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Optical Properties of Tlinse2<Au> Single Crystals

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Abstract: - This paper presents the results of studying the surface microrelief in 2D and 3D models and analyzing the spectroscopy of a three-junction TlInSe2<Au> crystal. Analysis of the results obtained showed that with a change in the composition of the TlInSe2<Au> crystal, sharp changes occur in the microrelief of its surface. An X-ray optical diffraction analysis of the TlInSe2<Au> crystal was experimentally carried out. Based on ellipsometric data, optical functions were determined - the real and imaginary parts of the dielectric permittivity of crystals, the coefficients of optical absorption and reflection, the dependence of energy losses and electric field power on the effective density, the spectral dependences of the real (σr) and imaginary (σi) parts, optical electrical conductivity were experimentally studied. The fluorescence spectra of the ternary compound TlInSe2<Au> were isolated and analyzed when excited by light with a wavelength of 532 nm. X-ray studies of TlInSe2<Au> showed that this phase crystallizes into tetragonal systems. Ellipsometric measurements showed that the real (ε1) and imaginary (ε2) parts of the dielectric constant are components of the dielectric constant tensor of the uniaxial joints under consideration and do not depend on the angle. Analysis of the dependence of the real and imaginary parts of the refractive index of the TlInSe2<Au> crystal on photon energy showed that the nature of the change in the real and imaginary parts of the dielectric constant does not differ significantly. When analyzing the spectral dependences of the real (σr) and imaginary (σi) parts of the optical electrical conductivity, it was noticed that the real part of the optical electrical conductivity increases exponentially in the energy range 0.894-3.505 eV. In the energy range of 0.654-2.91 eV, the imaginary part of the optical electrical conductivity increases linearly, reaches a maximum value, and decreases at an energy of 2.91 eV. At 3.6 eV, an inversion of the imaginary part of the optical electrical conductivity of the TlInSe2<Au> compound is observed. From the graphs of the effective power density versus electric field energy losses, it is known that the effective power density increases significantly in the energy range of 0.805–3.52 eV. The fluorescence spectrum of the ternary compound TlInSe2<Au> upon excitation with light with a wavelength of 532 nm has been studied and it has been established that this phase has luminescent properties.

Keywords: Optical properties of TlInSe2, tetragonal systems, real and imaginary dielectric permittivity, real and imaginary optical electrical conductivity.

I. INTRODUCTION

The study of the crystal structure of the TlSe compound is of particular importance. The thallium atoms in this binary compound have a different crystal structure. The main properties of this compound are determined by trivalent (Tl^{+3}) thallium atoms located in tetrahedra. Based on those real experimental results, a new class of $A^{III}B^{III}C_2^{VI}$ type triplet compounds was discovered by partially replacing trivalent Tl atoms with trivalent In^{+3} and atoms in the TlSe compound. The study of both the structures and physical properties of this type of crystals has shown that some of those compounds have a layered, and some have a chain crystal structure.

$A^{III}B^{III}C_2^{VI}$ type ternary compounds [1] attract the attention of researchers due to their promising application in electro-optical, optoelectronic, and linear optical devices. These compounds are characterized by optical anisotropy, birefringence, significant coefficients of nonlinear susceptibility, high photosensitivity, high strain sensitivity, bright luminescence, switching ability with memory, etc. The presence of these properties in combination with a significant band gap makes these crystals a promising material for solving practical problems [2,3]. Therefore, the study of the physical properties of compounds of the above type is an urgent task. Among the compounds of the above type, $TlInSe_2$ occupies a special place. This compound has high tensoresistive properties [4], high photosensitivity [5], switching properties with memory [6–9], etc. The electrical and photoelectric properties of $TlInSe_2$ single crystals were studied in [10, 11, 12]. As a result of these studies, the prospects of these crystals as receivers of near-IR and X-ray radiation were established. The effect of iso- and heterovalent active substitutions on the physical features of $TlInSe_2$ has been studied. It has been found that when exposed to sunlight, the n-*Si*- p-$TlInSe_2$ heterojunctions generated a photo-emf of up to 100 mV and a short-circuit current of 200 μA/cm^2. Current-voltage characteristics were studied in [13]. It has been established that $TlInSe_2$ and solid solutions based on it have

