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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

INFLUENCE OF IONIZATION RADIATION ON THE IMPEDANCE, DIELECTRICAL AND ELECTRICAL PROPERTIES OF $TlInS_2$, $TlGaSe_2$ Crystals

Specialty: **2225.01 – Radiation Materials Science**

Field of science: **Physics**

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GENERAL CHARACTERISTICS OF WORK

The actuality of the subject. In recent years, the study of semiconductor materials has caused widespread scientific and technological interest. In this regard, development of solid state electronics in nanoelectronics - increases the requirements for the creation of devices such as supercapacitors, ionizers (extreme high capacity capacitors), electronic converters.

As it is known, solid crystalline materials used in industry have a real structure, which is characterized by the presence of defects. Some of these are defects that occur during the synthesis of crystals. Others are defects caused by the temperature of solids or the effects of ionizing radiation.

Currently, $TlInS_2$ and $TlGaSe_2$ compounds belonging to the class of $A^3B^3C_2^6$ semiconductors are widely studied. $TlInS_2$ and $TlGaSe_2$ single crystals have a layered structure. One of the unique features of these crystals is the strong anisotropy of physical properties due to the specificity of their structures. Because $TlInS_2$ and $TlGaSe_2$ single crystals are optically active, they have high photo sensitivity over a wide spectrum and are one of the applications of optoelectronics. On the other hand, the fact that these crystals have a layered structure is conducive to the formation of polytypes within them and, consequently, to changes in their physical properties. These types of semiconductors have unique properties. At present, there is a need for a systematic study of the dielectric, electrical, optical and photoelectric properties of these materials. This allows us to identify the whole complex of physical processes that take place in them. The study of the optical properties of these materials is necessary for both practical application and a thorough study of the electron-energy structure.

Many methods are used to develop the nature and applications of semiconductor materials. The method of gamma-ray irradiation and ion implantation has been widely used in recent years. Radiation-related effects occur as a result of the interaction of gamma rays with the sample. These effects reduce the effectiveness of the target substance and create residual defects. The main principle of the ion implantation method is the injection of high-speed ions into the target. It is possible to change both the physical and chemical nature of materials by the method of ion implantation. As a result of implantation with ions, both the area of use and the service life of materials can change significantly. For this reason, this method used is one of the special ways to improve and develop the properties of samples in technology, especially in semiconductor technology.

Despite the extensive study of $A^3B^3C_2^6$-type compounds in recent years, difficulties in their practical application remain due to the lack of information on some of their physical properties. In particular, the Laboratory of Radiation Physics of Ferroelectrics of the Institute of Radiation Problems has achieved significant results in this area. Thus, $TlInS_2$ and $TlGaSe_2$ single crystals have been extensively studied at temperatures at lower than room temperature. They found that $TlGaSe_2$ crystals have ferroelectric phase at the temperature lower than 107K and phase mismatch at the temperature range of 107-119K. In the meantime, the spontaneous polarization of the $TlInS_2$ crystal has been studied at low temperature. The results were published in high-impact journals. It should also be noted that $TlInS_2$ and $TlGaSe_2$ layered crystals are studied over a wide temperature range in the Laboratory of Radiation Physics of Irregular Solids of the Institute of Radiation Problems. However, at temperature higher than room temperature, the phase transitions in $TlInS_2$ and $TlGaSe_2$ crystals and their nature have not been studied. Also, the dielectric, electrical, impedance properties of $TlInS_2$ and $TlGaSe_2$ layered crystals over a wide temperature range and the effect of ionizing radiation on these properties have not been studied.

The purpose of the dissertation:

It consists of studying the effect of ionizing radiation on the impedance, dielectric and electrical properties of $TlInS_2$ and $TlGaSe_2$ crystals over a wide temperature range and over a wide frequency range.

Research methods:

$TlGaSe_2$ and $TlInS_2$ single crystals were synthesized by the Bricman-Stockbar method. In order to obtain $TlGaSe_2$ and $TlInS_2$

single crystals, cylindrical quartz ampoules (0.23-0.25 m in length and 0.01-0,-2 m in diameter) with a diameter of $(2.3\text{-}2.5)\cdot10^{-2}$m were used. Quartz ampoules were placed in the furnace under vacuum and with the components at an angle of 10-15 degrees, leaving 1/3 in the air. By placing the ampoule in this way, it was possible to speed up the synthesis process and increase the surface area of the alloy. The process was continued by heating the furnace at a speed of 0.16-0.20 K/sec. At the end of the process, the temperature of the furnace was lowered to room temperature and the crystal was removed from the furnace. And thus the process of synthesis (cultivation) of samples was completed.

The radiation source of $TlGaSe_2$ and $TlInS_2$ single crystals was irradiated in a γ-25 device consisting of the isotope Co^{60}. It is possible to conduct physicochemical and biological research with this research method. The gamma source system consists of tubes and cassettes with rods connected to the lower and upper holders inside. The rods connected to the lower and upper holder are made of the Co^{60} isotope and are lined up (symmetrically) throughout the round. For proper irradiation, the size of the sample to be irradiated must be smaller than the size of the chamber. Depending on the placement of the samples to be irradiated, the doses received by the samples also vary.

