

The Growth of Single Crystals of InGaSe₂ Compounds, Their X-Ray-Phase Analysis, Electronic Structure and Optical Functions

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ABSTRACT

Growing of InGaSe₂ single crystals has been carried out by employing the Brijman-Stockbargor methods. On the base of X-ray-analysis it has been found that the given phase is crystallized into tetragonal symmetry. The temperature dependence of electric conductivity has been studied. Band structure has been computed. Optical functions, effective masses of electrons and holes have been calculated. Origin of formation of valence and conductance bands as well as the width of forbidden band for InGaSe₂ have been determined.

Keywords: Band Structure; Optical Functions; InGaSe₂

1. Introduction

During last years great quantity of works has been devoted to the study of $A^{111}B^{V1}$ type semiconductor compounds that is related with interest to their specific physical properties. A nature of chemical bonds in these compounds causes specific features as layered and chain structure which are important from both fundamental and technological points of view. In particular, layered semiconductors create rising interest with their possible optoelectronic application [1]. Chain compounds of this type possess higher coefficients of photo- and tensile-sensitivity as well as the switching properties with memory [2-5]. Their two-dimensional structural anisotropy as well as the specific optical and photoelectric properties attract researchers working for successfully learning of the processes occurred in these compounds.

The $A^{111}B^{111}C_2^{VI}$ type chalcogenides are representatives of layered and chain $A^{111}B^{V1}$ type semiconductors. Although, in latest years the ternary semiconductor chalcogenides are intensively studied, however a negligible number of papers have been devoted to the study of InGaSe₂ and InGaSe₂ [6-10]. Similarly to other semiconductor compounds these materials may have large range of application broadening from the use in solar elements up to nonlinear optical systems. In addition, they may easily intercalated by impurity ions, atoms and molecules assuming real predictions for development of the monitored super-lattices on their basis.

First X-ray structural researches showed the InGaSe₂

like other representatives of $A^{111}B^{111}C_2^{VI}$ type compounds possess tetragonal structure [11]. In more latest researches these crystals were considered to be in monoclinic symmetry [10], at the same time information was given about multi-type modifications with other crystalline structures. In this connection a structure of single crystal of InGaSe₂ has been investigated in detail, the HRTEM electron diffraction of selected region (SAED) has been carried out. In these investigations was used the HF-200 TEM equipped with emitting-field gun. To obtain the images of back scattering of electrons which is observed upon chemical contrast between phases with different chemical compositions the Cambridge S-100 SEM was used [10].

The present paper is devoted to the growth of single crystals of InGaSe₂ compounds, their X-ray-phaseanalysis, investigation the electro-conductivity, computation the band structure and optical functions.

2. The Experimental Method

The single crystals of InGaSe₂ have been undergone to growth by the Brijemena-Staockbarger method. The double-wall quartz ampoules with evacuated external part were used for minimization of the convection effects. First, ampoules were cleaned by use the mixture of fluoric acid and distilled water (with volume proportion 1:3) and then with pure alcohol. After performance of the chemical purification the evacuated ampoules were put into dryer at 1000°C for 12 hours. After dehumidification

under 1000°C temperature the ampoules were cooled and filled with highly cleaned elements in stoichiometric proportions.

To reduce the risk of explosion of ampoule the blend was slowly heated (with speed of 0.5°/minute) from temperatures 200°C - 250°C. The melt was kept under 950°C temperature during 48 hours for obtaining homogeneous. Then the furnace was undergone to cooling with speed of 0.6 mm/hour with replacement from hot place to colder one with 350°C.

After obtaining of the single crystals they were undergone to the X-ray-phase analysis after their obtaining. Decoding of diffractogram of InGaSe₂ showed that the given phase is crystallized into tetragonal symmetry with lattice parameters $a = 8.0138 \text{ \AA}$ and $c = 6.953 \text{ \AA}$. Diffractograms are shown in **Figure 1**, results of X-ray-phase analysis are given in **Table 1**.

For analysis of the electric properties the samples of single crystals were obtained from large pieces (sizes of 2.2 mm × 1.0 mm × 1.0 mm) by cutting with diamond knife. The process of polishing with rotary disk was nec-

essary for obtaining the bulk samples with parallel surfaces. To obtain the best polishing process the mixture of 1 mm α -aluminum and 0.005 mm β -aluminum were used. After polishing the samples were washed in pure ethyl alcohol then twice in distilled hot water. Then the samples were put for dehumidification without any thermal processing. Accurate determination of the sizes of sample that is needed for exact calculation of the electric properties has been carried out by optical microscope.