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switching properties with memory [14-16]. In [17,18], the results of studying the acoustophotovoltaic effect in $TlInSe_2$ and solid solutions based on it were presented. The band structure was studied in [19-21]. It is shown that the valence band can be conditionally divided into three groups. The lowest one with four bands near 12.6 eV owes its origin to the *4s* states of *Se*. Another group of four bands in the 4÷5.5 eV region is mainly due to *6s* states of *Tl* atoms and *5s* states of *In*. The upper group of ten bands in the region 0÷3.5 eV is mainly formed from *4p* states of *Se* atoms, *6p* states of *Tl* atoms and *5s* states of *In* atoms. Thus, the analysis of published data shows that the $TlInSe_2$ compound occupies a special place among the $A^{III}B^{III}C_2^{VI}$ compounds. This paper presents the results of an experimental and theoretical study of the optical properties of the $TlInSe_2$<*Au*> compound. It was found that $TlInSe_2$ compounds crystallize in the tetragonal syngony.

II. Experimental Part

Single crystals of $TlInSe_2$ were obtained by zone melting and Bridgman–Stockbarger method. X-ray diffraction studies were carried out on a Bruker 2D-Phaser X-ray diffractometer. The crystals were characterized by X-ray diffraction methods [22,23].

Raman scattering and luminescence spectra were studied on a three-dimensional confocal Raman microspectrometer Nanofinder 30 (Tokyo Instruments), excitation wavelength λ=532nm. The cross-sectional radius of the laser beam incident on the crystal was 4 μm. The studies were carried out in backscattering geometry. The radiation receiver was a cooled CCD camera (-70 ^{0}C) operating in the photon counting mode. All measurements were made at an exposure time of 20sec and excitation power of 10mW. The accuracy of determining the position of the spectral line was no more than 0.5 cm^{-1}. Ellipsometric studies were carried out using a JAWoollam M2000 DJ spectroscopic ellipsometer at room temperature. To study the optical parameters of the ternary compound $TlInSe_2$ with *Au* impurities, we carried out spectral ellipsometric studies, which are a highly sensitive and accurate optical method for studying the surfaces and interfaces of these media. This method is based on studying the change in the state of polarization of reflected light after its interaction with the surface of the interfaces between these media. The basic equation of ellipsometry, which relates the ellipsometric parameters and the complex values of the Frenkel reflection coefficients r_p and r_s p and s components of elliptically polarized light, is written in the form [24-27], the results of an ellipsometric study and calculation of the dielectric functions of $TlInSe_2$<*Au*> are given on the figures.

III. Results And Discussion

X-ray study of $TlInSe_2$<*Au*> showed that this phase crystallizes in the tetragonal syngony, unit cell parameters a=8,02 A°, c=6.83 A°, etc. Symmetry group I4/mcm=D_{4h}^{18}. The X-ray diffraction pattern of this phase is shown in Fig.1.

Spectroscopic ellipsometry is the main methodology recognized in the world as a global standard for the study of permittivity [28,29]. Unlike well-known and long-used techniques for measuring the intensities of reflected or transmitted light, the ellipsometric approach uses the polarization state of light. The measurement was carried out in the photon energy range from 0.7 to 6 eV. The permittivity ($\varepsilon = \varepsilon_1 + i\varepsilon_2$),where the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the permittivity, extracted from ellipsometric measurements, did not depend on the angle and corresponded to the component $\vec{E} \perp \vec{C}$ ($\vec{E}$ is the electric vector of the incident light, $\vec{C}$ is the optical axis) of the permittivity tensor of the considered uniaxial joints. The angles of incidence of light for measurements varied from 60° to 75° with a step of 5°. The obtained values of the permittivity were practically independent of the angle. The real and imaginary parts of the permittivity for $TlInSe_2$ <*A*> are shown in Fig.2. The imaginary part of the permittivity has a direct dependence on the distribution of the density of states for optical transitions.