Ion implantation of samples was implanted in a UNIMAS 79 accelerator. During implantation, the sample was placed at an angle of 10° in front of the source and implantation was performed at room temperature. Implantation was performed using light ions (H^+ and He^{2+}). During the extraction process, ions are extracted from the source with the help of a magnetic field and implanted on a sample placed on a holder. Electrostatic lenses placed in the accelerator distribute ion radiation. In this time, the amount of ion flux is determined using the screen. A variable electric field was used to evenly irradiate the surface of the sample. The samples were placed on the handle in the implant chamber in the accelerator. Thus, the implantation dose of the samples could be calculated by measuring the electric charge flowing from the holder where the samples were placed. Then, modeling of ionizing radiation was given by using

SRIM simulation software. During the calculation, 10^6 ions were taken and calculated. The spectra were constructed by calculating the depth distribution of ions in the samples, the distribution of repulsive atoms, and the vacancies created by the implant ions in the sample.

The dielectric constant (ε) and tangent of the dielectric loss angle ($tg\sigma$) of the samples were measured using the E7-25 impedance measuring device. Measurements were made with a temperature difference of 1K, in the temperature range of 300-600K and in the frequency range 25Hz-1MHz.

The optical properties of the samples were investigated by the combined light scattering (Raman) method before and after exposure to ionizing radiation. The studies were performed on the NTEGRA Spectra LS PNL spectrometer. Helium / Neon laser was used as a laser in the spectrometer. The wavelength of the helium / neon laser is 632.8 nm. In order to make the experiment more effective, a laser with this wavelength was chosen. As the laser microscope used is confocal, illimunases only one point on the sample. Since the main condition is that the crystal surface is homogeneous, the combined scattering spectra of light (Raman) were taken at several points. Spectral solutions were not worse than ± 0,5 sm^{-1}. The combined scattering spectra of light (Raman spectrum) were studied at 300K room temperature. In order to minimize the thermal effect in the studied samples, the radiation power on the sample was weakened to the level of 600 μW - 2 mW. The size of the beam falling on the sample is about 1 micron. Signal accumulation time as a rule time was typically 0.5 to 1 minute. Each case in the size of the scattering spectrum of light was divided into Lorentzian peaks by using the least square procedur (solution).

The following issues have been resolved to achieve the goal:

1) Observation of anomalies in the temperature ε (T) dependence of the dielectric constant in the $TlGaSe_2$ crystal at temperatures T_1 = 415K, T_2 = 500K and T_3 = 532K;
2) Observation of anomalies in the temperature dependence of dielectric constant in the $TlInS_2$ single crystal at temperatures of 330K, 410K, 490K, 570K and 600K;

3) The electrical conductivity of $TlGaSe_2$ və $TlInS_2$ crystals have ion conductivity at temperature higher than 400K and is defined that this conductivity increase with the effect of gamma beams;
4) While the electronic components dominantes in conductivity at temperature lower than 400K at dependence of $TlInS_2$ crystal in the consant electric field, a rapid increase in the value of ion conductivity is observed with increasing temperature (higher than 400k);
5) It was shown that the numerical value and relaxation time of the dielectric constant of the $TlGaSe_2$ crystal implanted with 150 kV He^{2+} ions decreased by 10 times. This decrease was due to the increase in the concentration of mobile ions in the crystal structure as a result of implantation;
6) Investigations of the Combined Scattering of Light spectra of (Raman spectrum) $TlInS_2$ crystals implanted with H^+ ions show a significant increase in the spectral properties of In and Tl ions and a decrease in the Tl content in the surface layer of the crystal. Also it is observed amorphization in the structure of the crystal after implantation;
7) In $TlInS_2$ crystals implanted with H^+ ions, the main reason for the decrease in the numerical value of the dielectric constant and the decrease in the relaxation time as a result of implantation is the increase in the concentration of mobile ions;

Scientific novelty of the research. For the first time in layered single crystals $TlInS_2$ and $TlGaSe_2$:

1) Phase transitions were observed in $TlGaSe_2$ and $TlInS_2$ crystals at temperatures ($TlGaSe_2$ - T_1 = 415K, T_2 = 500K and T_3 = 532K), ($TlInS_2$-330K, 410K, 490K, 570K and 600K) respectively.
2) It was determined that $TlGaSe_2$ and $TlInS_2$ crystals had ionic conductivity at temperature higher than 400K and the activation energies from the ln (ε), ln (σT) dependencies were calculated.
3) The dispersion which was characterized by a decrease in the real and imaginary parts (Z' and Z'') of the impedance with the inerease of the freguency of the electric field and shifting toward the higher freguency region with the increase of the temperature was observed in the $TlGaSe_2$ and $TlInS_2$ single crystals, in the

frequency range of $25 \div 10^6$ Hs. The average relaxation period ($\tau = 1.54 \bullet 10^{-6}$ san) was determined In the frequency dependence of the imaginary part of the electrical module (M") of the TlGaSe crystal.

4) It was determined that, the strong change in the frequency and temperature dependence of the real and imaginary parts of the dielectric constant in $TlGaSe_2$ crystals under the influence of 20Mrad gamma rays is the result of the mobility of Tl ions and their activation in the temperature range.
5) The share of ions in the kinetics of electrical conductivity was estimated in the constant electric field of the $TlInS_2$ crystal at a temperature T = 470K. It was, found out that the share of ions in the electrical conductivity before irradiation is 78%, and after irradiation with 20 Mrad gamma rays is 82%.
6) The study of the real and imaginary parts of the dielectric constant and impedance of $TlInS_2$ crystals implanted with H+ ions in the range of 300-550K showed that the main reason for the decrease in the numerical value of dielectric constant and relaxation time was due to increased concentration of mobile Tl ions.
7) Amorphization in the structure of $TlInS_2$ crystals was observed as a result of the study of the combined scatter spectra of light after implantation with H^+ ions.
8) The depth distribution of atoms in the $TlGaSe_2$ crystal implanted with He ions has been given by using the SRIM (The Stopping and Range of Ions in Matter) simulation program. The distribution of He^{2+} ions in Tl cavities has been determined at a depth of 1000 nm.