3. Results and Discussions

By use the thermoelectric energetic graduation we observed that the investigated samples demonstrate the p-type conductivity. Temperature dependence of conductivity was measured in the 300 - 900 K temperature range. Note that, up to present paper the studies of temperature dependence for electric resistivity of InGaSe₂ single crystal have been carried out in the temperature range of 4.2 - 300 K. The results indicate exponential character of dependence in agreement with relationship $\exp(-E/kT)$ where k is the Boltzmann constant, E refers to the activation energy. Thermal energy of activation for majority carriers (holes) is 51.8 meV. The resistivity of $\rho = 1.51 \times 10^{-3} \Omega \cdot \text{cm}$ was measured at a room temperature.

In the present paper the temperature dependence of electric conductivity of InGaSe₂ has been investigated in the temperature range of 300 - 900 K. From results presented in **Figure 2** it follows that in the investigated range of temperature the electric conductivity increases with temperature. Width of forbidden gap determined from the high-temperature slope of temperature dependence for this phase is in good agreement with that one calculated on the basis of band structure of InGaSe₂.

Width of forbidden gap determined from the high-temperature slope of temperature dependence for this phase is in good agreement with that one calculated on the basis of band structure of InGaSe₂. In this paper the band spectrum has been studied, the genesis of electron states was determined and optical functions have been calculated for InGaSe₂ crystal. We have carried out calculation of the electron states on the basis of theory of functional of local electron density. For this aim the method of pseudo-potential was employed on the basis of plane waves. Nonlocalized pseudo-potentials were constructed according to the diagram presented in [12]. Screening of ion pseudo-potential was made through the function given by Khabbard and Shem [13]. In expansion of wave function of electrons 3800 plane waves have been used. Calculation was made at symmetrical points Γ , T , N , P as well as over the lines connecting them.

The lattice's parameters are determined through minimization the ionic energy and the structural parameters are optimized by use the Gelman-Feynmann forces. The

Table 1. Results of X-ray-phase analysis of InGaSe₂.

θ	d_{ex} (Å)	d_{cal} (Å)	hkl	J/J_0
12°56'	4.0015	4.0019	200	6
12°2'	3.1750	3.1801	211	100
15°48'	2.8321	2.8317	220	13
17°4'	2.6364	2.6275	202	17
17°42'	2.5338	2.5360	310	14
24°21'	1.8679	1.8724	411	40
27°39'	1.6614	1.6592	332	36
34°7'	1.3785	1.3746	530	8
49°53'	1.1780	1.1780	532	10

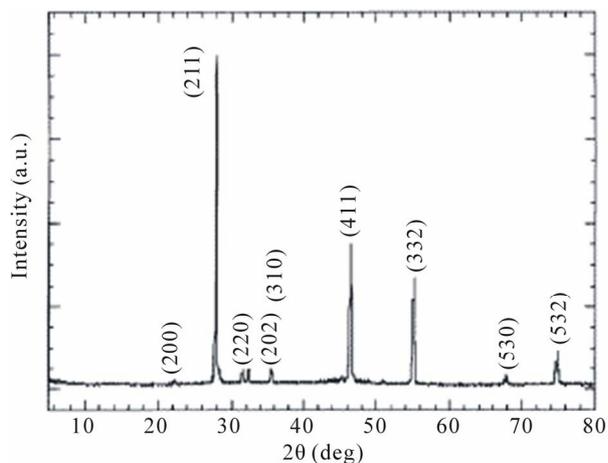


Figure 1. Diffractogram of InGaSe₂ single crystal.

