THE ELECTRIC AND OPTICAL PROPERTIES OF THE LAYERED SEMICONDUCTOR $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$

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The single crystals of the intermediate phase of system $(GaIn)_2S_3$-Fe4 of composition $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ have grown from the melt by Bridgemen method. The single crystals are layered, the symmetry is orthorombic, grating constants in the hexagonal device a=3,786·2, c=36, 606Å, sp.gr. R3m, z=16.

The edge of the optical absorption in the wide energy photon interval has been investigated and the forbidden band width E_g=1,843eV for $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ have been defined.

The structure In-$Ga_{0.5}Fe_{0.25}In_{1.25}S_3$-In has been prepared and its VAC and the temperature dependence in the temperature interval 100÷360K have been studied. The parameters of the given structure: 12.56 $cm^2/V\cdot$ sec, $n_k=1.55\cdot10^{10}$ cm^{-3}; $D_k^*=2\cdot10^{-2}$; $d_k=5.6\cdot10^{-9}$ cm; $\Delta\varepsilon$ =0.497eV have been calculated by the method of the differential analysis.

1. Introduction

The significance of the physical-chemical and structural study of substance with semiconductor properties is obvious. The synthesis and single crystals growth, the study of their physical-chemical and structural peculiarities, phase-formation regularities and the mechanism of structural phase transition have a great scientific –practical mean. In this aspect Ga_2S_3 – In_2S_3 system compounds are perspective objects for the solution of questions of the structurization, polymorphic, polytype, methods of the phase stabilization and the clarification of characteristics physical-chemical properties.

The phase equilibrium in Ga_2S_3 – In_2S_3 quasi-binary cut of the triple system Ga-In-S were for the first time studied by authors [1], where the formation of just one triple phase GaInS, melting uncongradually, was established. It should be noted that in these papers there is a visible discrepancy in the state diagram and values of hexagonal cell parameters. Neither was determined the crystal structure of the compound.

Judging from experimental facts on the presence of some polymorphy modifications in sesqui chalcogenide of A_2S_3 (A-Al,Ga,In) type, authors [2-6] investigated in details the phase –formation in the given system.

Applying the method of chemical transport reaction (CTR), the presence of polymorphy phases line, polytype forms and three independed compounds (table 1) was established. As result of *X*-ray analysis of crystals, obtained from before synthesized contents $Ga_{0.5}In_{1.5}S_3$ and $GaInS_3$ in various temperature gradients.

To reveal the influence of multivalent tetrahedral atoms on the stabilization of polymorphy modifications $(GaIn)_2S_3$, partially substituting tetrahedral placed atoms Ga and In by atoms Cu and Sn (conserving the total balance of the valence) by the method of direct synthesis, authors [7,8] realized 2H and 3R polytypes, having the layered structure of polytype line a=3.82Å, c=15Å·n (n=2,3) and a=6.52Å, c=18Å·n (n=2).

The present paper are dedicated to structural research, definition of nature of optical transitions and current – conduction mechanism of layered $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ single crystals in a wide temperature range (100÷360K).

Table 1
Crystallographic data of polymorphic phases and polytype forms of compounds of $(GaIn)_2S_3$

The content of the phase	Sp.gr.	a, Å	b, Å	c, Å	Z
$GaInS_3$	P3m1	3.81		18.19	2
$GaInS_3$	P3m1	3.81		54.61	6
$GaInS_3$	$P6_1$	6.65		17.92	6
$GaInS_3$	$P6_3mc$	3.81		30.62	10/3
$GaInS_3$	P3m	3.81		45.89	5
$GaInS_3$	$Bb2_1m$	19.06	6.19	3.81	4
$Ga_{0.5}In_{1.5}S_3$	P3m1	3.84		12.33	1
$Ga_{0.5}In_{1.5}S_3$	R3m	3.81		100.04	11
$Ga_{0.67}In_{1.33}S_3$	2H	7.64		74.00	8
$GaInS_3$	R3m	3.82		63.41	6
$Ga_{0.25}In_{1.75}S_3$	C2/m	6.55	3.72	12.62 $\beta=100^0$	4
$GaInS_3$	Shpinell Str.type	10.79			8

The present paper is devoted to the structural investigation of the layered single crystals $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$, definition of the character of the optical transitions and conduction current mechanism in the wide temperature interval (100÷360K).