Theoretical and practical significance of the research:

The results obtained in the dissertation can be widely used in the development of electronic converters, extreme high capacitance capacitors, supercapacitors for convenient use in nanoelectronics, food microbatteries, corememory cores, electricity and systems for the collection of optical information.

Studies show that, there is a "memory effect" in layered crystals of $TlGaSe_2$ and $TlInS_2$ that is observed to maintain a low resistance state for a long time after the external field is cut. This period is more than ≈ 50 hours for $TlGaSe_2$ and $TlInS_2$ layered crystals.

The following tasks have been solved to achieve the goal:

- Synthesis of $TlInS_2$ and $TlGaSe_2$ compounds and to grow of single crystals;
- Gamma irradiation of $TlInS_2$ and $TlGaSe_2$ crystals and make implantation with light ions (H^+, He^{2+});
- To investigate the electrical conductivity of $TlInS_2$ and $TlGaSe_2$ crystals in the wide temperature range (290-550K) and in a wide frequency range (20-10^6Hz) before and after gamma radiation and light ions implantation;
- To study of ionic conductivity properties of $TlInS_2$ and $TlGaSe_2$ crystals before and after implantation with light ions (H^+, He^{2+}) and gamma radiation;
- To find out the properties of the complex impedance spectrum of $TlInS_2$ and $TlGaSe_2$ crystals before and after implantation with light ions (H^+, He^{2+}) and gamma radiation;
- To explore the dielectric relaxation events of $TlInS_2$ and $TlGaSe_2$ crystals before and after implantation with light ions (H^+, He^{2+}) and gamma radiation;
- To investigate of Raman spectra of the $TlInS_2$ crystal before and after implantation with light ions (H^+, He^{2+});
- Modeling of ionizing radiation for $TlInS_2$ crystals;

Approbation and application. The results of the dissertation were report at the following conferences: “10-я международная конференция Ядерная и радиационная физика” (8-11 сентября 2015 г., г. Курчатов, Республика Казахстан), “52-ая Школа ПИЯФ по Физике Конденсированного Состояния” (Санкт – Петербург, Россия 12-17 марта 2018), “XII-th International Conference Ion Implantation and Other Applications of Ions and Electrons” (Lublin,Poland 18-21 July 2018), II Международный научный форум «Ядерная наука и технологии» 12-я Международная конференция «Ядерная и радиационная физика» 1-я Международная конференция «Ядерные и радиационные технологии в медицине, промышленности и сельском хозяйстве» (24-27 июня 2019 г. Алматы, Казахстан), The ninth international conference “Modern problems of nuclear physics and nuclear technologies” (24-27 September 2019, Tashkent, Uzbekistan).

Published scientific works: The content of the dissertation is published in 12 scientific works, including 7 articles in Republican and foreign journals, 5 conference materials. Two of the articles abroad in journals included in International databases, two are co-authors has been published.

Structure, volume and main content of dissertation work. The dissertation consists of the introduction, 4 chapter, results and list of 198 used literature. 62 figures, 6 tables and 249970 (174 page) symbols were used throughout dissertation.

CONTENT OF WORK

In the introduction, actuality of dissertation topic has been justified; the purpose of the research, scientific novelty and practical significance of the research has been shown; information about main provisions to be defended, degree of approbation, published works has been given and the main content of the chapters of dissertation work is briefly explained.

Chapter I of the dissertation consists of 30 pages. In the first chapter, literature data on structural and phase transitions, superion phase transitions of $A^3B^3C_2^6$ type semiconductor-ferroelectrics, implantation of semiconductors and radiation defects caused by ionizing radiation were collected and analyzed. From the analyzed literatures, it can be said that the both impact of gamma quanta and ionizing rays during implantation on semiconductor materials are little-studied fields.

In Chapter II synthesis of $TlGaSe_2$ and $TlInS_2$ single crystals and production by Bridgman-Stockbarger method is shown in detail and a description of the device is given. Also, schemes of γ-25 device (consisting of Co^{60} isotope) and UNIMAS 79 ion accelerator, E7-25 impedance measurement method to study electrical and dielectric properties and scheme and working principle of Raman spectroscopy device are described. This chapter provides detailed information on the lasers used in the Raman spectroscopy.

In the third chapter of the dissertation, the changes in the electrical and dielectric properties of $TlGaSe_2$ and $TlInS_2$ crystals before and after exposure to 20Mrad gamma rays has been studied using the E7-25 impedance measuring device. In addition, the optical properties of the $TlInS_2$ crystal were studied with the help of the Combined Scatter Spectrometer of Light (Raman spectrum). The methods used provide extensive information about the structural changes in these crystals as a result of the action of gamma rays, the electrophysical and optical properties of the crystals. Thus, under the influence of 20 Mrad gamma rays, in $TlGaSe_2$ and $TlInS_2$ crystals depending on the temperature an increase in the real and imaginary parts of the dielectric constant was observed. This is the result of the mobility of Tl ions in crystals and their activation in the temperature range. The dielectric and electrical properties of the crystals have been investigated and the existence of bounce conductivity has been determined based on the results of σ(T) studies.

