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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**STRUCTURES, ELECTRONIC AND OPTICAL PROPERTIES OF
TlIn_{1-x}Ga_xC₂ (C- Se, Te) CRYSTALS**

Speciality: 2220.01- “Semiconductor Physics”

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INTRODUCTION

Relevance of the topic and degree of elaboration.

Semiconductors are widely used in the electronic industry. Previously, simple substances such as germanium, silicon, selenium, and binary semiconductor compounds were used for this purpose. However, since the second half of the last century, three- and multi-component semiconductor materials began to attract the attention of specialists engaged in the study and application of semiconductors. This fact is directly related to the fact that the development of various areas of the electronic industry requires the purchase of semiconductors whose electronic and other physical properties can be controlled. An important role in solving the specified problem is played by the acquisition of multicomponent semiconductors, consisting of various elements with different fundamental parameters, and a complex study of both their structure and the physical processes taking place. The analysis of the available scientific literature shows that the lattice parameters undergo serious changes when the chemical composition of multicomponent semiconductor crystals $A^{III}B^{III}C_2^{VI}$ (C-Se,Te) is changed, as well as under the influence of high hydrostatic pressure. Changes in the structure can significantly affect the electrophysical, optical parameters, transformation effect, tensor-resistive, and other properties. Another attractive feature of these crystals is that they have a chain and layered structure, because of which they differ from other crystals with a complex chemical composition by high anisotropy of their physical properties. The specified properties created a stimulus for intensive research of these crystals in the last decades.

Since the beginning of the last century, it has been determined by the discovery of the crystal structure of the compound TlSe that this compound is of special importance. Thus, the thallium atoms in this binary compound are in different crystal positions. Some of them behave as trivalent, while others behave as monovalent. The main semiconductor properties of this compound are determined by

trivalent (Tl^{+3}) thallium atoms located in tetrahedra . That is, in reality, the chemical formula of TlSe compound is $TlSe \rightarrow Tl^{+}Tl^{3+}Se_2$. Based on those real experimental results, a new class of triplet compounds was discovered by partially replacing trivalent Tl atoms with trivalent In $A^{III}B^{III}C_2^{VI+3}$ or Ga $^{3+}$ atoms in the TlSe compound. The study of both the structures and physical properties of these types of crystals has shown that some of these compounds have a layered, and some have a chain crystal structure. It was suggested that the chemical formulas of those compounds $Tl^{+}In^{+3}(Ga^{3+})X_2^{VI}$ should be general, and later this opinion was confirmed by precise structure analysis. The existence of triple compounds of the indicated type in reality has been confirmed once again by the electronic structures of the elements forming these compounds. For example: when the compound TlSe - $Tl^{+}Tl^{3+}Se_2$ is formed, the outer electron layers of the chalcogen pair are completed to neutral argon $3s^23p^6$, krypton $4s^24p^6$ and xenon $5s^25p^6$, respectively, and indium atoms $5s^25p^1$ and occurs due to $4s^24p^1$ electrons of gallium atoms. The study of the crystal structures, zone structures and fundamental physical properties of the indicated type of compounds has been intensively conducted and is being studied by scientists from all over the world. The results of those studies showed that these compounds have high strain sensitivity, high photosensitivity in a wide frequency range, and memory switching properties. In the following years, studies of new, multi-component $TlInX_2$ - $TlGaX_2$, $InGaX_2$ - $TlInX_2$ systems were carried out with mixed substitution of trivalent Tl, In and Ga elements in triple-type compounds $A^{III}B^{III}C_2^{VI}$. These materials have also been found to be quite valuable materials. However, due to objective and subjective reasons, those substances were not studied in more detail. That is, the study of this type of crystals was episodic and not systematized. So, certain physical-chemical analyzes of these systems were conducted and some properties were studied. For this reason, there is a great need for a more detailed study of the indicated types of crystals and to reveal their practical possibilities.

The object and subject of the research: $TlIn_{1-x}Ga_xSe_2(Te_2)$, $InTl_{1-x}Ga_xSe_2(Te_2)$ is the study of the optical and electronic properties of the crystal structures of the systems.

The goals and objectives of the research: in connection with the mentioned, the aim of the dissertation work was to investigate the electrophysical, photoelectric, optical, tensor-resistive properties and conversion effect of the crystals of $InTl_{1-x}Ga_xC_2^{VI}$ group IIIB elements obtained by mixing each other $TlIn_{1-x}Ga_xC_2^{VI}$.

By solving the issues outlined below, it was possible to achieve the set goal.

1. Cultivation of monocrystals of solid solutions of systems $TlIn_{1-x}Ga_xSe_2(Te_2)$, $InTl_{1-x}Ga_xSe_2(Te_2)$ in a suitable technological mode, convenient for research;

2. Conducting stoichiometric and X-ray phase analyzes of crystals belonging to these systems, determining the regularities of the dependence of lattice parameters on the composition, studying the microrelief of surface structures;

3. Studying the electrophysical properties of the specified type of crystals and determining the fundamental semiconductor parameters;

4. Investigating the dependence of the optical and photoelectric properties of the studied crystals on the composition and the influence of external factors;

5. Determining the laws of change of tensiresistive properties depending on the mechanical effect and the effect of light;

6. Researching the acoustophotovoltaic effect, which occurs due to the simultaneous effect of sound and electromagnetic waves;

7. Study of volt-ampere characteristics depending on the composition of crystals and the influence of external factors.

Research methods: conducting dissertation experiments RIGAKU MiniFlex 600 X-ray diffractometer (roentgenograms), JEOL JSM 6610-LV scanning electron microscope (stoichiometry), J.A. Woollam M-2000 DI spectroscopic ellipsometer (ellipsometer), Keithley 6487 picoammeter (volt-ampere characteristic), Nanofinder[®] 30 - 3d laser Raman microscopy system (Raman and luminescence), Solver Next scanning probe (probe) microscope AFM (survey of surface microrelief) were used.

The main provisions for the defense:

1. $TlIn_{1-x}Ga_xSe_2(Te_2)$ and $InTl_{1-x}Ga_xSe_2(Te_2)$ technology of growing perfect single crystals of crystals;
2. $TlIn_{1-x}Ga_xSe_2(Te_2)$ and $InTl_{1-x}Ga_xSe_2(Te_2)$ stoichiometric surface microrelief, X-ray phase analysis, electrical properties of crystals. As a result of the research, it was found that the replacement of Tl atoms with In and Ga atoms in the specified type of crystals occurred as a result of the change in the ratio of the ionic compound to the covalent compound of the chemical bond and the decrease in the width of the zone where the change of the lattice constants is prohibited according to Vegard's law;
3. Explanation based on the thermal-electronic model of the change in electrical conductivity in compounds $TlInSe_2$ and $TlInTe_2$ in a high-intensity electric field depending on temperature;
4. $A^{III}B^{III}C_2^{VI}$ patterns of variation of the memory conversion effect in type crystals and their structural analogues depending on the composition of the crystals and temperature;
5. Mechanical deformation and tensor-resistive properties of electromagnetic wave $TlIn_{1-x}Ga_xSe_2(Te_2)$ and $InTl_{1-x}Ga_xSe_2(Te_2)$ crystals and piezomodulation effect;
6. $TlIn_{1-x}Ga_xSe_2(Te_2)$ and $InTl_{1-x}Ga_xSe_2(Te_2)$ features of the acoustophotovoltaic effect caused by the influence of sound and electromagnetic waves acting on each other perpendicularly at the same time in crystals;
7. Study of ellipsometric effect in type $A^{III}B^{VI}$ crystals and calculation of optical functions of those crystals;
8. Analysis of the combination scattering spectrum of light in those crystals.