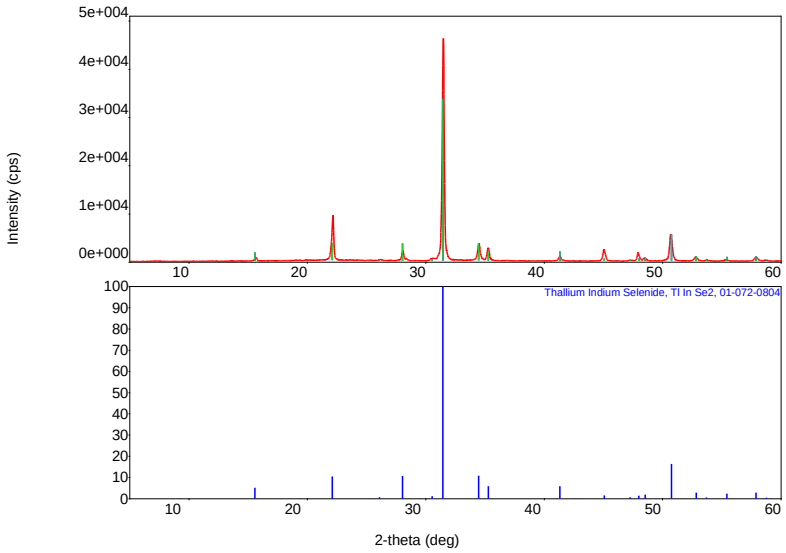

Fig.1. X-ray pattern of *TlInSe₂ <Au>*

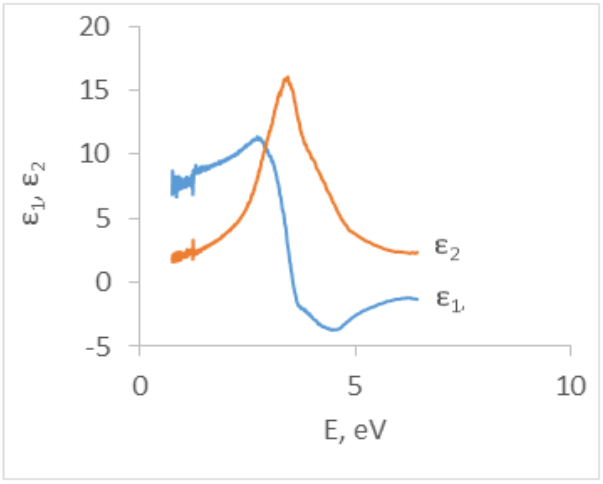

Fig. 2. Real and imaginary parts of the permittivity of *TlInSe₂<Au>*

Figure 3 shows the photon energy dependence of the real and imaginary parts of the refractive index *TlInSe₂<Au>*, which are related to the dielectric function by the following expressions $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$. As can be seen, the nature of the change in the imaginary and real parts of the permittivity does not differ significantly, i.e. at relatively low energies ε_r, both ε_i increase, reaching their maximum value, ε_r at an energy of 2.64 eV (11.06), $\varepsilon_i$at an energy of 3.42 eV (16), and then decrease with increasing energy, significant deviations in the dependences $\varepsilon_r(E)$ are $\varepsilon_i(E)$not observed. Based on the values of the real and imaginary parts of the permittivity, the real and imaginary parts of the refractive index of *TlInSe₂<Au>* were determined. The principal refractive index (*n*) is given by

$$n = \sqrt{\frac{1}{2}(\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2})}$$

and the imaginary part of the refractive index (*k*) is given by

$$k = \sqrt{\frac{1}{2}(-\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2})}.$$

Dependence n(E) begins n (0.79) = 2.68 and reaches its maximum value (3.53) at an energy of 2.74 eV. Then, with increasing energy, it decreases to n (0.83) at an energy of 6.44 eV (Fig.3).

