JOTCS A
Journal of the Turkish Chemical Society
Section: A
Chemistry
TURKISH CHEMICAL SOCIETY

Synthesis of $FeIn_2Se_4$ and Related Compounds

Aliye Rzayeva

Nakhchivan Branch of Azerbaijan NAS, Institute of Natural Resources, Az 7000, Nakhchivan, Azerbaijan

(This article was sent to the 6th Physical Chemistry Congress in Zonguldak, 2017 and accepted as a peer-reviewed article)

Abstract: Indium is transferred by the tartaric acid in the strong complex in aqueous medium. Then the selenizing solution (solution of selenium in borane) is added. The voluminous sediment of yellow color is formed. This $FeIn_2Se_4$ compound was prepared from $FeSO_4.7H_2O$ and In_2Se_3. Composition of the determined differential thermal analysis and by chemical analysis. Phase analysis of $FeIn_2Se_4$ is studied using the X-ray and chemical analysis. The compound $FeIn_2Se_4$ crystallized in hexagonal symmetry, a = 4.012 Å, c = 39.21 Å. Morphological investigations have been performed using scanning electron microscopy. Optical absorption is measured using a spectrophotometer, the value of band gap on the basis of the spectrum, which has been read from the dispersed solution of $FeIn_2Se_4$ is calculated. Two endothermic effects were observed in the differential thermal analysis of $FeIn_2Se_4$. In the system T_g = 1158 endothermic effect corresponding to the melting point of the compound. The qualitative analysis of this sediment has shown the presence of indium and selenium. In various experiments are produced sediments of different colors when medium pH changes. The set of experiments has been carried out to specify color change and hydrogen ions concentration impact. In this iron indium selenide, the efficiency is 92.2 %.

Keywords: Iron indium selenide, differential thermal analysis, sedimentation speed, chemical analyses, scanning electron microscopy (SEM).

Submitted: May 23 2017. **Accepted:** December 22, 2017.

Cite this: Rzayeva A. Synthesis of FeIn2Se4 and Related Compounds. JOTCSA. 2017;4(sp.is.1):93–102.

DOI: **To be assigned.**

***Corresponding author. E-mail:** aliye.rzaeva@mail.ru.

INTRODUCTION

Binary and ternary chalcogenides of indium group elements are promising functional materials of modern electronic engineering. Many of these compounds and multicomponent phases based on them have photoelectric, thermoelectric, ferroelectric, optoacoustic, and other useful properties.

The work (1) reports that In_2Se_3 single-crystal thin layer preparation has been carried out for the first time by means of mechanical peeling and investigation of (α→β) crystalline phase transitions, and corresponding changes of electrical properties in these thin layers are also given in this work. As opposed to bulk single-crystals, β-phases can remain in single-crystal thin layers at the room temperature. The single-crystal nature of the layers before and after a phase transition ensures unique determination of changes in electrical resistance. In particular, the β-phase has resistivity in 1 – 2 orders less than the α-phase. In addition, we find that the temperature of (α→β) phase transitions increases as much as 130 K if the layer thickness decreases from ~87 nm to ~ 4 nm. These single-crystal thin layers are ideal for research of phase transitions scaling behavior and electrical properties changing in connection to this process.

The work (2) determines boundary conditions and formation zone of indium(III) sulfide and indium(III) selenide with deposition by thiocarbamide and selenocarbamide. Potentiometry of indium chloride, $InCl_3$, has been carried out in the hydroxide solution concentration range of 0.0001 – 0.100 mole/L.

$Fe_2In_2Se_5$, a polytype of $FeIn_2Se_4$, has been synthesized by conventional solid-state reaction of their constituent elements. The product of the reaction was sequentially used as starting material in the crystal growth process carried out by chemical transport using iodine as the transporting agent. The crystal structure of a new polytype of this compound was determined using single crystal techniques with data collected with a CCD-based diffractometer (3). Single crystals of the ternary compound $FeIn_2Se_4$ have been grown by directional solidification in a vertical Bridgman geometry, and their composition, structure, and melting point have been determined. The relative length change of $FeIn_2Se_4$ has been measured on a dilatometer using oriented single-crystal samples, and its thermal expansion coefficients have been determined (4). The dielectric constants and tangent angle of dielectric loss at different frequencies and temperatures for layered monocrystals of $FeIn_2Se_4$ are explained and their experimental values are defined. The big value of ε is connected by electrons with hop exchange between defects, having in crystal are defined. It is established that angle tangent of dielectric loss decreases in inverse proportion with the frequency (~1/ω) (5).