2. Experimental results and discussion

2.1. The single crystals growth.

The crystallization from the melt by Bridgemen method of $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ has been carried out in the following mode and constants: the quantity of the beforehand synthesized substance ~5,6gr, the melt high is 30mm, the diameter of the container from the quartz is 8mm, the initial temperature is ~1273K, the cooling velocity is ~290K/h, the annealing band is 673K, the annealing time is 30 hours. The experiment result was successful. The all mass of the sample was crystallized in the form of the disoriented crystal blocks, which have absolute cleavage and easily crush on the thin layers of the needed forms and sizes. About the quality of the

grown single crystals can see on the given Laue photograph (fig.1).

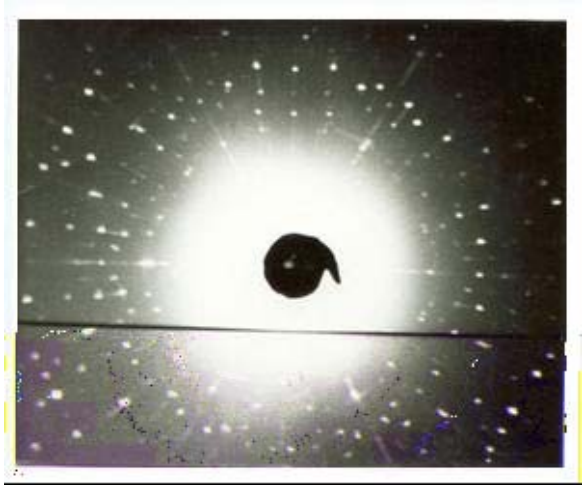

Fig.1. Laue X-ray diffraction for $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$

2.2. X-ray investigations.

For the definition of the crystal lattice parameters, symmetry and the structural type were obtained. The following roenthgenodifractional experiments: 1) by Laue methods and pumping were adjusted the crystalographical directions and defined their values: 2) the roenthgenoflections fro the plane-parallel planes for the definition of the character of the diffraction type ool were obtained; 3) powder diffractogram (DRON-20; N_i is filter, limit is $0,5^\circ<2\theta<70^\circ$).

On the base of the calculations and analysis of the obtained results it was established, that single crystals $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ are crystallised in the rombohedral lattice with periods, in the hexagonal device a=3.786·2Å, c=36.606Å; sp. gr. R3m, z=16, V=1817.57Å, V_s = 37.86Å^3.

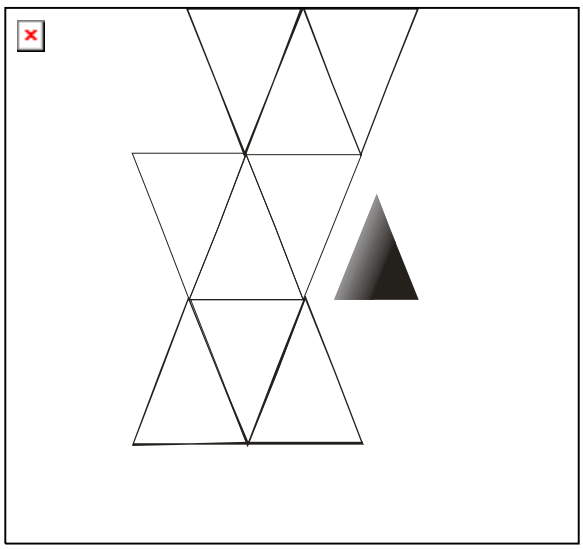

Fig.2. The variant of distribution of atoms in the lattice of $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$

By the crystalochemical analysis it is established that investigated single crystals are triple-packet polytype of the set c=12·nÅ and its structure is polytype on the base of $Ga_{0,5}Fe_{1,5}S_3$ structure in the ordered variant. The variant of atom distribution in the lattice is given on the fig.2. As it is seen from the figure, the layer consequence is correspond to the variant -$c$kk$c$- and the "a" period of the lattice is total because of the statistical filling of the octahedron empties. It is need to note, that in the difference from the changing atoms of Cu and Sn, the iron atoms stabilize the formation of the another kind of polytype, but not one- and divalent cations.

2.3. Optical properties.

For the definition of the electron effect mechanisms in the single crystals $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ the optical investigations in the wide interval of photon energy were carried out.

On the device, constructed on the base of the monochrometer MDR-12, the transmitted spectrums T of single crystals $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ at the wave length 400-800nm were obtained. The different single crystal samples by the thickness 10÷40mkm were investigated.

The optical absorption coefficient α has calculated from the experimental values of T, using the formulae [9]

$$T = (1 - R)^2 \exp(-kd), \qquad (1)$$

here R is the reflection coefficient, d is the sample thickness. The spectral dependence of optical absorption coefficient $\alpha(h\nu)$ for the samples from $Ga_{0,5}Fe_{0,25}InS_3$ is given on the fig.3a.