Scientific novelty of the research:

- $A^{III}B^{VI}$ type ternary and quaternary compounds and solid solutions stoichiometric analysis and surface microreliefs were studied.
- $TlInSe_2-TlGaSe_2$ and $TlInTe_2-TlGaTe_2$ crystals was performed.
- $TlIn_{1-x}Ga_xSe_2(Te_2)$ and $InTl_{1-x}Ga_xSe_2(Te_2)$ by studying VACH of crystals, it was determined that those crystals have memory

converter properties and the threshold voltage at which conversion occurs in them is controlled depending on the composition and temperature of the crystals.

- $TlIn_{1-x}Ga_xSe_2$ single crystals were studied and it was found that they have high strain sensitivity coefficients and can be controlled depending on the value of light and mechanical deformation.

- New piezomodulation and AFV effects were discovered and studied in the studied crystals. It has been shown that it is possible to control the observed effect by changing the frequency of electromagnetic and sound waves.

- $TlInSe_2$ and $TlInTe_2$ the conductivity of its compounds in strong electric fields was studied.

- $A^{III}B^{III}C_2^{VI}$ the light combination scattering spectra and luminescence phenomena were studied in the type compounds.

- $TlInX_2^{VI} - TlGaX_2^{VI}$ the study of ellipsometry in type crystals was carried out.

- $TlInX_2^{VI} - TlGaX_2^{VI}$ the real and imaginary parts of the dielectric functions and optical constants of type crystals were studied.

- A new acoustophotovoltaic effect was discovered and studied in the studied crystals.

Theoretical and practical significance of the research: The results obtained in the dissertation can be useful in the interpretation of the chemical dependence properties of kinetic effects in multicomponent semiconductor crystals, conversion phenomena with and without memory, effects such as tensoresistive and piezomodulation. $TlIn_{1-x}Ga_xSe_2(Te_2)$ and $InTl_{1-x}Ga_xSe_2(Te_2)$ strain gauges that allow detecting and measuring small deformations of memory elements based on crystals, optoelectronic devices used in the visible and near-infrared regions of the spectrum, in the preparation of high-sensitivity memory elements, a device that allows for the to celebrate of weak magnetic field and weak changes in light intensity creation is possible.

Approbation and application: 7 scientific articles covering the topic of the dissertation work were published in foreign journals, 11 scientific articles and conference theses were published in the journals

of our Republic and 1 textbook. The main results of the dissertation were discussed at the following conferences:

- "XXII Republican scientific conference of doctoral students and young researchers, ASPU, 22-23 November, 2018;
- on "Perspectives of application of soft magnetic alloys in information technology and military industry" International Scientific-Practical Conference, Baku, 09-10 October, 2019;
- "V International Scientific Conference of Young Researchers" dedicated to the 98th anniversary of the birth of national leader Heydar Aliyev, Baku Engineering University, 29-30 April, 2021;
- Current issues of personnel training in energy specialties Republican scientific conference, Sumgayit State University, 25-26 November, 2021.
- It was discussed in the scientific seminars of the Faculty of Physics and Mathematics of Nakhchivan State University.

The name of the organization in which the dissertation work is completed: Nakhchivan State University

Personal participation of the author: The main goal of the research and the issues to achieve them were indicated by the author, the directions of the research were determined, the results were processed, systematized and discussed. At the same time, the author directly participated in the preparation and conduct of laboratory and experimental studies.

The total volume of the dissertation is indicated by indicating the volume of the structural sections of the dissertation separately: Dissertation consists of 177 pages - introduction, 4 chapters including 4 tables and 69 pictures, 193 titles of bibliography, appendices, without tables, without bibliography and bibliography 38951 consists of a sign.

The main content of the dissertation: In the introduction, the relevance of the topic of the dissertation is justified, the purpose, scientific novelty, practical importance and the main provisions of the work are defined, and a brief summary of the existing theoretical and experimental works on the issues considered in the dissertation is given.

Chapter I of the dissertation work is devoted to the solution of technology issues. At the beginning of the chapter, the characteristics of IIIB and VI subgroup elements of the periodic system, which are the primary elements in the research work, are justified as being the basic elements in the research work. In the next part of the chapter, the possibility of obtaining new triple and quadruple combinations by rationally replacing the III B subgroup elements of the periodic system is analyzed and justified. In this chapter, an analysis of literature data on the study of the structures and fundamental physical properties of compounds of type $A^{III}B^{III}C_2^{IV}$ was carried out, and three-component compounds of type $A^{III}B^{VI}$ and their research levels were analyzed until this research work. In this chapter, the actuality of the topic of the dissertation, which was analyzed by collecting and analyzing the available literature data on the research of $TlInSe_2$ - $TlGaSe_2$ and $InTlSe_2$ - $InGaSe_2$ systems, is substantiated.

Chapter II of the dissertation is devoted to the solution of technology issues. At the beginning of the chapter, brief information on growing monocrystals of the synthesis of $TlInSe_2$, $TlInTe_2$, $InGaTe_2$ compounds, which are the main materials of the dissertation work, was given, and examples of experimental results were shown. In the next part of the chapter, the X-ray phase analyzes of the crystals, which are the research objects, were carried out. It was determined that the variation of the lattice constants depending on the composition varies mainly according to Vegard's law. This is due to the fact that both solute and solvent atoms have different sizes, so the introduction of Ga atoms into the $TlInTe_2$ lattice produces two effects: the crystal structure of the $TlInTe_2$ compound undergoes a static homogeneous deformation and the local shifts generated by each Ga atom is happening.

Thus, the determined X-ray values of the lattice constants of solid solutions and the interatomic distance take their values averaged over all lattices of the crystal. Homogeneous deformation causes, at least partially, the concentration dependence of X-ray calculated lattice constants of $TlIn_{1-x}Ga_xSe_2$ solid solutions. The local shifts caused by dissolved Ga atoms lead to distortion of the lattice to one degree or another, and changes in its shape and size. It depends on the

position of the alternating atoms in the lattice. Local deformations lead to attenuation of X-ray reflection intensities and diffusion scattering around regions.

On average, the distortion of the lattice means that the remote effect is kept. In an ideal three-dimensional, averaged lattice, statistical deviations from the mean state occur.