MATERIALS AND METHODS

In this paper, obtaining conditions of $FeIn_2Se_4$ compounds in aqueous and organic media are cited. An aliquot of 10 mL is taken from the indium chloride solution (0.1 M) and tartaric acid solution is added, whereupon indium transits into a firm complex. The complex is so firm that indium hydroxide is not formed at the action of ammonia solution at pH 1 – 12. Without tartaric acid, indium and ammonia form $In(OH)_3$ at pH > 3.5. Indium is converted into the firm complex with the aim to carry out the reactions in alkaline medium. The selenizing reagent is prepared by dilution of elementary selenium (amorphous or melt) in sodium borohydride solution. During the reaction, pH of indium solution is regulated within the limits of 10 – 11, and selenizing reagent is added in stoichiometric quantity. A bulky sediment in black color is formed. The qualitative analysis of this sediment has shown the presence of indium and selenium. In various experiments are produced sediments of different colors when medium pH changes. The set of experiments has been carried out to specify color change and hydrogen ions concentration impact. The results are given in Table 1.

Table 1. Dependence of indium selenide color and deposition completeness on medium pH. [In] = 0.1 M, [Se] = 0.1 M, temp. 323 – 333 K

№	$InCl_3$, mL	Se Soln., mL	pH	Sediment, mg	Sediment color	Sediment formula
1	10	15	8	178.1	black	In_2Se_3 + Se
2	–	–	9	231.2	brown	In_2Se_3
3	–	–	10	233.7	yellow	In_2Se_3
4	–	–	11	227.5	yellow	In_2Se_3

It is evident from the table data that selenium in the first experiment is partly hydrolyzed and mixed with the sediment; therefore complete deposition of indium selenide does not occur (separate experiments are carried out to ascertain selenium solution behavior at various pH values; it is ascertained that selenium is partly deposited from the solution at pH lower than 9). At the rest of experiments resulting sediments consisting of In_2Se_3. Sediments are washed by distilled water and dried at 33 K.

The thermal analysis of the produced In_2Se_3 sediment is carried out in the presence of air by the derivatograph NETZSCH STA 449F3. The composition of resulting indium selenide corresponds to the formula In_2Se_3. Also result of EDX (Energy dispersive X-ray Spectroscopy) of indium selenide (Figure 1).

Element	**Weight %**	**Atomic %**
Se	56.08	64.99
In	43.92	35.01
Totals	100.00	

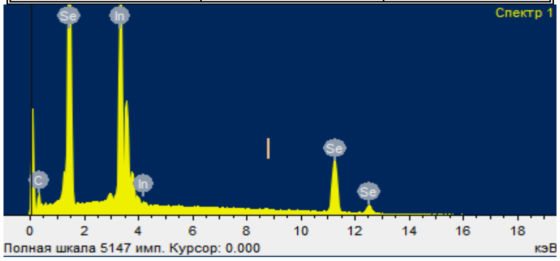


Figure 1. The results of the compound's elemental analysis.

The results in this table correspond to stoichiometric composition of the compound. The view of nanoparticles elementary spectrum is presented in the figure stated below.

Effect of temperatures (413, 433, 453 K) on emerging, growing and forming nanorods is studied at the solvothermal method of In_2Se_3 producing (1.09 μ – 230 nm), forms nanorods are taken. The compound obtained in aqueous medium does not form at the room temperature. Morphology of the obtained compounds was studied at the electronic microscope TM-3000 Hitachi.

As initial components for the synthesis of compounds $FeIn_2Se_4$ were used In_2Se_3 and $FeSO_4.7H_2O$. In_2Se_3 was mixed with $FeSO_4.7H_2O$ in the aqueous medium in the molar ratios 2:3 ($FeIn_2Se_4$) with the presence of acetic acid (pH=3-7), at 293-353 K. The synthesis of iron indium selenide ternary chalcogenide semiconductors has been used the primary components of indium(III) selenide with iron(II) sulfate in ethylene glycol media (pH-4-5). The quantity of reagents is determined according to the stoichiometry during the reaction. The experimental ware in a Teflon ditch is located in the autoclave. Test within 10 hours at 413 – 443 K to temperature remains in the furnace. Both water and organic media received deposits are filtered by the glass filter, washed with 0.1 M acetic acid, ultrapure water and ethyl alcohol at last, then dried in vacuum oven at 353 K for analysis.