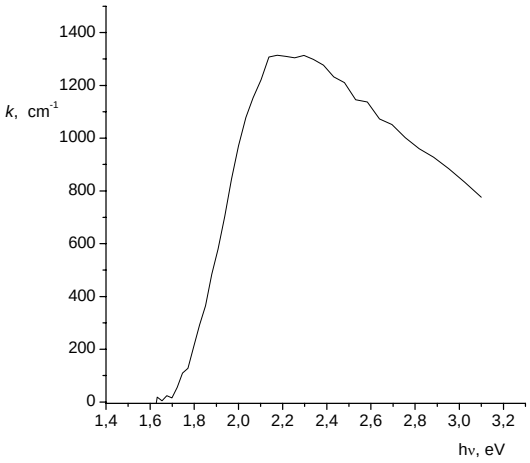

Fig.3 a. Spectral dependence of $k(h\nu)$ for $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$

As it is seen from the figure, at the absorption energy $h\nu \sim\sim Eg$, k strongly increases and achieves the value 10^3sm^{-1}, and in the big energy region its slowly decrease is observed.

The theory of the interband optical transitions [10] shows, that k in the dependence on the photon energy $h\nu$ changes according to the expression:

$$k(h\nu) = A(h\nu - E_g)^r \qquad (2)$$

where h is Plank constant, ν is frequency, A is constant, r is quantity, having values 2,3,1/2, 3/2 in the dependence on the optical transition nature. The obtained results have been analyzed on the base of the theory of the direct transition [9].

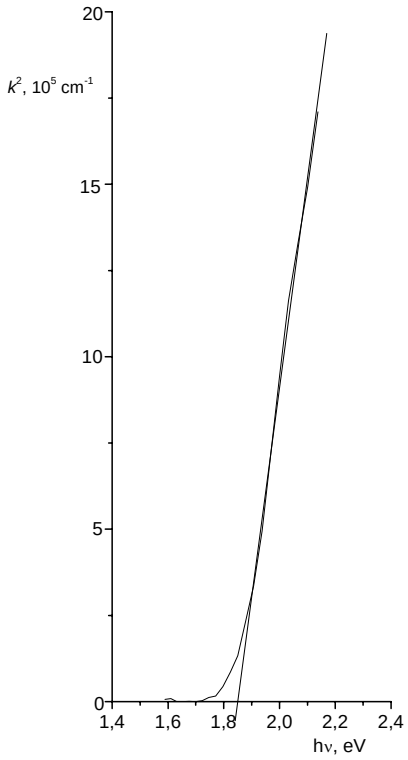

Fig.3 b. Spectral dependence of $k^2(h\nu)$ for $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$

In the region of the longwave absorption edge, the experimental data were given in the coordinates $k^2 \sim h\nu (r=1/2)$ (fig.3,b). It is seen that at the energies $h\nu \geq 1{,}85$eV the k values are well laid on the line in the coordinates $k^2=f(h\nu)$. The line dependence k^2 on $h\nu$ is the evidence that intrinsic absorption edge in the single crystals $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ forms by the direct allowed optical transitions.

The values of the forbidden band width for the direct allowed transition, which are 1,843eV are obtained by the extrapolation of the lines $k^2=f(h\nu)$ to the value k=0.

2.4. Electric properties.

The injection effects have been studied by the way of the investigation of volt-ampere characteristics (VAC) of structures In-$Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ –In (in the sandviche form) in the electric fields till $3 \cdot 10^5$ V/cm in the temperature interval 100÷360K with the aim of the revealing of the charge transition mechanism, definition current carrier movement and their concentrations, trap parameters (activation energy, concentration and e.t.c.) in the single crystals $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$.

The typical VAC for the investigated samples are presented on the fig.4. With the increase of the electric field from $5 \cdot 10^2$ till $3 \cdot 10^5$V/sm, the current changes in the wide interval ($10^{-4} \div 4 \cdot 10^4$A). It is especially seen, that in spite of the big change of the electric field, the ohmity destroys after the 10^5V/sm. Starting from 10^5V/smthe current increases faster and on the VAC line the quarter region is observed.