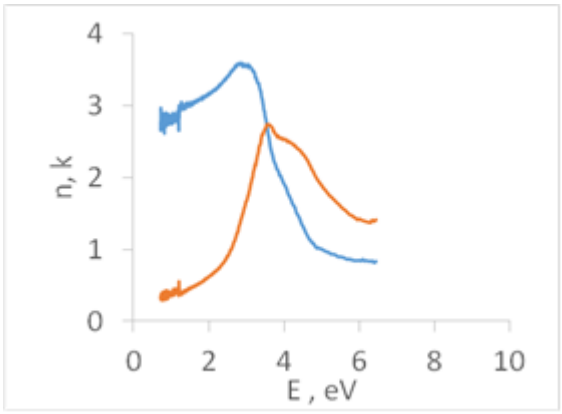

Fig. 3. Refractive indices *n* and extinction *k* for *TlInSe₂<Au>*

As follows from the spectral dependence, k(E) starts from an energy of 0.67 eV, then the imaginary part of the refractive index increases, reaching its maximum value at an energy of 3.50 eV (2.66), a smeared maximum is observed at an energy of 4.11 eV (2.493), then k(ω) decreases to 1.41 at an energy of 6.44 eV.
The results of calculating the optical absorption of *TlInSe₂<Au>* are determined by the formula

$$\alpha(\omega) = \frac{2}{c}\omega k(\omega)$$

The calculation results are shown in Fig.4.

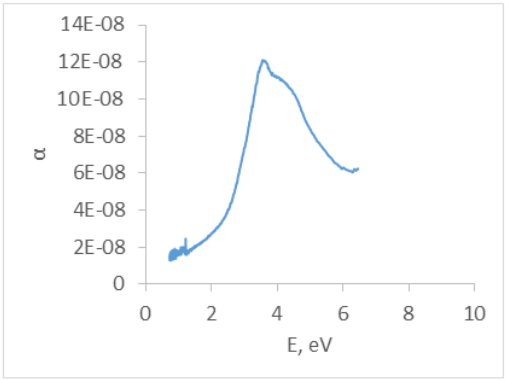

Fig. 4. Optical absorption spectrum α for *TlInSe₂<Au>*.

As follows from Fig. 4 $\alpha(E)$, starting from the energy of 1.92 eV to 3.74 eV, it increases almost linearly, reaching its maximum value (1.85) at an energy of 3.74 eV, then at an energy of 4.1 eV a diffuse minimum is observed.
The frequency dependence of the reflection coefficient is determined by the formula

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

and is shown in Fig.5. As follows from Fig. 5, the frequency dependence of the reflection coefficient has an almost similar character, i.e. in the energy range of 1.5-3.72 eV, the reflection coefficient increases from 0.479 to 4.736, at an energy of 3.832 a deep minimum (0.479) is found, then up to an energy of 4.736 eV R increases to a value of 0.502, and with a further increase in energy to 6.294 eV it monotonically decreases up to 0.363.

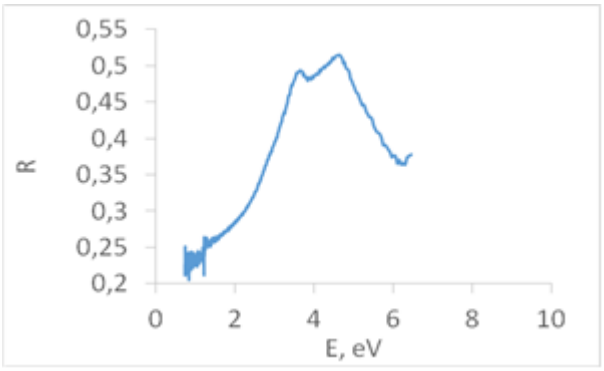

Fig. 5. Spectrum of optical reflection of *TlInSe₂<Au>*compound.

The characteristic function of electron energy losses is determined by the formula

$$Im(-\varepsilon^{-1}) = \frac{\varepsilon_i}{\varepsilon_r^2 + \varepsilon_i^2}$$

and the effective density of states is determined by the formula

$$g_{eff}(\omega) = \varepsilon_i(\omega) \cdot (\hbar\omega)^2$$

Changes in *TlInSe₂<Au>* compound's effective density of states are shown in Fig.6.b, from which it follows that in the energy range 0.805–3.52 eV, a strong increase in the effective density of states of the *TlInSe₂<Au>* compound is observed, reaching its maximum value at an energy of 3.52 eV. Further, a decrease in the density of states of *TlInSe₂<Au>* to an energy of 6.44 eV is observed, and an insignificant response is observed at an energy of 4 eV. With a further increase in energy to 4.91 eV, a strong decrease is observed. In the energy range of 4.91-5.95 eV, a relatively weak decrease is observed, and in the energy range of 5.95-56.44 eV, a slight increase is observed.