Comparasion of the temperature dependence of the dielectric constant of the $TlGaSe_2$ crystal before and after irradiation with gamma rays is given in Figure 1. The study have conducted in the range of 275-550K and in the frequency field of 25Hs-1MHs. As it can be seen from Figure 1 (a), for the first time in the $TlGaSe_2$ crystal, at certain values of temperature (T_1 = 415 K, T_2 = 500 K və T_3 = 532 K), a sharp increase in the dielectric constant was observed. Also, at the $T>T_c$ low-frequency dielectric dispersion is observed and the characteristic dependence ε'(T) predominates in the measured value of ionic conductivity ε'. Temperature dependence of dielectric constant of $TlGaSe_2$ crystal after exposure to gamma quanta the numerical value of the dielectric constant increased by about 3 times (Figure 1 (b)). ln(ε)(1000/T) dependence was formed and activation energies were calculated. It is equal to ΔE_a^1 = 0.54eV, ΔE_a^2 = 0.4 eV in the absence of irradiation, and to ΔE_a^1 = 0.5eV, ΔE_a^2 = 0.38eV after the impact of 20Mrad gamma quanta. It is known that such a dependence of the dielectric constant indicates that ionic conductivity predominates at temperatures above the critical temperature. In our previous studies, we have shown that the ionic conductivity of this type of single crystal is related to the mobility of Tl ions. Because, the Ga-Se bond in the $TlGaSe_2$ crystal is more durable than the Tl-Se bond. Receiving higher values of dielectric constant in the $TlGaSe_2$ crystal at low frequencies are based on the mechanism of ionic polarization. This occurs due to the irregualiton in Tl^+ lower cage (weakly bound Tl ions).

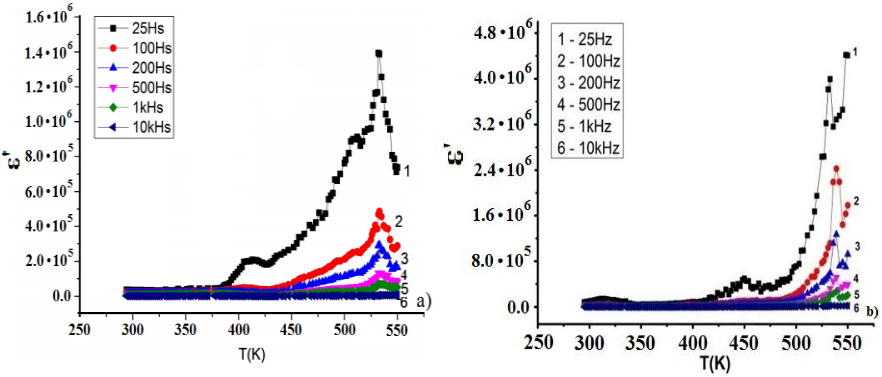

Figure 1. Temperature dependence of dielectric constant of $TlGaSe_2$ crystal before (a) and after irradiation (b) with γ-quanta

Temperature dependences of the real part of the dielectric constant of the $TlInS_2$ single crystal before (a) and after (b) irradiation with γ-quanta have shown in Figure 2 (a,b). The studies were performed in the frequency range of $10\text{-}10^6$ Hz and in the temperature range from room temperature to 600K. In this way, the temperature dependence of the dielectric constant ε'(T) of the $TlInS_2$ crystal both before and after irradiation with 20 Mrad γ-quanta have investigated.

As it can be seen from Figure 2(a), in the single crystal $TlInS_2$ at temperatures of 330K, 410K, 490K, 570K, and 600K phase transitions are observed and the numerical value of the real part of the dielectric constant increases sharply with increasing temperature.

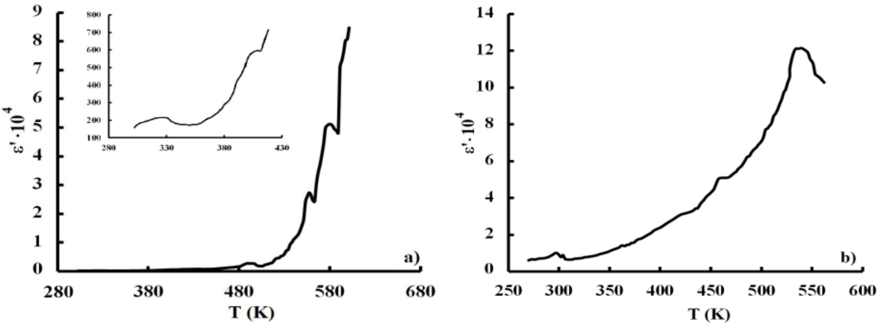

Figure 2. Temperature dependence of dielectric constant of $TlInS_2$ crystal before (a) and after irradiation (b) with γ-quanta

A sharp increase is can be more clearly observed in the value of the dielectric constant starting from a temperature of 490K. The increase in dielectric constant can be correlated with an increase in the concentration of ion carriers as a result of temperature rise. As can be seen from Figure 2 (b), with effect of γ-quanta, the real part of the dielectric constant increased. This is due to the increase in the concentration of the carriers as a result of the impact of γ-quanta and the increase in the mobility of the carriers as a result of the increase in temperature. For a non-irradiated $TlInS_2$ crystal, the activation energies were calculated using the 1/T dependence of ln(ε) (ΔE_a^1 = 0.3eV, ΔE_a^2 = 0.22eV). In Figure 2(a), the temperature range of 290-430K is enlarged has given at the top of the figure. The goal is to observe the maximums in this temperature range (330K and 410K). The experimental points in the 1/T - ln(ε) dependence are collected on a straight line. This indicates that the $TlInS_2$ single crystal has ionic character. After exposure to gamma rays (Figure 2 (b)), phase transitions has been observed on the temperature dependence of the dielectric constant, at temperatures of 290K, 410K, 470K and 550K, and activation energies (ΔE_a^1 = 0.29eV, ΔE_a^2 = 0.2eV) has been calculated by forming a 1/T - ln (ε) dependence. After exposure to gamma rays, the activation energies decrease and the dielectric constant slides towards the upper temperature range. As in the $TlGaSe_2$ crystal, the ln(ε) (1000/T) dependence line changes linearly both before and after irradiation for $TlInS_2$ crystal. This indicates that the dielectric constant has ionic character and diffusion of Tl^+ ions is occuring in vacancies of the bottom cages of the sample. As a result of the phase transition in the $TlInS_2$ crystal, the lower cage of Tl ions is observed to melt. This is a characteristic case for ion-conducting compounds. Big numerical value of dielectric constant in the paraelectric phase before and after irradiation allows these materials to be used in an ionizing environment.