In order to determine the morphology of the individuality of the synthesized compounds, X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), differential thermal analysis (DTA), and chemical analysis were studied.

The morphology of the patterns was carried out with scanning electron microscopy. The synthesized samples are not found to shape in aqueous medium. But it has been ascertained that the nano- and microparticles are formed at 413-443 K in organic medium. The results obtained from SEM analysis showed that, depending on the type of organic solvents are different of particles shape (Figure 2).

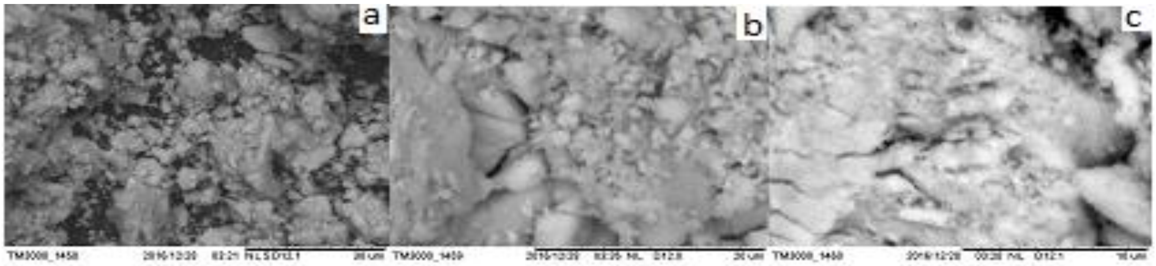


Figure 2. SEM photographs of $FeIn_2Se_4$ compound (*a*) at 413 K in aqueous medium and (*b, c*) at 443 K in ethylene glycol.

X-ray powder diffraction of $FeIn_2Se_4$ compounds have been studied (Bruker D8 ADVANCE, CuK_α, $\lambda = 1.5406$ Å, $0 < 2\Theta < 80°$). The compound $FeIn_2Se_4$ crystallized in hexagonal symmetry $\alpha = 4.012$ Å, $c = 39.21$ Å (3). Our experimental XRD patterns agreed with those calculated from the structural data reported in the literature (Figure 3).

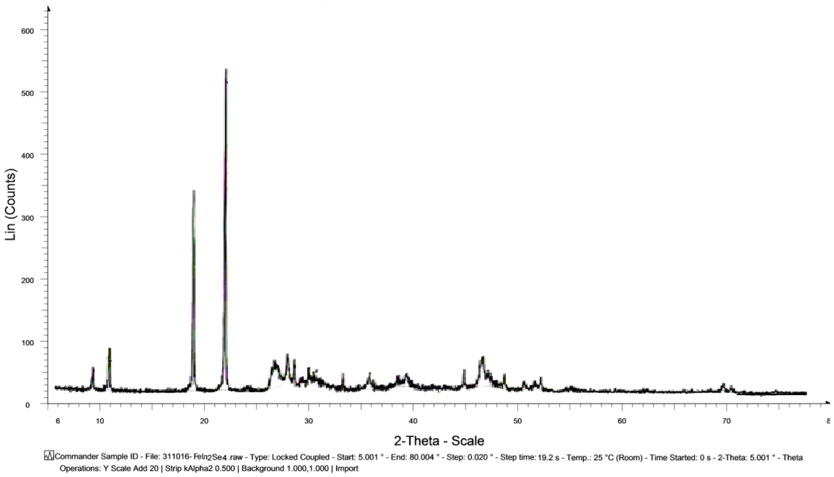
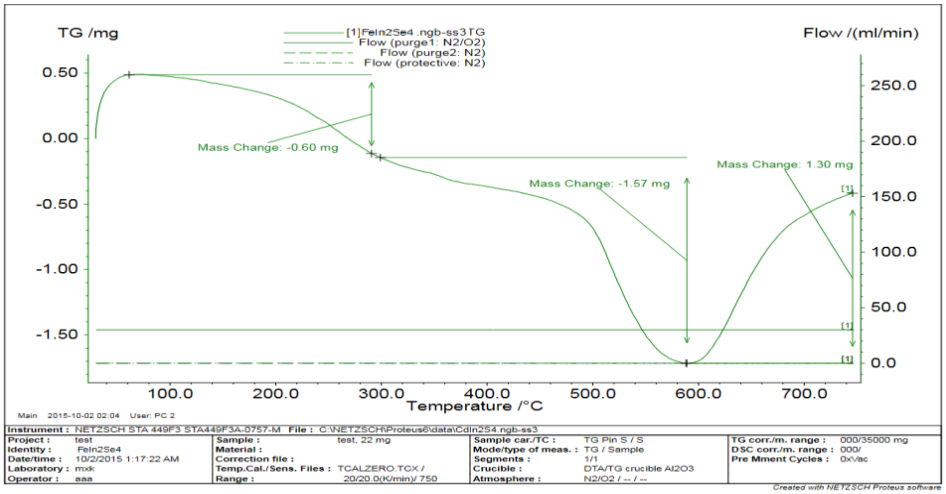


Figure 3. XRD of $FeIn_2Se_4$.