Thus, although the periodicity is statistical, it is actually kept accurate. It is obvious that the deviations of the atoms from their ideal states depend on the difference in the ionic radii and concentration of the alternating In (1.66\AA) and Ga (1.39\AA) atoms. Note that the ionic radii of In and Ga atoms are 16% different from each other.

Even if the sizes of atoms and interatomic bonds are the same, this in itself cannot always ensure isomorphism. In addition, pairs of atoms that replace each other isomorphically in the same type of structure may not have this property in other types of structures. This is not surprising, because isomorphism is not a property of the structure as a whole, but of atoms in isolation. If the structure has a complex chemical formula and the size of the lattice is large, then the requirements for the size of the atoms replacing each other should be slightly relaxed. Because in the mentioned case, the interatomic equilibrium should be slightly softened due to the slight displacement of other atoms of the lattice. Let us add that in TlInTe_2 or TlInSe_2 compounds, the bonds formed by Ga and In atoms, which are isomorphous replacements for each other, can be considered as part of the ionic bonds. In the end, we can note that the general structure of reflexes observed in X-ray images is preserved when In atoms are replaced by Ga atoms in TlInTe_2 compound, additional reflexes do not appear. But in the case of the mentioned substitution, the intensity of the reflexes observed in the radiographs changes. This feature is also observed in the X-ray images of the $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ system .

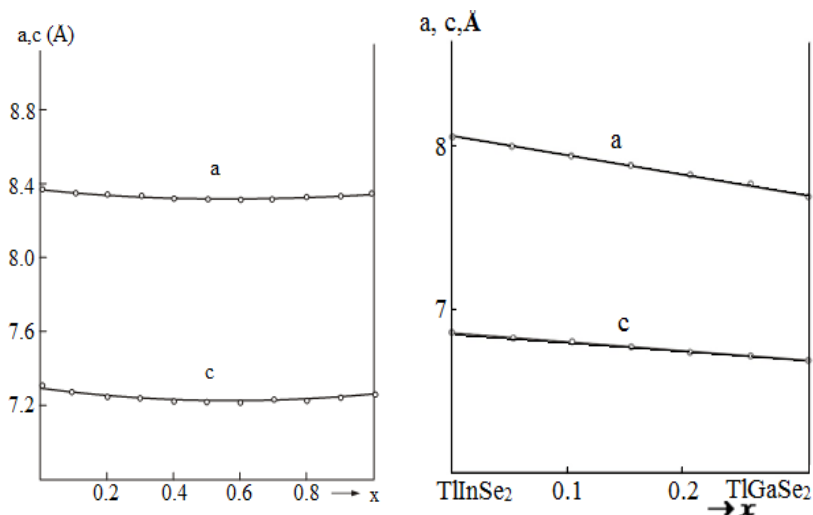


Figure 1. Composition dependence of lattice constants of TlIn_{1-x}Ga_xTe₂ (a), TlIn_{1-x}Ga_xSe₂ (b) crystals

In the next part of the chapter, the experimental results of schematic and X-ray phase analysis of the research objects, as well as the results of the study of the microreliefs of the surfaces of compounds and solid solutions in the 2D and 3D modes with the atomic force microscope are given. The following sections of the chapter give brief information about the methods of measuring the kinetic effects of crystals. In this chapter, information about the method used in the VACH study of the same crystals is also reflected.

Chapter III of the dissertation, the results of the research of the temperature dependence of the specific electrical conductivity - Hall and thermo-electric coefficients of TlIn_{1-x}Ga_xSe₂ and InTl_{1-x}Ga_xCe₂ solid solutions were reported. It was determined that these crystals are typical semiconductor materials. The temperature-dependent variation of the Hall conductivity in the studied crystals occurs according to the $T^{-2/3}$ law, which indicates the longitudinal acoustic scattering of charge carriers in the studied crystals.

The analysis of the composition dependence of the width of the forbidden zones of TlIn_{1-x}Ga_xCe₂ crystals showed that the width of the

forbidden zone increases when trivalent In atoms are replaced by trivalent Ga atoms in the compound $TlInSe_2$ (Figure 2).

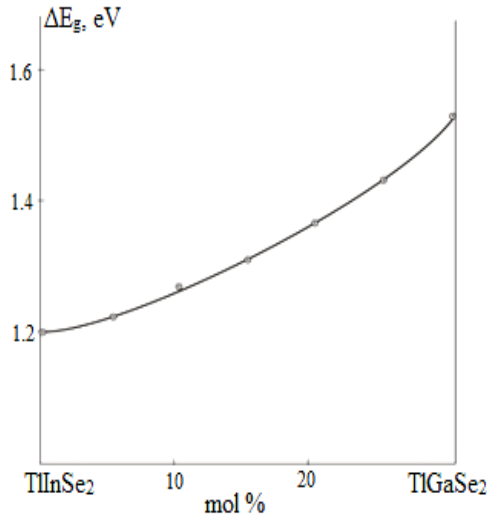


Figure 2. $TlIn_{1-x}Ga_xSe_2$ dependence of the width of forbidden zones of crystals on composition

Thus, by calculating the zone structures of both $TlInTe_2$ and $TlGaTe_2$ and $TlInSe_2$ compounds, it was determined that the ceiling of the valence zones of those compounds is formed by p states of thallium, indium, selenium and tellurium atoms. It is natural that if indium atoms are replaced by gallium atoms in these compounds, since gallium atoms with 4p electrons participate instead of indium atoms with 5p electrons in the formation of the ceiling of the valence zone, the zone shifts to lower energies and the width of the forbidden zone decreases in that direction.

In the next part of the chapter, the results of the study of VACH characteristics of $TlIn_{1-x}Ga_xSe_2$, $InTl_{1-x}Ga_xSe_2$ crystals in static mode are given. It was determined that the I(U) dependence obeys Ohm's law at small voltage values in the studied samples. However, in samples with different compositions, starting from a certain value of

the voltage, the sample jumps from a state of high resistance to a low resistance, and the dependence of the current on the voltage becomes non-linear. The characteristic is S-shaped. It was found that the temperature of the sample remains constant in the region where Ohm's law is satisfied. However, in the region of negative differential resistance, the temperature increases and usually this temperature is higher than the ambient temperature. In the area of high currents, the S-shaped characteristic is more clearly formed. In particular, the VAcH of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystals are given in the figure (Figure 3).