The spectral characteristic of the imaginary part of the reciprocal of the complex permittivity is shown in Fig. 6a. As follows from Fig. 6a, no deviations are observed on Im(-ε^{-1}). Im *(-ε^{-1})* increases in the energy range of 0.76-6.397 eV from 0.028 to 0.337.

The real and imaginary parts of the optical electrical conductivity of *TlInSe₂<Au>* are determined using the following formulas

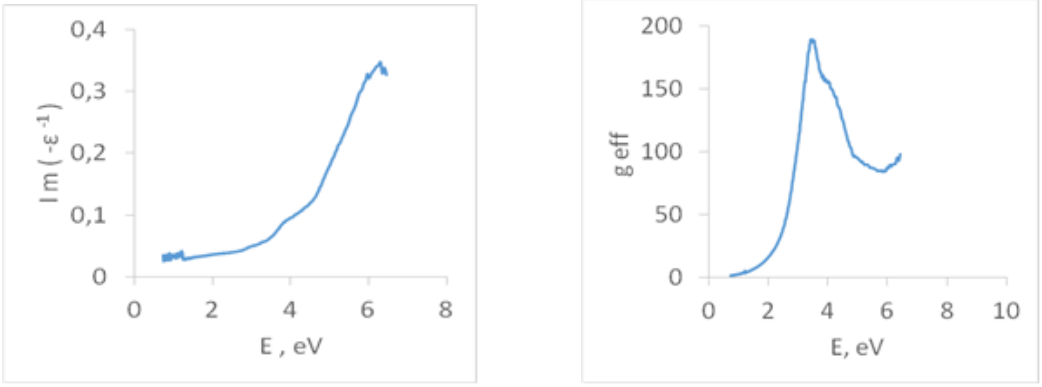

Fig.6. Dependence of the characteristic function of energy losses (a) and effective density of states *(b)* for *TlInSe₂<Au>*

$\sigma_r = \frac{\omega\varepsilon_i}{4\pi}$, $\sigma_i = -\frac{\omega\varepsilon_r}{4\pi}$

The results of calculating the real and imaginary parts of the optical electrical conductivity are shown in Fig.7. As follows from Fig.7, the real part of the optical electrical conductivity in the energy range 0.894-3.505 eV increases exponentially (curve 1). Reaching its maximum value (4.022) at an energy of 3.505 eV, it decreases to 6.449 eV (1.143).

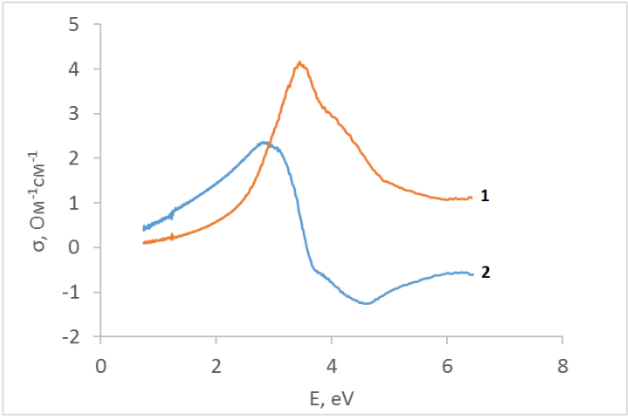

Fig. 7. Spectral dependence of real (σ_r)-1 and imaginary (σ_i)-2 parts of the optical electrical conductivity of the *TlInSe₂<Au>* compound

The imaginary part of the optical electrical conductivity (curve 2) in the energy range 0.654-2.91 eV increases linearly, reaching its maximum value, decreases at an energy of 2.91 eV, and at 3.6 eV an inversion of the imaginary part of the optical electrical conductivity of the *TlInSe₂<Au>* compound is observed. Subsequently, there is a slight decrease σ_i in the range of 3.81-4.65 eV, with a further increase in energy to 6.449 eV, a slight increase in the imaginary part of the optical electrical conductivity is observed.