The thermogravimetric analysis of the produced $FeIn_2Se_4$ sediment is carried out in the presence of air by the derivatograph. The results are shown in Figure 4.



Instrument : NETZSCH STA 449F3 STA449F3A-0757-M **File :** C:\NETZSCH\Proteus6\data\CdIn2S4.ngb-ss3

Project :	test	**Sample :**	test, 22 mg	**Sample car./TC :**	TG Pin S / S	**TG corr./m. range :**	000/35000 mg
Identity :	FeIn2Se4	**Material :**		**Mode/type of meas. :**	TG / Sample	**DSC corr./m. range :**	000/
Date/time :	10/2/2015 1:17:22 AM	**Correction file :**		**Segments :**	1/1	**Pre Mment Cycles :**	0xVac
Laboratory :	mxk	**Temp.Cal./Sens. Files :**	TCALZERO.TCX /	**Crucible :**	DTA/TG crucible Al2O3		
Operator :	aaa	**Range :**	20/20.0(K/min)/ 750	**Atmosphere :**	N2/O2 / -- / --		

Figure 4. TGA of $FeIn_2Se_4$.

As evident from Figure 4, the sample is heated between at 293-1073 K temperature. The rate was 40 mL/s. This time, mass loss is 3.47 mg. Mass loss up to 300° C temperature (0.60 mg) occurs due to the free selenium. But mass loss up to 600° C (1.57 mg) occurs due to the oxidation of the selenium contained in the combination. Mass lost between 600-750° C temperature is due to the elements in the compound. All these show that the composition of resulting iron indium selenide corresponds to the formula $FeIn_2Se_4$.

The crystallinity of the alloys was controlled by differential thermal analysis with an HTP-70 pyrometer with Thermoskan-2 device. Differential thermal analysis of $FeIn_2Se_4$ compound is observed endothermic effects. In the system T_g = 1158 (Figure 5) endothermic effect corresponds to the melting point of the combination (6).

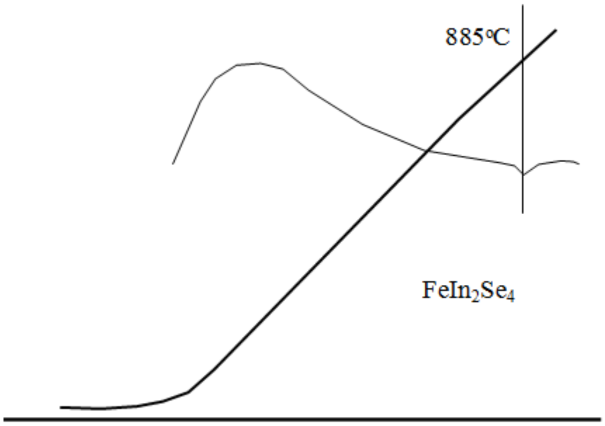


Figure 5. The DTA of $FeIn_2Se_4$.

The optical absorption spectra have shown that functional group peaks existed before process of the transformation to the compound of $FeIn_2Se_4$ and then process in in the infrared region.