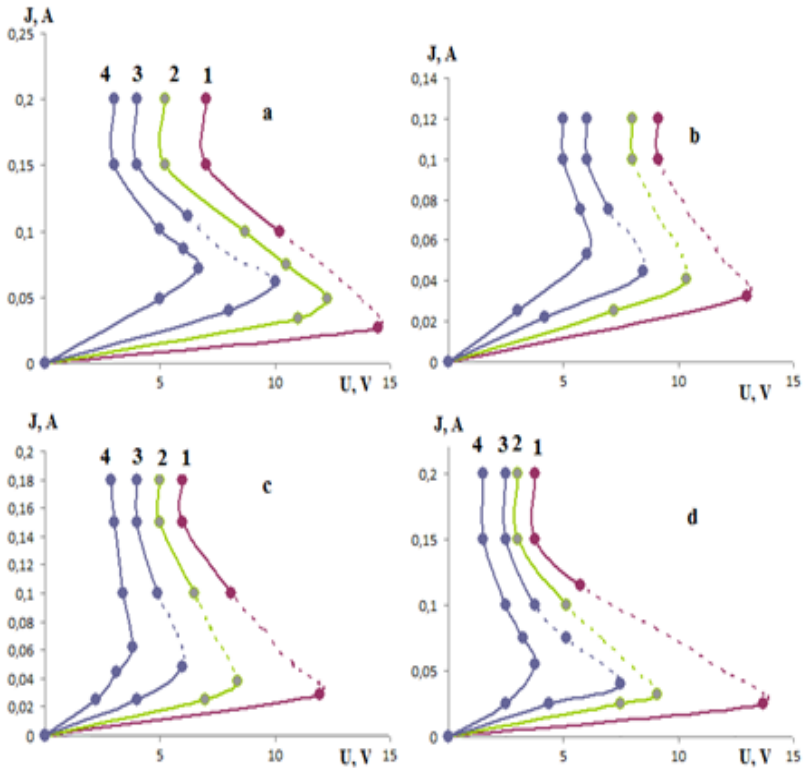


Figure 3. VAcH of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystals at different temperatures (1– 80 K; 2 – 120 K; 3 – 220 K; 4– 300 K): a) $x=0.02$; b) $x=0.04$; c) $x=0.06$; d) $x=0.08$.

Analysis of the results shows that as the ambient temperature decreases, there is a migration of the astana voltage –that is, it shifts to higher values, and an increase in the ambient temperature is accompanied by a narrowing of the area with negative resistance in the Volt-Ampere characteristic.

The main characteristics of this region are its width, slope, threshold voltage, threshold current, as well as holding voltage and holding current. For this reason, Coul heat plays a key role in the conversion. Because for the astana voltage (U_a) the condition $\frac{dI}{dV} < 0$ is paid, the corresponding astana voltage corresponds to the small values of the current.

Note that, the occurrence of conversion effect in $TlIn_{1-x}Ga_xCe_2$ crystals can be explained based on the electrothermal model of conversion. According to this model, temperature affects the threshold voltage U_a as much as it affects the shape of VACH. It follows that the threshold current decreases as the threshold voltage increases. As can be seen, the VACH of the studied samples changes sharply depending on the ambient temperature. Threshold voltage U_a and threshold current I_a change depending on the temperature, which causes an increase in the threshold current and a decrease in the threshold voltage in $TlIn_{1-x}Ga_xSe_2$ and $InTl_{1-x}Ga_xC_2$ crystals. This indicates that the electrothermal mechanism prevails during conversion (figure 4).

Threshold power also depends on the ambient temperature. The report shows that P_a decreases proportionally with increasing temperature. From what has been said, it is clear that as the temperature increases, the number of random collisions, as well as the number of free charge carriers, increases due to the increase in temperature. All these facts indicate that the increase in temperature is the reason for the reduction of threshold strength.

It is clear that conversion effects in thick samples occur as a result of thermal effects. During the electronic-thermal mechanism of the effect, the combined effect of the electric field and temperature on the semiconductor should be taken into account. So, at this time, the semiconductor changes from a state of high resistance to a state of low resistance. The thermal effect of the mechanism is mainly

determined by the temperature dependence of the thermal capacity, thermal conductivity and resistance of the active region.

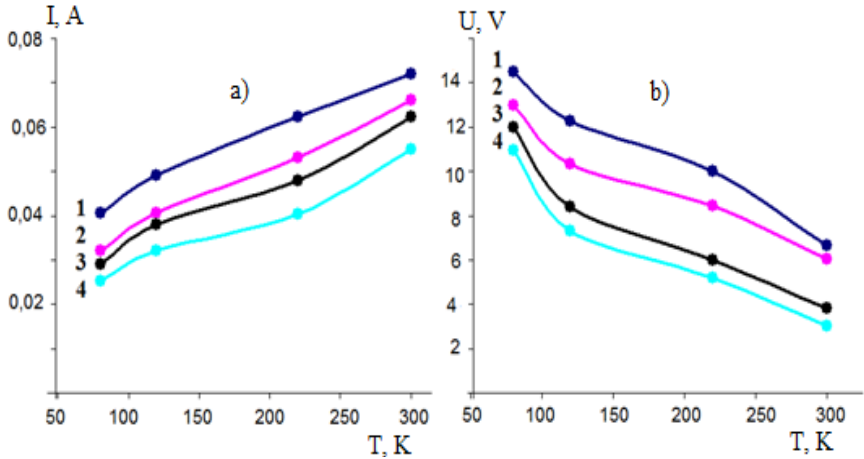


Figure 4. Temperature dependences of the threshold voltage (a) and threshold current (b) of crystals $\text{TIIn}_{1-x}\text{Ga}_x\text{Se}_2$: 1) $x=0.02$; 2) $x=0.04$; 3) $x=0.06$; 4) $x=0.08$.

The S-like curve for the studied crystals is shown as the threshold current in the negative resistance (NR) region, which is well expressed at high currents. In the $I(U)$ curve, a certain part of NR is better expressed at low ambient temperatures. From the obtained results, it can be seen that the reduction of the voltage of the straight transition was characteristic for all the crystals we studied in each subsequent transformation and up to the non-threshold areas of nonlinearity in VACH. Super linear part of VACH

$$J=aU+bU^2+cU^3$$

can be clearly expressed by the trinomial. Here, the numerical values of the coefficients a , b , and c are easily determined and take different values for different compositions. These obtained results show that the appearance of NR regions in $\text{TIIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystals is related to electrothermal processes. In electrothermal processes, small local deviations are allowed, which lead to the formation of areas of high current density. Such an increase in current density is usually

accompanied by the formation of high-density fringes in the samples. The high current density generated in those channels causes the generation of Coul heat. Also, with an increase in temperature, the electrical conductivity increases, which in turn leads to the passage of a high current. When this state is stable, it is observed that heat radiation is equal to heat loss. The steady state of VACH, especially the NR region, can be elucidated by electrothermal approximation. In the case of small currents, this is considered completely normal.

In the next part of the chapter, the results of the study of tensor-resistive properties of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystals depending on the influence of mechanical deformation and electromagnetic waves are given. It was determined that the strain sensitivity coefficient decreases when In atoms are replaced by Ga atoms in the $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystal. This reduction is observed in all samples studied. As the temperature increases, the strain sensitivity coefficient increases linearly. One of the interesting properties found in these crystals is the change in strain sensitivity coefficients when they are affected by electromagnetic waves. This change can be controlled depending on the intensity and spectral composition of the light. Figure 5 shows the dependences of strain sensitivity coefficients of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystals exposed to different radiations on mechanical deformation. The analysis of the obtained results shows that [101] when stretching along the axis, the relative number of heavy holes moving in that in connection with this, direction increases and, the conductivity decreases. The reason for redistribution of charge carriers in the valleys is due to the existence of extremums in the zonal structures of crystals under different conditions during unidirectional deformation. That is [101] of the crystal during stretching in the direction of the arrow [100] and [110] since compression of the directions occurs, as a result [001] the extremum on the axis shifts upwards and accordingly [100] and [110] the minima on the arrows are decreasing.

