this composition is a two-phase mixture of FeIn₂Se₄ and FeSe.

Fig.1. Phase diagram of the FeSe–In₂Se₃

The refined T - x diagram of the FeSe-In₂Se₃ system (Figure 1) is slightly different from that given in [30]. First, the melting point of the compound FeIn₂Se₄ determined by us is significantly higher than the value (1163 K) specified in [30]. There are also discrepancies in the coordinates of the eutectic, eutectoid and peritectoid equilibria and the length of the homogeneity regions of the β_1 , β_2 , β_3 , and β_4 phases.

Refinement of the crystal structure of the FeIn₂Se₄

The lattice type and unit cell parameters for the powder sample FeIn₂Se₄ were determined based on the obtained powder XRD pattern. Figure 2 displays the XRD pattern and the intensities differences between the experimental and calculated by Rietveld method data.

The refined unit cell parameters are shown in Table 1, and the atomic positional parameters are given in Table 2.

The crystal structures of MB₂X₄-type layered compounds consist of seven-layer packets [31].

Table 1. Refined structure parameters and interatomic distances of the FeIn₂Se₄

Structure parameters	FeIn ₂ Se ₄
Space group	$R\bar{3}m$
Lattice parameters:	
a (nm)	0.40219(13)
c (nm)	3.9161(25)
Cell volume(nm ³)	0.5486(50)
Density (g/cm ³)	5.4604(50)
R-Bregg (%)	2.964

These packets are formed from atomic layers in the following sequence: X-B-X-M-X-B-X. If we characterize the structure of these packets in polyhedra, it can be shown that they consist of three polyhedral layers. In this case, the central layer consists of octahedra connected by common edges. This layer of octahedra is surrounded on two sides by layers of tetrahedra that are connected by vertices. Tetrahedral positions are occupied by B atoms, and the central layer of octahedra is only occupied by M atoms.

Fig.2. Observed and calculated powder diffraction pattern and difference plot for FeIn₂Se₄.

Table 2. Atomic positional parameters in FeIn₂Se₄

Atom	Multiplicity of positions	x	y	z	Atom type and relative occupation
Fe	3	0.00000	0.00000	0.00000	Fe+2 1
In	6	0.33333	0.66667	0.0896(12)	In+3 1
Se1	6	0.33333	0.66667	0.0276(14)	Se 1
Se2	6	0.66667	0.33333	0.1187(16)	Se 1

Fig.3. Occupancy of metal positions in the FeIn₂Se₄ crystal structure.

Conclusion

A new scheme of phase relations in the quasi-binary system FeSe–In₂Se₃, somewhat different from the previously given in the literature, has been constructed. It was shown that the only ternary compound of the FeIn₂Se₄ system melts congruently at 1195 K and forms eutectics with both the initial binary compounds. The eutectic coordinates determined by us differ from the literature data. The crystal structure of FeIn₂Se₄ is refined by treatment of the powder diffractogram using the Rietveld method.

Obtained experimental results can be used for choosing the composition of solution-melt for the growth of the high-quality crystals of intermediate phases which are of interest as magnetic semiconductors.

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FeSe–In₂Se₃ SİSTEMİNİN FAZA DİAQRAMI**F.M.Məmmədov**

FeSe–In₂Se₃ kvazibinar sistemi DTA və RFA metodları ilə yenidən tədqiq edilmiş və onun T – x faza diaqramı qurulmuşdur. Müəyyən edilmişdir ki, diaqram əvvəldən ədəbiyyatda veriləndən bir qədər fərqlənir. Sistemdə 1195 K-də konqruent əriyən FeIn₂Se₄ birləşməsi əmələ gəlir. Bu birləşmə hər iki ilkin binar birləşmələrlə evtektika əmələ gətirir. FeIn₂Se₄ birləşməsinin kristal quruluşu ovuntu rentgenoqramının nəticələri əsasında Ritveld metodu ilə dəqiqləşdirilmişdir.

Açar sözlər: FeSe–In₂Se₃ sistemi, faza diaqramı, FeIn₂Se₄ birləşməsi, evtektika, Rietveld metodu, kristal quruluş.

ФАЗОВАЯ ДИАГРАММА СИСТЕМЫ FeSe–In₂Se₃**Ф.М.Мамедов**

Квазибинарная система FeSe–In₂Se₃ была повторно исследована методами ДТА и РФА и построена ее фазовая диаграмма. Установлено, что диаграмма несколько отличается от ранее приведенной в литературе. В системе обнаружено соединение FeIn₂Se₄, конгруэнтно плавящееся при 1195 К. Это соединение образует эвтектику с обоими исходными бинарными соединениями. Методом Ритвельда на основании порошковых дифракционных данных уточнена кристаллическая структура FeIn₂Se₄.

Ключевые слова: система FeSe–In₂Se₃, фазовая диаграмма, соединение FeIn₂Se₄, эвтектика, метод Ритвельда, кристаллическая структура.