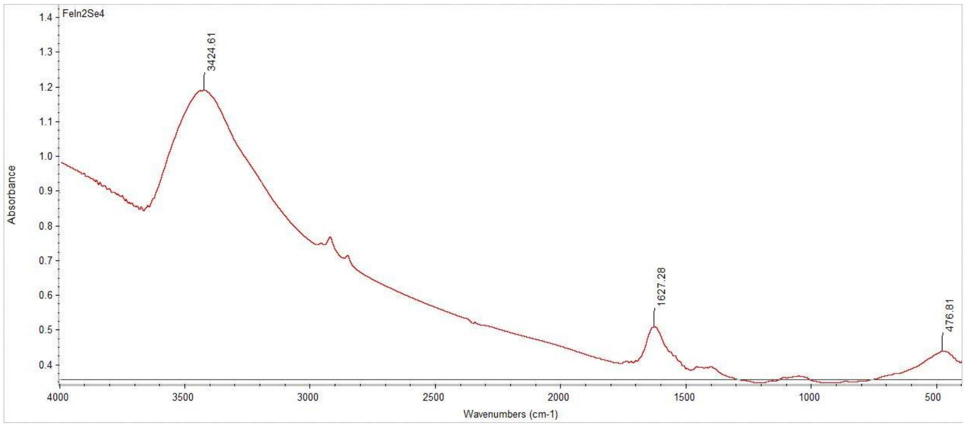


Figure 6. IR spectrum of $FeIn_2Se_4$.

As known, absorption spectrum leads to the emergence of a number of functional groups certain of peaks infrared region. On the figure, we observed great energies manifested in the region for the compound $FeIn_2Se_4$ a peak 3424-1627 cm^{-1} is suitable group $O-H$ absorbing water, and compatible peak 476 cm^{-1} merger is compatible with (Figure 6).

The chemical analysis of produced sediments is carried out. The sediments are decomposed by nitric acid, evaporated up to isolation of salt mixture. Then distilled water and some drops of hydrochloric acid are added to the mixture, and all that is moved to a graduated flask. Iron is determined by methods known in solution (7). Selenium and indium are appointed by the method of the photo-colorimeter (Table 2).

Table 2. The chemical analysis of $FeIn_2Se_4$

Pattern, g	Components, g					
$FeIn_2Se_4$	Fe		In		Se	
0. 5425	Theo.	Pract.	Theo.	Pract.	Theo.	Pract.
	0.253	0.251	0.093	0.091	0.196	0.199

The table shows that the combination of chemical analysis is consistent with formula of $FeIn_2Se_4$.

CONCLUSIONS

The results of these experiments have shown that there is no difference between the combination of the formation of the compound in both organic and non-organic environments. The difference is the combination of nano- and microparticules in the organic environment. This is important in the semiconductor area.

It is known that the production of ternary chalcogenide semiconductor materials in polar and low-polarity organic solvents is of great practical importance recently, since impurities are less in composition of the compounds obtained in an organic solvent medium. Furthermore, the formation of nanoparticles and microparticles is very easy. Information on the production of iron indium selenide in ethylene glycol medium is almost absent in the literature and the present work represents a first step in this direction.

X-ray powder diffraction of $FeIn_2Se_4$ crystallized in hexagonal symmetry $a = 4.012$ Å, $c = 39.21$ Å. In this article, we report the mechanism of synthesis and results of $FeIn_2Se_4$. Endothermic effects is observed in the differential thermal analysis of $FeIn_2Se_4$ ($T_g = 1158$). The thermogravimetric analysis of the produced $FeIn_2Se_4$ sediment is carried out in the presence of air by the derivatograph. The results iron indium selenide corresponds to the formula of $FeIn_2Se_4$.

ACKNOWLEDGMENTS

This paper was submitted first to the IV Physical chemistry congress, 15-18 May, 2017, Zonguldak, Turkey.

REFERENCES

1. Chaiken A. [and others]. Structural and electronic properties of amorphous and polycrystalline In_2Se_3 films. *Journal of Applied Physics,* **94** (2003), http://dx.doi.org/10.1063/1.1592631.
2. Tulenin S.S. [and others]. Deposition conditions, the composition and structure of the chemically deposited films of In_2Se_3. *Journal of Inorganic Chemistry*, **61**(2016), http://doi.org/10.1134/S0036023616040227.
3. Cedeno C. [and others]. The crystal structure of $Fe_2In_2Se_5$, a $FeIn_2Se_4$-related polytype. *Journal of Physics and Chemistry of Solids.* **66** (2005), 2049–2051.
4. Bodnar I.V. [and others]. Growth, structure, and thermal expansion anisotropy of $FeIn_2Se_4$ single crystals. *Inorganic Materials,* **46** (2010), 604–608.
5. Niftiyev N.N. [and others]. Electrical properties of monocrystal $FeIn_2Se_4$. *Journal of Semiconductors,* **37** (2003), 173–175.
6. Reil S., Haeuseler H. Journal of Alloys and Compounds **270**, 83 (1998).
7. Scheler V.R., Powell A.R. Analysis of minerals and ores of rare elements, *State scientific and technical publishing house*, Moscow, **447**, (1962).