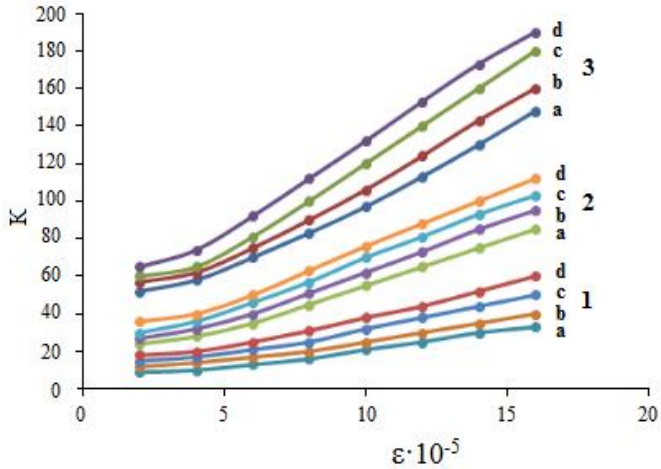


Figure 5. Dependences of optical illumination of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystals on mechanical deformation at different values, where 1 - $x=0.2$, 2 - $x=0.4$, 3 - $x=0.6$, (a) $L=0$, (b) $L=103 \text{ Lk}$, (c) $L=104 \text{ Lk}$, (d) $L=5 \cdot 104 \text{ Lk}$.

In the next part of the chapter, the results of the piezomodulation of the electrical conductivity of the $\text{TlIn}_{0.9}\text{Ga}_{0.1}\text{Se}_2$ crystal are given. The analysis of the obtained results showed that the amplitude of piezophotoconductivity depends linearly on the light intensity $\Delta\sigma_{pf} = \frac{1}{VR_y}(\Delta V_0 - \Delta V_{op})$. As can be seen from Figure 6, the piezo signal is almost identical to the value of deformation at 6000 Lk illumination and when $I_f = 0$, $\varepsilon_{01} = 8 \cdot 10^{-5}$ and $\varepsilon_{05} = 25 \cdot 10^{-5}$.

The experimental results show that the detected piezophotorestrictive effect can expand the possibilities of recording dynamic processes.

Through our research, it was determined that weak magnetic fields can be precisely determined at a given frequency based on the tensoresistive and piezophotorestrictive effects found in the $\text{TlIn}_{0.9}\text{Ga}_{0.1}\text{Se}_2$ crystal.

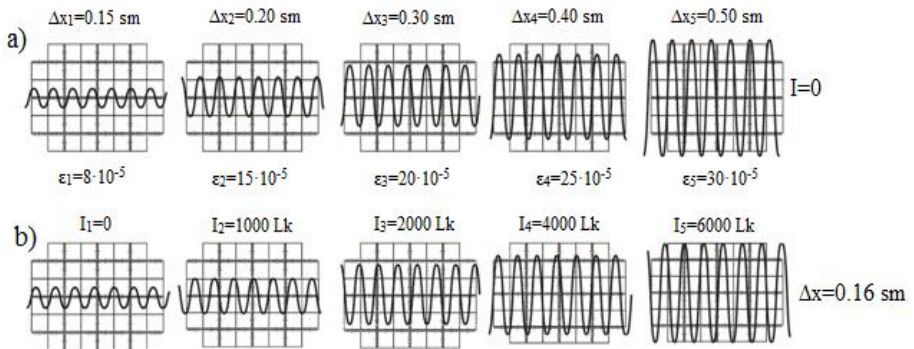


Figure 6. Modulation of the piezoelectric conductivity of $\text{TlIn}_{0.9}\text{Ga}_{0.1}\text{Se}_2$ single crystal at $0.5 \cdot 10^{-6} \text{ Ohm} \cdot \text{cm}^{-1}$ depending on the degree of deformation (a) and

It should be noted that, $\text{TlIn}_{0.9}\text{Ga}_{0.1}\text{Se}_2$ it is possible to calculate the value of magnetic fields at given frequencies on the basis of tensorresistive and piezoresistive effects found in the crystal.

Chapter IV of the dissertation, is devoted to studying the optical properties of research objects. Combined light scattering microspectroscopy (LCS) is one of the effective methods for detecting internal stresses in crystals. Combined light scattering microspectroscopy is one of the effective methods for detecting internal stresses in crystals. In Chapter IV, paragraph 1, the Raman scattering of type $\text{A}^{\text{III}}\text{B}^{\text{VI}}$ compounds is discussed. For each cm of the diffraction grating used in the study, there were 1800 lines. The exposure time was 1 min.

The phonon frequencies in the Raman spectra of the crystals under study have been determined: $\text{InSe}\langle\text{Ge}\rangle$ (40 sm^{-1} , 105 sm^{-1} , 180 sm^{-1} v 230 sm^{-1}), $\text{TlSe}\langle\text{Ge}\rangle$ (38 sm^{-1} , 142 sm^{-1} , 159 sm^{-1}), InGaTe_2 (100 sm^{-1} , 123 sm^{-1} v 142 sm^{-1}), TlGaSe_2 (42 sm^{-1} , 52 sm^{-1} , 129 sm^{-1} , 189 sm^{-1}), $\text{Tl}_2\text{InGaSe}_4$ (46 sm^{-1} , 109 sm^{-1} , 189 sm^{-1} , 271 sm^{-1}). The Raman spectra of the compounds $\text{InSe}\langle\text{Ge}\rangle$, $\text{TlSe}\langle\text{Ge}\rangle$, InGaTe_2 , TlGaSe_2 , $\text{Tl}_2\text{InGaSe}_4$ obtained at room temperature are shown in Figs. 7.