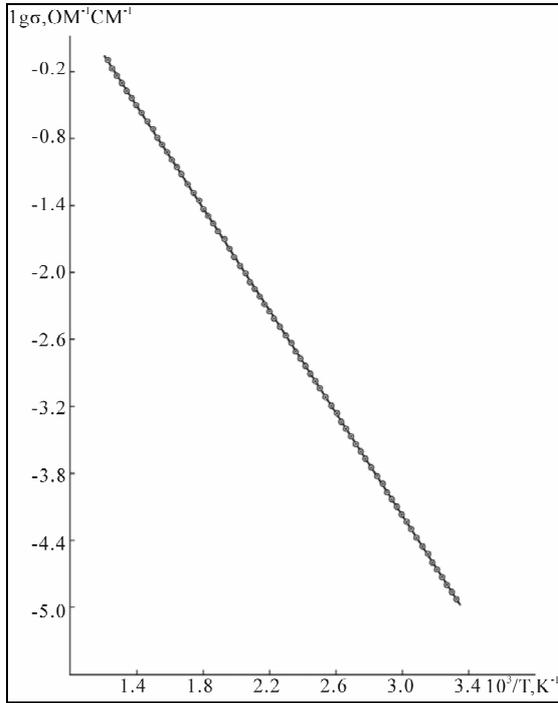


Figure 2. Temperature dependence of electric conductivity for InGaSe₂ single crystal.

minimization process was occurred providing condition $|F| < 3 \frac{mRy}{a.u.}$. For the lattice and chalcogen the optimized parameters are $a = 8.0138 \text{ \AA}$, $c = 6.953 \text{ \AA}$ and $x = 0.1720$ respectively.

The table of unreduced and binary unreduced representations of wave vector groups for space group D_{4h}^{18} were obtained in [14]. Here also are demonstrated condition of agreement between unreduced representations of simple groups and double-value group D_{4h}^{18} and view of Brillouin zone for volume-centered tetragonal lattice. The band spectrum of InGaSe₂ is presented in **Figure 3**. Where the top of valence band was taken as the ground energy. The main feature of valence zone is that it consists of three pronounced sub-bands separated by forbidden values of energy. The lower sub-band consisting of four zones is about $-10/(-11) \text{ eV}$ and apart from others by wide energy gap of order -6 eV . Results of theoretical-group analysis carried out by use of the symmetry properties of InGaSe₂ crystal show that these valence bands are obliged with their origin to 5 s states of Se. Next group located in energy level near -5 eV consists of four valence bands originated from s-states of In and Ga atoms. The top subzone consisting of ten bands of $\approx 5 \text{ eV}$ width is originated from p-states of In, Ga and Se atoms.

In [10] the X-ray photoemission spectrum of valence band of InGaSe₂ is demonstrated. Experimentally was shown that photoemission spectrum consists of three more pronounced regions. The observed peaks about

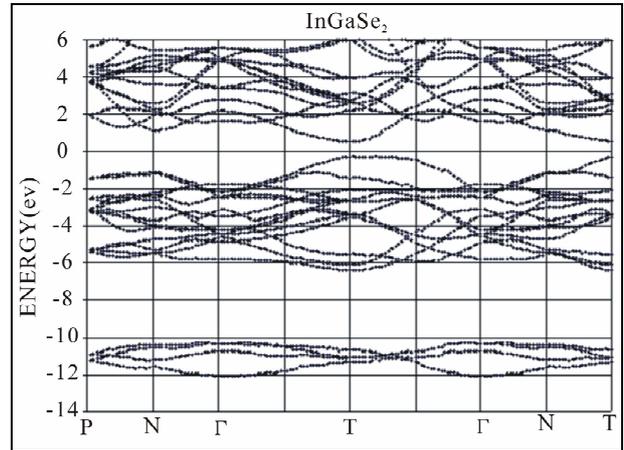


Figure 3. Band structure of InGaSe₂ compound.

-13.5 eV and -4 eV correspond to s-states of Se and Ga-Se bonds respectively. Complex of features about $-5/0 \text{ eV}$ corresponds to both Ga-Ga and Ga-Se bonds that is in a good agreement with our band spectrum calculations and theoretical-group analysis.

Top of valence band as well as the bottom of conductivity band are located at point *T* with high symmetry on the surface of Brillouin zone and lower energetic transition occurs at this point. Other minimum of conductivity band is located at high symmetrical point *N*. For the width of forbidden band our calculations gives 0.95 eV and extremity of fundamental absorption is originated by direct transitions.