The temperature dependences of the tangent of the dielectric loss angle of $TlGaSe_2$ and $TlInS_2$ crystals at different frequencies has been studied before and after irradiation with gamma quanta. The results show that as the frequency increases, maximums of tgδ(T) slides towards upper temperature range, and the numerical value of tgδ decreases. In both samples, the tangent of the dielectric loss angle increases with increasing temperature and reaches a maximum at a given temperature. Then it decreases again with increasing temperature. This decrease is called relaxation reduction. This is typical for Debay-type relaxation processes. Under the influence of gamma radiation, value of the dielectric loss angle had been decreased by more than 2 times and chaoticity was observed in temperature dependencies.

Broadband impedance spectroscopy is a very useful method for studying the structure, dynamics and relaxation of solids. This information is important for the purchase of new materials and for the development of those materials. In this chapter, the impedance spectra of $TlGaSe_2$ and $TlInS_2$ crystals have been studied at four constant temperatures (293K, 323K, 372K, 431K) and in the 25-1MHz frequency range. The temperature dependence of the real part of the impedance for the $TlGaSe_2$ crystal had shown comparatively before and after irradiation. As the temperature increases, real part of the complex impedance decreases. It is a common case for the real part of the impedance to decrease at high frequencies. As the frequency of the applied alternating electric field increases, the impedance begins to decrease because of the dipoles noncompliance with field changes at high frequencies, as well as the effects of electrode polarization. Under the influence of ionizing radiation, the value of the real part of the complex impedance increases and a certain chaoticity can be observed. Under the influence of gamma rays, real part of the complex impedance decreases with increasing frequency.

The electronic sum of conductivity in the $TlInS_2$ crystal has been determined by the Wagner polarization method. In Wagner's method , change in electrical conductivity with temperature in a constant electric field for ionic or charged solid electrolytes with electron-ion characteristics is observed. This is based on the formation of a polarization process in the crystal. This creates a double electric layer at the sample/electrode boundary. Because loaded ions are trapped at the isolation electrode sample/electrode boundary, mobile ions accumulate at the negatively charged electrode as a result of the electric field. Kinetic study of time dependence the conductivity for the $TlInS_2$ crystal in the 0-60Mrad dose range has shown in Figure 3.

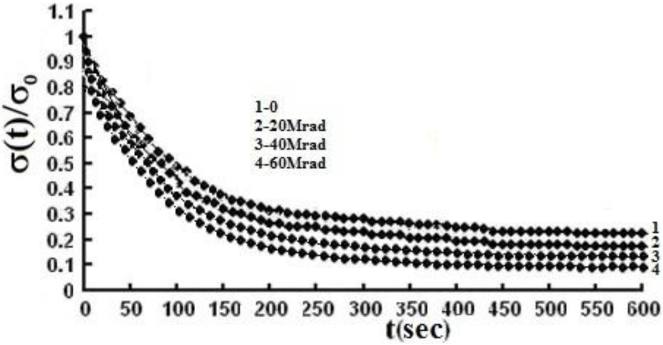

Figure 3. At T = 470K, the kinetics of the electrical conductivity of the $TlInS_2$ crystal irradiated with γ-rays: 1-0; 2-20Mrad; 3-40Mrad; 4-60Mrad

As can be seen from Figure 3, the electrical conductivity initially decreases exponentially and remains unchanged after a certain time. The nonlinear decrease of electrical conductivity occurs more rapidly at relatively high temperatures. Decrease in current with time (in the field of stable electricity) is the result of the mutual compensation of the volume loads near the isolating electrodes. And the results show that as the radiation dose increases, role of hte electrons in the total conductivity decreases and the role of ions increases. Ion share was calculated at 470K temperature before and after the effect of 20 Mrad γ-quanta. The share of ions in the non-irradiated $TlInS_2$ crystal is 78%, and 82% after exposure to 20Mrad γ-rays.

Electrical modulus formulas are often used to study the relaxation processes that occur in ion-conducting material. The complex electrical module can be expressed as $M^{*} = 1/\varepsilon^{*} = M' + jM''$. Because it is possible to determine the duration of relaxation with the help of processes occurring in electrical conductivity. At the same time, the effect of blockage of the electrodes goes down to a minimum. A M' to M″ diagram (Cole-Cole diagram) has been formed on a complex plane for the M* complex electrical module.

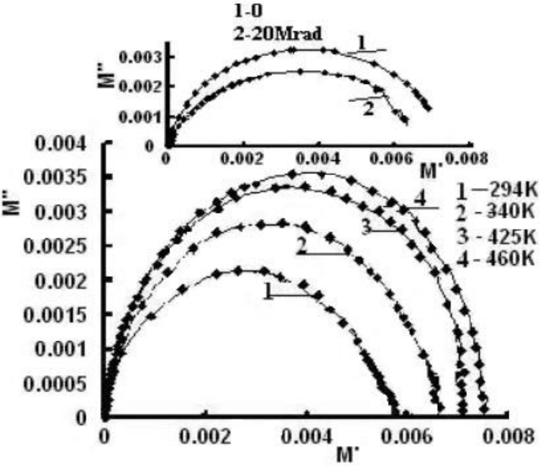

Figure 4. M'' - M' diagram for complex electrical module at different temperatures for $TlInS_2$ combination: 1- 294K; 2-340K; 3-425K; 4-460K. The appendix of the figure shows the diagram M'' - M' at 386K: 1-0; 2-20 Mrad.