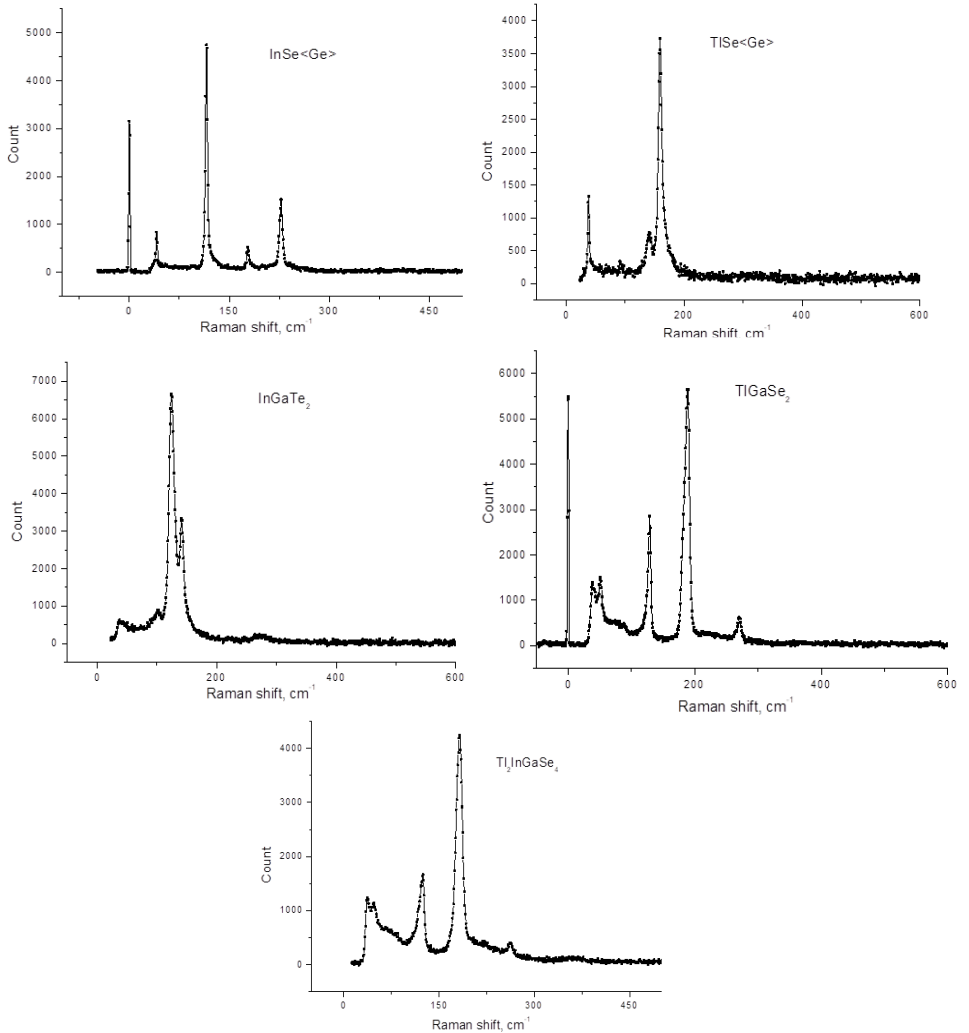


Figure 7. Combination scattering of light spectra of InSe<Ge>, TlSe<Ge>, InGaTe₂, TlGaSe₂, Tl₂InGaSe₄

As it is known, the main methodology of studying the dielectric permeability of materials all over the world is the ellipsometric spectroscopy method. In this method, the degree of polarization of the sample is determined by the effect of light passing

through the surface of the sample and reflected from it. Taking into account these mentioned, we have conducted the study of ellipsiometry in $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ type crystals. Researches were conducted in the energy range of $0.7 \div 6$ eV. The light beam falling on the sample was angled from 60° to 75° in 5° steps. Comparing the energy dependences of the real and imaginary parts of the dielectric permittivity obtained by ellipsiometry, it was found that the real part of the dielectric permittivity reached its maximum value at 2.4 eV, and the imaginary part at 3.42 eV. Based on these values of dielectric constant, the optical functions of the studied crystals were determined. The real and imaginary part of the dielectric constant of the TlInSe_2 crystal doped with Au is given in Figure 8.

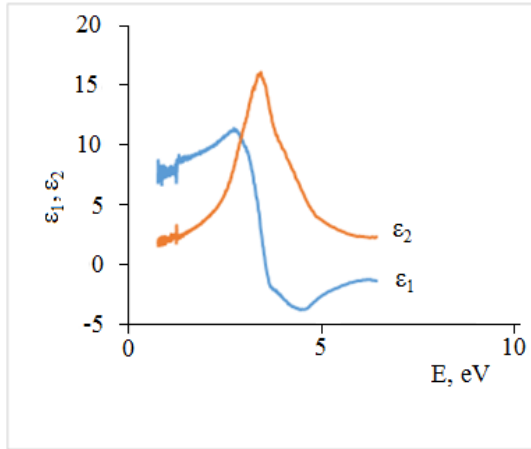


Figure 8. Real and imaginary parts of dielectric constant of $\text{TlInSe}_2\langle\text{Au}\rangle$ crystal

The real part of the refractive index based on the dielectric constant

$$n = \sqrt{\frac{1}{2}(\epsilon_r + \sqrt{\epsilon_r^2 + \epsilon_i^2})},$$

and the imaginary part

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

calculated with formulas.

It can be seen from the dependence of $n(E)$ that the real part of the refractive index of the crystal $n(0.79)=2.68$ takes its maximum value (0.53) at the energy value of 2.74 eV. After that, n takes its minimum value ($n=0.83$) at the value of 6.44 eV of energy. As can be seen from the energy dependence of the imaginary part, $k(E)$ increases from the energy value of 0.67 eV. It takes its maximum value at the energy value of 3.50 eV. A spread maximum is observed at the energy value of 4.11 eV. Then k decreases to the energy value of 6.44 eV (Figure 9, a).

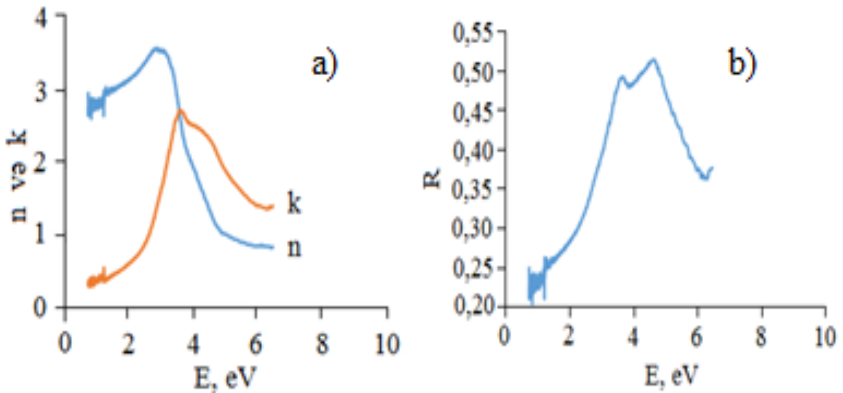


Figure 9. Dependence of the real and imaginary parts of the refractive index of the $\text{TlInSe}_2\langle\text{Au}\rangle$ crystal on the photon energy (a), spectrum of the optical reflection (b) coefficient

The absorption coefficient was calculated using the following formula,

$$\alpha = \frac{4\pi k}{\lambda}$$

Here, k is the extinction coefficient, λ is the wavelength, and π is a constant of 3.14.

As can be seen from the picture, light absorption occurs from the energy value of 0.55 eV and gets its maximum absorption energy at the value of 4.55 eV (Figure 10).