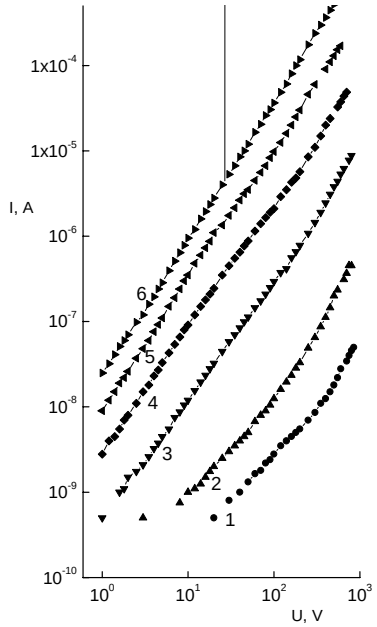

Fig.4. Volt-ampere characteristic of $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ single crystal at temperatures: 1-131K; 2-236K; 3-270K; 4-300K;5-317K;6-340K.

This fact is proved in the graphics of the temperature dependence of the current at the different electric fields (fig.5), including the region of the carrying out of Ohm law and nonlinear region of VAC. It is seen that inclination of the curves 1-3 is the same, but inclination of the curve 4 is slowly decreases.

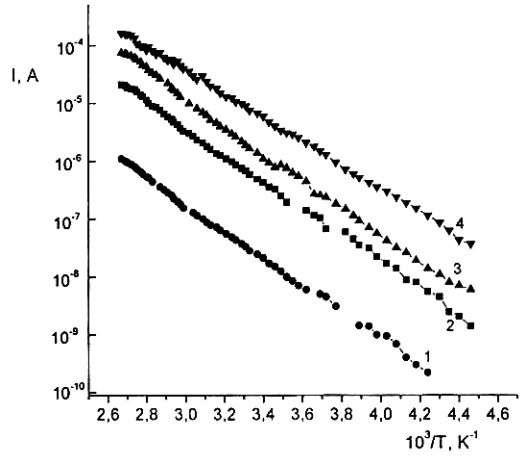

Fig.5. The dependence of $\alpha \sim U$ at T=300 K.

For the clarifying of the current change mechanism in the single crystals $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ in the dependence on the electric current and the temperature, the obtained results were analyzed on the base of the method of injective spectroscopy [11], i.e. power current I dependence on voltage $U(I \sim U^{\alpha})$.

$$\alpha = \frac{d \lg I}{d \lg U} = \frac{U}{I} \frac{dI}{dU} . \qquad (3)$$

Such approach allows to more clearly realize the VAC structure, to fix its special points and to border the injection mode [12-14].

The dependence $\alpha(U,I)$ at the temperature 300K has the one experimental point (α_{min}=0,677 at U_{min}=180V(I_{min}=4,65.10^{-6}A) (fig.6).

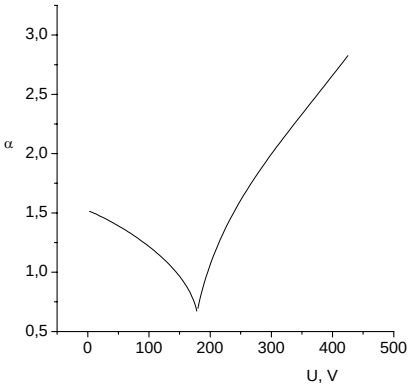

Fig.6

The local levels in the forbidden band (E_t=0,52eV), trapping the injected charge carriers, in the result of which the slow current increase takes place, are defined by the formulae

$$E_t = kT \ln\left[2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} \frac{3(1+\alpha_m)e\mu SU_m}{2\alpha_m^2(5-8\alpha_m^2)LI_m}\right] \quad (4)$$

where

$$2\left(\frac{2\pi m^* kT}{h^2}\right) \approx 10^{19} - \text{“}^{-3}\left(\frac{m^*}{m}\frac{T}{300K}\right)^{3/2} = N_c$$

is the effective state density in the conductivity band, m_n=0,4m_e is the effective mass, h is Plank constant, k is Bolzman constant, T is Kelvin temperature, L is samples thickness, S is contact area.

The definitions of the main carrier movement by formulae (1) (μ=12,56sm^2/V·sec) give the possibility to estimate the initial (I=0) contact concentration of these carriers by the formulae

$$n_{k0} = \frac{\exp\left\{\sqrt{1-\alpha_{\min}}\left(\sqrt{1-\alpha_{\min}}-1\right)\right\}}{1-\sqrt{1-\alpha_{\min}}} \frac{I_{\min}L}{e\mu SU_{\min}} \quad (5)$$

According to [11] VAC approximation

$$V >> |V_k| = \frac{2\pi|\rho_k|L^2}{\varepsilon} \quad (6)$$

(here $|\rho_k| = en_k$ -) is the density module of the space charge of the cathode, V_k is the cathode strength), when the applied shifting is in many times more than volume back strength, caused by the charge(or recombination) barrier in the semiconductor, the approximation Mott-Gerni takes place

$$j = \frac{e\mu n_{k0}}{L}V >> \frac{8\pi e^2 \mu n_{k0}^2 L}{\varepsilon}$$

which is the result of the noncreation of the space charge because of the high value of the field.