Optical functions for InGaSe₂ were calculated by known method given in [15]. For determination the spectral dependence of imaginary part of complex dielectric constant we have used relationship

$$\varepsilon_i(E) = \frac{N}{E^2} \sum_{k \in BZ} \sum_{v,c} |\mathbf{e} \cdot \mathbf{M}_{cv}(\mathbf{k})|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - E) \quad (1)$$

here integral

$$\mathbf{e} \cdot \mathbf{M}_{cv}(\mathbf{k}) = \mathbf{e} \cdot \int \psi_{ck}^*(\mathbf{r})(-i\hbar\nabla)\psi_{vk}(\mathbf{r})d^3r.$$

is taken over the volume of elementary cell of crystal and indicates matrix element of operator of linear momentum $p = -i\hbar\nabla$; indices *v* and *c* numerate the states of valence and conductivity bands respectively; *e* indicates unit vector of polarization. During summation over the Brillouin zone the elementary cell of inverse lattice was divided into 64 parts of equal volumes and *k*-points were randomly selected in them. Totally were taken 3000 points and those gave continuously (regular) histogram. Constant *N* is determined from condition of normalization of histogram

$$\int_0^\infty E \varepsilon_i(E) dE = \frac{\pi}{2\hbar^2} \omega_p^2 = \frac{\pi}{2\hbar^2} \cdot \frac{4\pi n_e e^2}{m_e}$$

where ω_p refers to plasma frequency of electrons and n_e indicates mean density of electrons in crystal.

Histogram was plotted with step of 0.2 eV and covered all transitions between zones $\nu \rightarrow c$ with energy up to 12 eV. Starting from small structure in histogram about 12 eV dependence $\varepsilon_i(E)$ was extrapolated according to formula $\varepsilon_i(E)_{E \rightarrow \infty} \approx E^{-3}$. Transitions from most lower bands having Se-5s origin as can be seen partially are found within the range of investigated spectral region. These bands are located far and as our studies show, broadening of spectral region and thus involves high energetic transitions from these bands into upper states of conductivity band does not give to dielectric constant significant contribution distinguished from extrapolation. Real part of dielectric constant was determined from Kramer-Kronig integral dispersion relation

$$\varepsilon_r(E) = 1 + \frac{2}{\pi} P \int_0^{\infty} E' \varepsilon_i(E') \cdot \frac{dE'}{E'^2 - E^2} \quad (2)$$

where P indicates the integral of principal meaning. Results of spectral functions calculations of InGaSe₂ compounds are given for $e//c$ and $e \perp c$ polarizations in **Figures 4** and **5** respectively. As can be seen from **Figure 4** calculated curves rapidly rise up to maximum. According to these figures maximum in the $\varepsilon_r(E)$ spectrum upon polarizations.

However in the $\varepsilon_i(E)$ spectrum for both polarizations maximum of main fringe which is related to transitions from upper part of valence zone to downer part of conductivity zone corresponds to 3.5 eV energy. For $e \perp c$ type polarization in the $\varepsilon_i(E)$ four additional peaks of 4.25 eV, 5.55 eV, 5.95 eV and 6.45 eV energies have been found. In the case of $e//c$ type polarization additional peaks are weak and located at energies 4.05 eV, 5.08 eV and 5.75 eV.

Maximum value of ε_i upon $e//c$ and $e \perp c$ polarizations are 24.9 and 14.95 respectively and such a difference belongs to chain InGaSe₂ crystals with high ani-

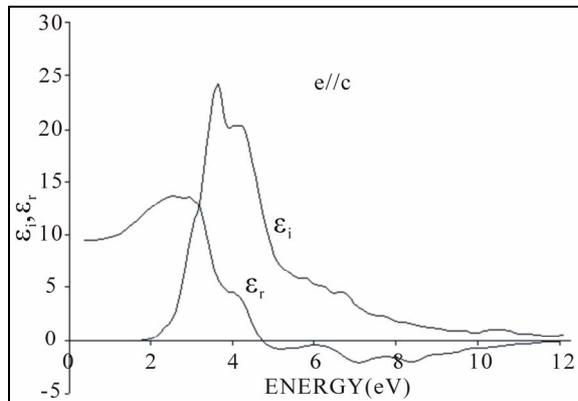


Figure 4. Spectral dependence of imaginary (ε_i) and real (ε_r) parts of dielectric constant of InGaSe₂ compound in the case of $e//c$ polarization.