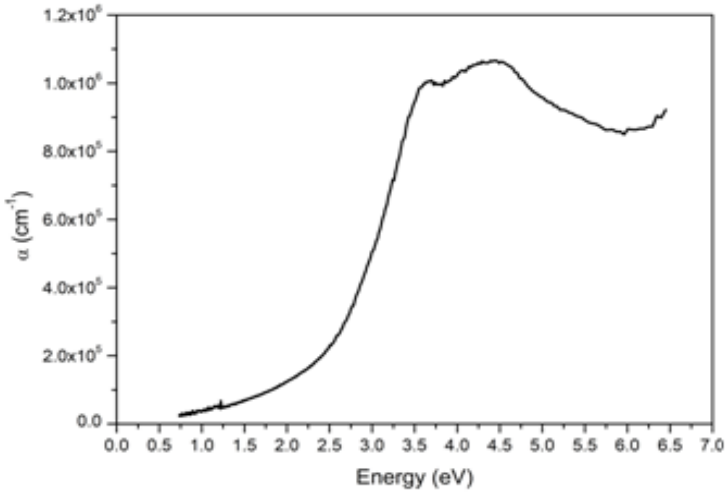


Figure 10. Spectrum of optical absorption coefficient α of TlInSe₂ <Au> crystal

The coefficient of return is calculated by the following formula,

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

The analysis of the obtained result showed that the coefficient of restitution increases in the energy interval of 1.5÷3.72 eV, a deep minimum is observed at the energy value of 3.832 eV, then it increases again to 4.73 eV and then monotonically decreases to 0.368 eV (Figure 11).

The characteristic functions of energy losses of electrons were calculated by the following formula.

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

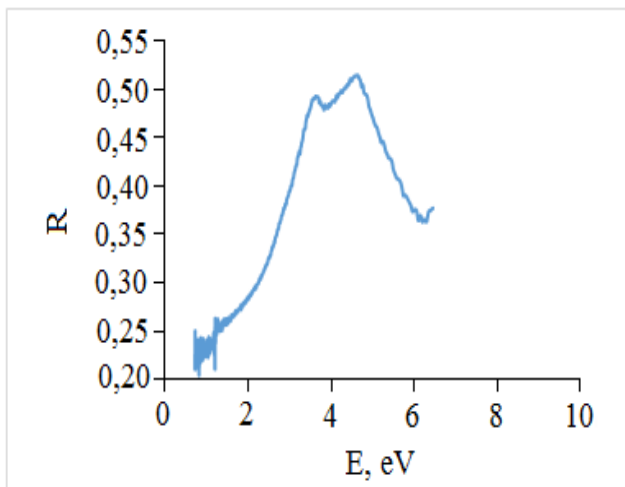


Figure 11. Spectrum of the optical reflection coefficient of the TlInSe₂ <Au> crystal

The analysis of the results shows that the effective density of TlIn Au combination TlInSe₂ <Au> increases sharply in the range of energy 0.805÷3.52 eV and decreases to the value of energy 6.44 eV, taking its maximum value (Figure 11,b). The analysis of the energy dependence of the electric loss showed that it increases from 0.28 to 0.337 in the energy range of 0.76÷6.397 eV (Figure 12,a).

The real and imaginary parts of the optical electrical conductivity of the compound are calculated by the following formula.

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

of Ge-doped InSe and quadruple TlIn₂GaSe₄ compounds were also determined based on the energy dependences.

In this chapter, the results of the study of the acoustophotovoltaic (APhV) effect in TlInSe₂ (Te₂) crystals of copper are reflected. The measurements were 0.2 ÷ 0.4 mm, width 1 ÷ 1.5 mm, and the distance between the symmetrical electrodes placed at the ends of the sample was 3 ÷ 7 mm.

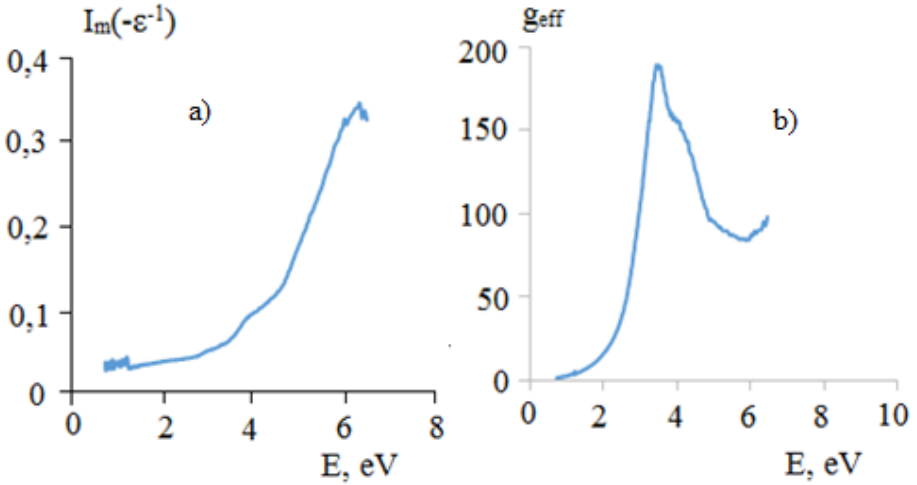


Figure 12. Energy dependence of characteristic functions of energy losses (a) and effective density (b) of TlInSe₂<Au>

The sample is placed on a sound wave radiator with a thin, solid acoustic contact or lubricant. In the event that sound waves and electromagnetic waves fall perpendicular to each other on the sample, it has been found that an electric current appears between the ends of the sample. Photovoltaic effect has different properties from known photoacoustic effects. When increasing the frequency of the acoustic wave during constant illumination with white light, the sign of the common APhV changes periodically. The spectral dependence of this effect also has its own characteristic. The intensity of the light falling on the crystal, the frequency and power of the acoustic wave, the distance between the electrodes, as well as the semiconductor material of the external fields by changing the orientation of the crystallographic axes, it is possible to change the spectral characteristics of the same crystal and control the process (Figure 13).

TlInSe₂, TlInTe₂ and TlGaTe₂ crystals showed that the short-circuit current does not always correspond to zero when $J_{\text{APhV}}(\hbar\omega)$ depends, on the contrary, $\hbar\omega_i = \hbar\omega_i^{\text{max}}$ $J_{\text{AFV}} \neq 0$ is often the case. However, this value of the short-circuit current can be both positive

and negative, depending on the frequency ω_s and power w_s of the sound wave, as well as the value of the distance between the electrodes.