Dependence of the electrical modules M''(M') before and after irradiation with 20Mrad γ-quanta can be seen from Figure 4 for $TlInS_2$ crystals at a temperature of 386K. As can be seen from Figure

4, the frequency dependences M"(f) and M'(f) are clearly defined in the diagram M" - M'. As can be seen from the appendix to Figure 4, a decrease is observed in the imaginary part of the electrical modulus M" of the $TlInS_2$ crystal irradiated with 20Mrad γ-quanta.

All information on the dynamics of the crystal lattice is obtained by conducting experiments with inelastic neutron scattering, Raman (Combined Scattering of Light) spectroscopy. In this chapter, Raman spectrum (Combined Scattering of Light) of the $TlInS_2$ crystal were studied using a He-Ne red laser at room temperature. 6 Raman (Combined Scattering of Light) lines were identified in the spectrum at a temperature of 300K. It was found that the maximum value intensity at room temperature is 291 cm^{-1} for $TlInS_2$. Thus, for the C_{2h}^6 symmetry geometric group, $10A_g$ phonons was observed via group-theoretical analysis. It should be noted that the total number of phonons observed and the polarization behavior exclude the C_s^4 symmetry group.

The fourth chapter of the dissertation presents the research results of $TlGaSe_2$ and $TlInS_2$ compounds implanted with light ions (H^+, He^{2+} ions) with the energy of 150KeV. Electrical, dielectric and Raman spectra (Combined Scattering of Light) has been studied by implantation of $TlGaSe_2$ and $TlInS_2$ crystals.

In Chapter 3, it was shown that, in ionically conductive $TlGaSe_2$ and $TlInS_2$ crystals, the conductivity increases exponentially with increasing temperature. Along with this increase, an exponential increase was observed in the numerical value of the dielectric constant. Dielectric constant gets bigger values at high temperatures. The reason of this is related to the displacement of Tl atoms on the ab surface. In this chapter, changes in the dielectric constant of the $TlGaSe^2$ crystal as a result of the impact of H^+ and He^{2+} ions are studied.

Figure 5 illustrates the temperature dependence of the real part of the dielectric constant of $TlGaSe_2$ crystals after implantation with H^+ and He^{2+} ions. Real part of the dielectric constant was investigated in a range from room temperature to 550K, and starting from 500K sharp increase is observed in value of the real part of the dielectric constant.

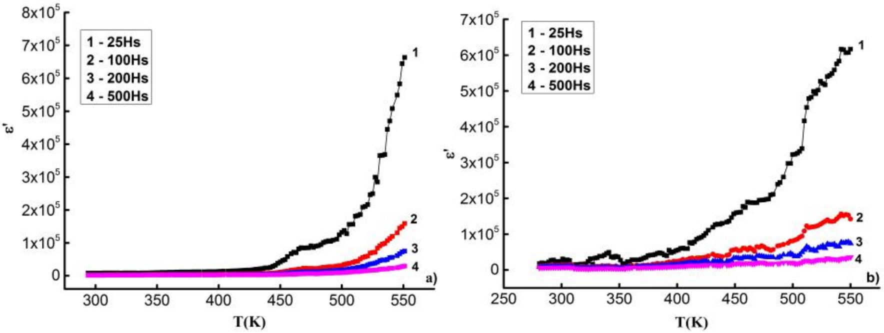

Figure 5. Temperature dependence of dielectric constant of $TlGaSe_2$ crystal (implanted with a-H^+; b-He^{2+} ions)

After implantation with H ions, phase transitions was observed in the $TlGaSe_2$ crystal at temperatures of 470K and 540K. Similarly, phase transitions was observed as a result of implantation with He^{2+} ions. After the impact of He^{2+} ions, the maximums of dielectric constant slides into the upper temperature range. Activation energies were calculated using the ln(ε)-1000/T dependence after the effect of implantation. Calculated activation energy values are as following: after implantation with H^+ ions ($\Delta E_a^1 = 0.45eV$, $\Delta E_a^2 = 0.36eV$), after implantation with He^{2+} ions, ($\Delta Ea^1 = 0.4eV$, $\Delta Ea^2 = 0.32eV$). Ion-type defects as a result of implantation play a key role in decrease of dielectric constant value. Along with the increase, certain anomalies were observed at 460K under the influence of H^+ ions.

The results of the study of the temperature dependence of the electrical conductivity of the $TlInS_2$ crystal before and after implantation with H^+ ions are given. Value of the electrical conductivity increases sharply, starting from 450K in the temperature dependence of electrical conductivity $\sigma(T)$ of the $TlInS_2$ crystal. This, as known from the literature, associated with ionic conductivity. Numerical value of electrical conductivity increases by two order after exposure to ionizing radiation.

Activation energies of $TlGaSe_2$ and $TlInS_2$ crystals after exposure to ionizing radiation were calculated and given in Table 1. As can be seen from Table 1, after exposure to ionizing radiation the activation energies decrease. The largest decrease was observed after implantation with He^{2+} ions with energy of 150KeV. In these crystals the main reasons of the decrease in activation energies after exposure to ionizing radiation is the increase in the concentration of mobile ions and the mobility of Tl ions.