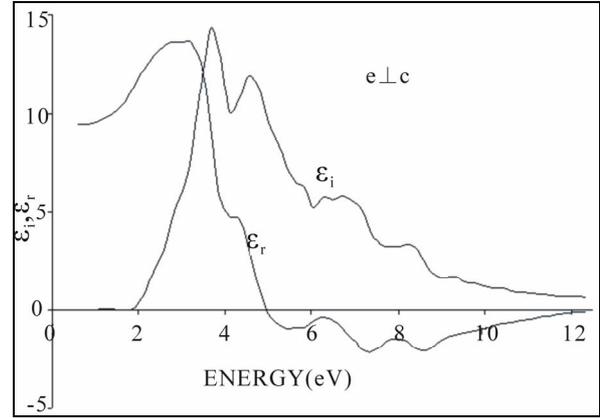


Figure 5. Spectral dependence of imaginary (ε_i) and real (ε_r) parts of dielectric constant of InGaSe₂ compound in the case of $e \perp c$ polarization.

sotropy. Limit values of $\varepsilon_r(E=0)$ are obtained as 9.5 and 9.1 upon $e//c$ and $e \perp c$ type polarizations respectively.

Components of tensor of inverse effective mass were determined by the formula m_0 is the resting mass of electron; δ_{ij} refers to Kroneker symbols; $\langle n_1 k_0 | P_i | n'_1 k_0 \rangle$ is the matrix element of operator of linear momentum

$P_i = -i\hbar \frac{\partial}{\partial x_i}$ at the extreme point k_0 for n and n' electron zones; $||n_1 k_0\rangle\rangle$ is the wave function of electron

$$\langle n_1 k_0 | P_i | n'_1 k_0 \rangle = \frac{1}{\lambda} \int \varphi_{n k_0}^*(r) P_i \varphi_{n' k_0}(r) d^3 r$$

λ refers to volume of elementary cell Energetic spectrum and $E_n(k_0)$ and appropriate wave function $\varphi_{n k_0}(r)$ at extreme point k_0 is determined from the Schrodinger single electronic equation

In the basis of plane waves

$$\sum_{G'} \left[\frac{\hbar(k_0 + G')}{2m_e} \delta_{GG'} + V(k_0 + G_1 k_0 + G') \right] \varphi_n(k_0 + G') = E_{n k_0} \varphi_n(k_0 + G) - V(k_0 + G_1 k_0 + G')$$

$v(k)$ is the Fourier view of crystalline pseudo-potential.

Calculation of InGaSe₂ zone structure shows that both maximum of valence and minimum of conductivity zones are located at point T of high symmetry $k_0 = 0.5b_1 - 0.5b_2 + 0.5b_3$. Here b_1, b_2, b_3 are basis translations of inverse lattice.

In our calculations components of tensor of inverse effective mass of electron were measured with an accuracy to 0.01 m_0 .

$$\begin{pmatrix} m_0 \\ m_e^* \end{pmatrix} = \begin{bmatrix} 2.32 & 0 & 0 \\ 0 & 2.32 & 0 \\ 0 & 0 & 2.95 \end{bmatrix}$$

Tensor components of inverse effective mass of holes is given by

$$\begin{pmatrix} m_0 \\ m_n^* \end{pmatrix} = \begin{bmatrix} 2.23 & 0 & 0 \\ 0 & 2.23 & 0 \\ 0 & 0 & 0.32 \end{bmatrix}$$

As can be seen tensors of inverse effective mass of both electrons and holes have diagonal view and therefore isoenergetic surfaces are described by rotational ellipsoids that is correspond to symmetry of InGaSe₂ crystal. Please do not revise any of the current designations.

4. Conclusion

Growing of single crystals, their X-ray-phase analysis, investigation of the temperature dependence of electric conductivity and determination of the width of InGaSe₂ forbidden band have been carried out. The electron structure was computed in the range of theory of functional of local electron density by employing the method of pseudopotential on the base of plane waves. Origin of valence and conductivity bands and width of forbidden band for InGaSe₂ have been determined. Real and imaginary parts of dielectric constant were calculated for the polarizations $e//c$ and $e \perp c$ in the energy range of (0 - 12) eV. Also effective masses of electrons and holes for InGaSe₂ were calculated.

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