In fact, the condition (3) is also the criteria of strength constant of the electric field in the structure. That's why the existence of the sublinear region on the VAC of structure In-$Ga_{0,5}Fe_{0,25}In_{1,25}S_3$-In with $0<\alpha_{min}<1$ degree, characterises the constant field mode on the intercontact layer, which allows to estimate also the transparency of the contact landing barrier Dk^*, its thickness d_k [11-15] and effective high $\Delta\varepsilon = kT\ln\frac{N_c}{n_{k0}}$.

Corresponding to the given formulae, the VAC processing gives the following parameters: n_k=1.55·10^{10}cm^{-3}; D_k^* =2·10^{-2}; d_k=5.6·10^{-9}cm; $\Delta\varepsilon$=0.497eV.

Conclusion.

In conclusion, we note that at the interaction in the system $(GaIn)_{2-x}S_3$-Fe_{1-x} in the difference from the edge consisting phases $GaFeS_3$ and $InFeS_3$, the intermediate phases of the layered structure of polytypes of trigonal modification of $Ga_{0,5}In_{1.5}S_3$ with lattice periods a=3,796, c=12,210A.

The single crystals of the composition $Fa_{0,5}Fe_{0,25}In_{1,25}S_3$ have been grown and it has established that its structure consist on the 3 packets with 3R symmetry with sera atom - *zkkz*. In the result of the statistical occupation of the tetrahedron and octahedron positions, the identification period of the lattice "a" increases in two times and become a=3,786.2, c=36,606Å.

By the crystal analysis it is established, that partial permutation of In and Ga atoms by the trivalent Fe atom, causes the stabilization of the polytype modification form $c=12\cdot n$Å. Besides the changes of Fe atom quantity in the composition give the possibility to control the forbidden band width, as with the increase of Fe atom quantity, the forbidden band width decreases (E_g for $Ga_{0.5}Fe_{0.5}InS_3$ - 1.885eV, where z=5.33 and for $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ -1.843eV, where z=16) in the comparison with the matrix modifications of $GaInS_3$ [16], the forbidden band width of which changes from 2,40 till 2,60eV.

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$Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ LAYLI YARIMKEÇİRİJİNİN ELEKTRİK VƏ OPTİK XASSƏLƏRİ

Brijman metodu ilə $(GaIn)_2S_3$–Fe sisteminin aralıq fazası olan $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ monokristalı yetişdirilmişdir. Monokristallar rombogdrik simmetriyalı təbəqəli quruluşa malikdir və qəfəsin periodu a=3.786x2, s=36.606 E, pr.qr. R3m, z=16.
Fotonların geniş intervalı üçün optik udulmanın kənarı tədqiq olunmuş və $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$ üçün qadağan olunmuş zolağın eni təyin olunmuşdur.
In- $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$-In strukturu düzəldilmiş və onun volt-amper xarakteristikası və 100÷360K temperatur intervalında temperatur asılılığı öyrənilmişdir. Differensial analiz metodu ilə göstərilən strukturun parametrləri təyin olunmuşdur: μ=12.56 sm^2/V sek, n_k=1.55 10^{10} cm^{-3}; D_k^* =2 10^{-2}; d_k =5.6 10^{-9} sm; $\Delta\varepsilon$=0.497 gV.

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ЭЛЕКТРИЧЕСКИЕ И ОПТИЧЕСКИЕ СВОЙСТВА СЛОИСТОГО ПОЛУПРОВОДНИКА $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$

Методом Бриджмена из расплава выращены монокристаллы промежуточной фазы системы $(GaIn)_2S_3$–Fe состава $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$. монокристаллы слоистые, симметрия ромбоэдрическая, периоды решетки в гексагональной установке a=3.786x2, c=36.606 Å, пр.гр. R3m, z=16.

Исследован край оптического поглощения в широком интервале энергии фотонов и определены ширины запрещенной зоны E_g =1.843 эВ для $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$.

Изготовлено структура In- $Ga_{0.5}Fe_{0.25}In_{1.25}S_3$-In и изучено его ВАХ и температурный зависимость в интервале температур 100÷360К. Методом дифференциального анализа вычислены параметры указанной структуры: μ=12.56 $см^2$/В сек, n_k=1.55 10^{10} $см^{-3}$; D_k^* =2 10^{-2}; d_k=5.6 10^{-9} см; $\Delta\varepsilon$=0.497 эВ.

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