Table 1. Activation energies for $TlGaSe_2$ and $TlInS_2$ crystals

$TlGaSe_2$		**$TlInS_2$**
unradiated	$\Delta E_a^1 = 0.54eV, \Delta E_a^2 = 0.4eV$	$\Delta E_a^1 = 0.3eV, \Delta E_a^2 = 0.22eV$
20Mrad	$\Delta E_a^1 = 0.5eV, \Delta E_a^2 = 0.38eV$	$\Delta E_a^1 = 0.29eV, \Delta E_a^2 = 0.2eV$
H^+	$\Delta E_a^1 = 0.45eV, \Delta E_a^2 = 0.36eV$	$\Delta E_a^1 = 0.26eV, \Delta E_a^2 = 0.19eV$
He^{2+}	$\Delta E_a^1 = 0.4eV, \Delta E_a^2 = 0.32eV$	$\Delta E_a^1 = 0.23eV, \Delta E_a^2 = 0.17eV$

This chapter presents the temperature dependences of the real (Z′) and imaginary (Z") parts of the $Z^*(f)$ complex impedance spectrum of $TlGaSe_2$ and $TlInS_2$ crystals implanted with H^+ and He^{2+} ions with an energy of 150 keV in the 25Hs-1MHs frequency range. Frequency dependencies at different temperatures have also been studied. With increasing temperature, the frequency dependence of the real part of the complex impedance gradually shifts, and the frequency dependence of the imaginary part of the impedance slides into the upper frequency range as a result of the impact of implantation. Decrease in the numerical value of the impedance is observed with increasing frequency of the electric field in the frequency dependence of the impedance. For the $TlInS_2$ crystal, relaxation time was calculated by forming the frequency dependences of the real (Z′) and imaginary (Z") part of the impedance at constant temperatures (300K, 405K, 470K, 530K, 590K). In $TlInS_2$ crystals at relatively high temperatures, relaxation time is around 10^{-3} seconds before irradiation, but decreases to $5x10^{-5}$ seconds as a result of irradiation.

Using the SRIM-2013 simulation program, in a $TlInS_2$ crystal implanted with H^+ and He^{2+} ions with 150keV energy distribution of ions at depth, vacancies created by implantation ions, and the distribution of repulsion atoms were calculated and mathematical models were given in the form of spectras.

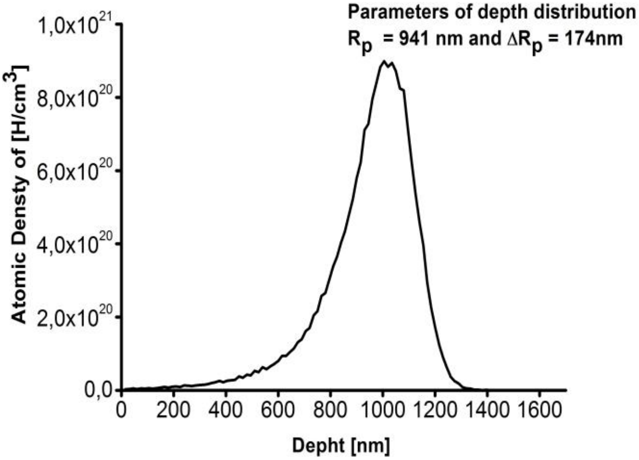

Figure 6. Distribution of implant (H^+) ions in $TlInS_2$ crystal at different depths

10^6 ions were taken as a basis during the calculation in the simulation program SRIM-2013. In Figure 6 the atomic density of the implantation ions (H^+) at depth in the $TlInS_2$ crystal has been shown. As can be seen from the figure, the distribution at maximum depth is R_p = 941nm. In general, the distribution of H^+ implant ions is in the depth range of 174-1350nm.

The distribution of vacancies at different depths in the $TlInS_2$ crystal is shown in Figure 7. As it can be seen from Figure 7, ions can create vacancies in the target atoms to a approximate depth of 950 nm. This is the maximum range observed in a $TlInS_2$ crystal implanted with (H^+) ions which have 150 keV energy. According to SRIM simulations, maximum distribution of Tl gaps is at depth of 1000 nm.

Also in this chapter, the combined scattering spectra of light before and after implantation of the $TlInS_2$ crystal with the H^+ and He^{2+} ions has been investigated and presented as comparision.

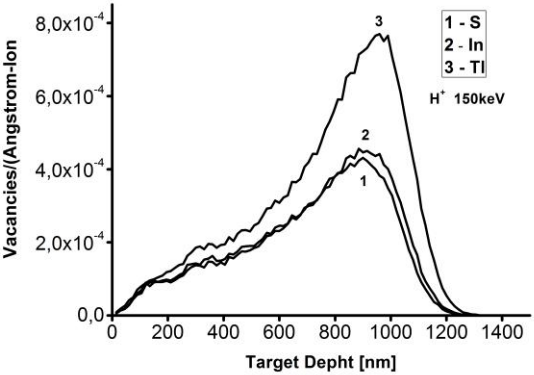

Figure 7. Distribution of vacancies in target atoms at different depths

Raman spectra (Combined Scattering of Light) captured on an NTEGRA Spectra LS PNL spectrometer at room temperature, in the 50-4000 cm^{-1} Raman range, and using a He/Ne red laser with a wavelength of λ=633nm. Comparision of Raman spectras (Combined Scattering of Light) of the $TlInS_2$ crystal before and after implantation with H^+ ions is given Figure 8. Six peaks (58.1, 81.2, 137.5, 180.1, 291.4, 346.2 cm^{-1}) were identified in the Raman spectra of the non-implanted $TlInS_2$ crystal. After implantation with H^+ ions, 4 peaks were identified. The maximum photosensitivity of the Raman spectrum after H^+ implantation was observed at the λ=194 cm^{-1} frequency. Compared to the initial case, the maximum photosensitivity of the implanted $TlInS_2$ crystal is reduced by 10 times approximately. Some differences was observed during comparision of Raman spectras (Combined Scattering of Light) before and after implantation. This is reflected as the decrease in the intensity of the lines and the disappearance of some of them. These effects depend on the ion masses which implant target sample.