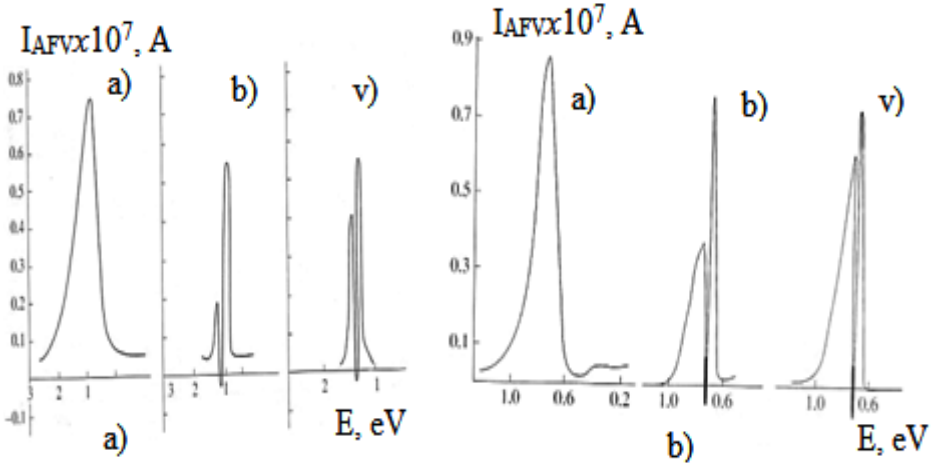


Figure 13. Spectral dependence of the short-circuit current of the APhV effect at 15 kHz (a), 35 kHz (b) and 50 kHz (v) sound frequency values in TI GaTe₂ (a) and TI InTe₂ (b) compounds.

The analysis of all the performed spectral measurements shows that the maximum of $(\hbar\omega_i = \hbar\omega_i^{\max})$ the specific conductivity in the dependence of $J_{AFV}(\hbar\omega_i)$ is a more sensitive point for controlling the value of the short-circuit current by changing the frequency and power of the sound, as well as the distance between the electrodes. $\hbar\omega_i = \hbar\omega_i^{\max}$ The recorded high sensitivity of the AFV effect at the spectral point is probably due to the fact that the positive and negative accumulated at this point balance each other. Frequency limits of electrons and holes are like:

$$\tau_n \gg T_s (\omega_s \tau_n \gg 1) \text{ and } \tau_p \gg T_s (\omega_s \tau_p \gg 1)$$

Here, τ_n - lifetime of electrons, τ_p - holes,

T_s - is the period of the sound wave.

Physically, this means that for charge carriers to interact effectively with each other, their lifetimes should be greater than the period of elastic waves ($qv\tau_{n,p} \gg 1$).

Since the lifetimes of electrons and holes in the crystals we studied are significantly different from each other, it is possible to limit the number of electrons or holes involved in the APhV effect by changing the frequency. Several mechanisms of this effect must be related to resonance excitation of anion radicals. Of course, the explanation of this effect described above cannot be taken for granted. Further research is needed for this. In addition, this effect, which was discovered in certain classes of crystals, has very wide application possibilities.

Recall that in the spectral characteristic $\hbar\omega_{01}$ and $\hbar\omega_{02}$ inverse points (that is, the points of change of the sign of J_{AFV}) are such characteristic points that the semiconductor does not react to the influence of sound waves or electromagnetic radiation, i.e., at these points, the crystal neither "sees" nor "hears". In the rest of the spectrum, especially at the maximum of the photosensitivity, the crystal has high sensitivity and the ability to receive sound is also very high.

Since light and sound must act at the same time for the creation of EMF, the "seeing" and "hearing" devices developed on the basis of this principle must have rare (and important) properties. So, these devices should "see" when there is sound (be "blind" when there is no sound or speech), and conversely, "hear" when there is lighting, for example during the day, and "deaf" when there is no lighting (at night).

Transducers working on this principle and made on the basis of solid bodies can be a model representation of the logical connection between vision and hearing of a living organism.

The problem of environmental protection, biological, medical, physical research requires the presence of a large number of recording devices to determine the concentration of atoms and molecules of various substances in liquid and gas mixtures studied in the atmosphere, industrial and residential areas.

MAIN RESULTS

1. A stoichiometric analysis of crystals studied by X-ray diffraction and atomic force microscopes was carried out. Their homogeneity was determined and it was shown that in the TlInC_2 system, when In and Tl atoms are alternately replaced by Ga atoms, the lattice constants decrease according to Vegard's law due to the smaller ionic radii of the substituting atoms.
2. By studying the temperature dependence of the electrical properties of $\text{TlInSe}(\text{Te})_2$ crystals, their fundamental physical parameters were determined. It is shown that when In and Tl atoms are alternately replaced by Ga atoms, the band gap increases due to the high energy of chemical bonds formed in the presence of Ga.
3. The change in electrical conductivity of TlInC_2 crystals depending on temperature and electric field strength in a strong electric field is associated with the thermionic emission mechanism.
4. By studying the current-voltage characteristics of $\text{TlIn}(\text{Ga})\text{C}_2$ crystals, it was established that these crystals have a transformative property. The threshold voltage and the region of negative differential resistance where the conversion occurs narrowly with increasing temperature. The results confirm charge transfer between electrodes within crystals based on the thermionic model. The cross-sectional area is explained by the presence of low-resistance filaments, which increase with increasing temperature and return to its previous state as the temperature decreases.
5. It has been established that $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ crystals [001] they have a high coefficient of strain sensitivity both in tension and compression in the direction of the crystallographic axis. This fact was explained by a change in the relative number of high and low trucks.
6. It has been established that when $\text{TlInSe}_2(\text{Te}_2)$, TlGaTe_2 single crystals are exposed to electromagnetic and sound waves in a

direction perpendicular to each other, $|001|$ for example, controlled by exposure to light and sound waves in the direction of the arrow. (electric current in a closed circuit). It is assumed that charge carriers released as a result of interaction with a photon and whose kinetic energy increases due to interaction with an acoustic phonon receive an additional impulse in the direction of propagation of the sound wave, causing the AFE effect.

7. It has been established that changes in the light incident on the strain gauge +cause a change in the strain resistance and piezoresistive coefficients of the sample. Registration of weak changes in light intensity is possible using devices based on tensor-resistive and piezoresistive effects discovered in the $\text{TlIn}_{0,9}\text{Ga}_{0,1}\text{Se}_2$ crystal.
8. In the Raman spectra of its crystals, the phonon frequencies are determined: $\text{InSe}<\text{Ge}>$ (40 cm^{-1} , 105 cm^{-1} , 180 cm^{-1} və 230 cm^{-1}), $\text{TlSe}<\text{Ge}>$ (38 cm^{-1} , 142 cm^{-1} , 159 cm^{-1}), InGaTe_2 (100 cm^{-1} , 123 cm^{-1} və 142 cm^{-1}), TlGaSe_2 (42 cm^{-1} , 52 cm^{-1} , 129 cm^{-1} , 189 cm^{-1}), $\text{Tl}_2\text{InGaSe}_4$ (46 cm^{-1} , 109 cm^{-1} , 189 cm^{-1} , 271 cm^{-1}). The vibration modes observed in the spectrum are consistent with the results of other authors available in the literature.
9. Using the method of spectral ellipsometry at a temperature of 300 K, the energy dependences of the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant of crystals of $\text{TlIn}_{1-x}\text{Ga}_x\text{Se}_2$ solid solutions with an improved surface were studied. The values of optical parameters (extinction coefficients, optical absorption and refraction coefficients) were calculated.

List of published scientific works related to the topic of the dissertation:

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