The fluorescence spectra of the ternary compound *TlInSe₂<Au>* were studied. A characteristic feature of the fluorescence spectrum is a strong separation of the chemical composition of the sample into elementary structure and processes associated with other dynamic changes in the sample.

The fluorescence spectrum has a small-time range of 10^{-8} sec. after absorbing light. During this time, the processes are completed at the molecular level. In the fluorescence spectrum, radiation, energy transfer, as well as the exchange of charges and energies between the components are reflected in short-term dynamic processes. All this is reflected in the study of the optical properties, structural features of the material, and in the processes detected by light streaks in narrow luminescence bands. The luminescence spectra were studied in the ternary compound *TlInSe₂<Au>*. The spectra were obtained by excitation of *TlInSe₂<Au>* with light with a wavelength of 532 nm. As can be seen from fig. 8 *TlInSe₂<Au>* has peaks at 625 and 650 nm. Both of these peaks are pronounced.

Analyzing the research results, we can conclude that in *TlInSe₂<Au>* sharply pronounced luminescence spectra are obtained. This allows us to conclude that the ternary compound *TlInSe₂* doped with *Au* has bright luminescent properties and is a promising material for solving practical problems.

IV. Conclusion

Using the X-ray diffraction method and based on ellipsometric data, the *TlInSe₂* compounds obtained by us with *0.1% Au* impurity were characterized as single crystals, their optical functions were determined, and the luminescent properties of these crystals were studied.

X-ray study of $TlInSe_2$<Au> showed that this phase crystallizes in tetragonal syngonia. Ellipsometric measurements revealed that the real (ε_1) and imaginary (ε_2) parts of the dielectric constant are components of the dielectric permeability tensor of the considered uniaxial connections and are independent of the angle. From the spectrum of the optical absorption coefficient of the $TlInSe_2$ <Au> crystal, it was found that light absorption occurs from the energy value of 0.55 eV, and α(E) increases almost linearly from 1.92 eV to 3.74 eV. It reaches a maximum (1.85) at 3.74 eV, a diffuse value at 4.55 eV, and then decreases. From the spectrum of the optical reflection coefficient, it was found that the reflection coefficient increases in the energy range of 1.5÷3.72 eV, a deep minimum is observed at the energy value of 3.832 eV, then it increases again up to 4.73 eV and then monotonically decreases to 0, decreases to 368 eV. From the energy dependence of the energy losses in the $TlInSe_2$<Au> compound, it was found that the energy losses increase from 0.28 eV to 0.337 eV in the energy range of 0.76÷6.397 eV. From the dependence of the effective density on the energy, it was known that the effective density increases sharply in the range of 0.805÷3.52 eV and decreases to the energy value of 6.44 eV, taking its maximum value. While the energy increases to the value of 4.91 eV, a partial weak decrease is observed in the interval of 4.91÷5.95 eV, and a weak decrease in the interval of 5.95÷6.44 eV. From the spectral dependence of the real (σ_r) and imaginary (σ_i) part of the optical electrical conductivity of the TlInSe2<Au> compound, it was known that the real part of the electrical

conductivity increases by an exponential law. After receiving its maximum value at the energy value of 3,505 eV, it decreases to the energy value of 6,449 eV. The imaginary part of the optical electrical conductivity increases with a linear law in the range of 0.654÷2.91 eV and decreases after reaching its maximum value. An inversion of the imaginary part of the optical electrical conductivity is observed at an energy value of 3.6 eV. Then, a weak increase in electrical conductivity is observed in the energy interval of 0.381÷4.65 eV.

Fluorescence spectra of TlInSe2<Au> ternary compounds revealed that the studied samples have bright luminescence properties and can be used as promising materials for solving practical problems.

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