Comparision of Raman spectrum (Combined Scattering of Light) of the $TlInS_2$ crystal before and after implantation with He^{2+} ions illustrated in Figure 9.

As in Figure 8, disappearance of some peaks and differences in the intensities of existing peaks under the influence of implantation can be seen here. In both figure, a new peak was formed at a frequency of 194 cm^{-1} under the influence of implantation. As it can be seen from both figures, amorphization occurs under the influence of implantation. As a result of the impact of light ions donor-type radiation defects occur.

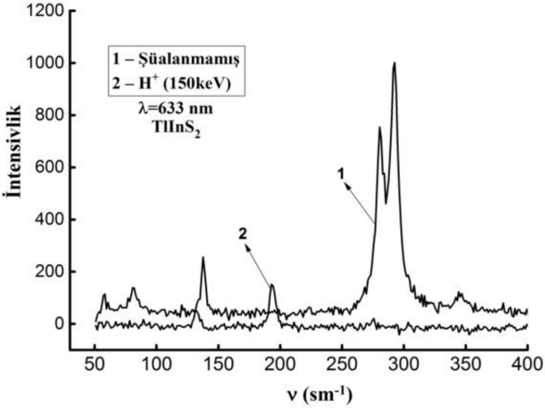

Figure 8. Raman spectra of $TlInS_2$ crystal (1-non-implanted, implanted with 2-H^+ ions)

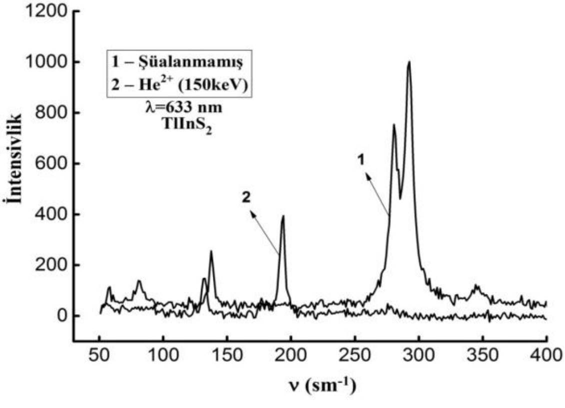

Figure 9. Raman spectra of $TlInS_2$ crystal (1-non-implanted, implanted with 2-He^{2+} ions)

MAIN RESULTS

1) For the first time, in the $TlGaSe_2$ crystal at temperatures T_1 = 415K, T_2 = 500K and T_3 = 532 K an sharp increase is observed in dielectric constant. It has been shown that the electrical conductivity in these phases has ionic character. Activation energies were calculated from the dependencies ln(ε) and ln(σ). Before irradiation, $\Delta E_a^1 = 0.54$eV, $\Delta E_a^2 = 0.4$eV and after exposure to 20 Mrad gamma rays, the activation energies are $\Delta Ea^1 = 0.5$eV, $\Delta Ea^2 = 0.38$eV. This is because of the irregularity in the lower cage of Tl^+ (weakly bounded Tl ions).
2) For the first time, in the $TlInS_2$ crystal anomalies was observed in the ε(T) dependence of the dielectric constant at temperatures of 330K, 410K, 490K, 570K and 600K. Activation energies are equal to $\Delta E_a^1 = 0.3$eV, $\Delta E_a^2 = 0.22$eV. In the 1/T dependence of ln(ε), the experimental points was formed on a straight line, which indicates that the conductivity has ionic character. After exposure to gamma rays, phase transitions was observed in temperature dependence of dielectric constant at 290K, 410K, 470K and 550K temperatures. Activation energies was calculated $\Delta E_a^1 = 0.29$eV, $\Delta E_a^2 = 0.2$eV. After exposure to gamma rays, the activation energies decrease and the maximums of dielectric constant slides into the upper temperature range.
3) It was determined that, in $TlGaSe_2$ single crystal, increasing frequency of the electric field in the $25 \div 10^6$ Hs frequency range cause dispersion in the maximums which is characterized by a decrease in the real and imaginary components of the impedance (Z' and Z''). The average relaxation time has been calculated from the frequency dependence of the imaginary part (M") of the electrical module of the sample ($\tau = 1.54 \bullet 10^{-6}$ san).
4) In the constant electric field, in the σ(T) dependence of the $TlInS_2$ crystal electron conductivity dominates at low temperatures, while the increase in the value of ionic conductivity was observed with increasing temperature. The kinetics of the electrical conductivity of the $TlInS_2$ crystal irradiated with γ-rays in the 0-60 Mrad dose range was presented. It was shown that, as the radiation dose

increases, the share of electrons in the total conductivity decreases, and as a result, the share of ions increases. It was, foundout that the share of ions in the electrical conductivity before irradiation is 78%, and after irradiation with 20 Mrad gamma rays is 82%.

5) The depth distribution of atoms in the $TlGaSe_2$ crystal implanted with H^+ ions has been given using the SRIM program and the distribution of H^+ ions in Tl cavities was determined at a depth of 1000 nm. Investigation of dielectric constant and imaginary and real parts of impedance at 300-500K in $TlInS_2$ crystals implanted with H^+ ions showed that, decrease in numerical value of dielectric constant and relaxation time is related to increase in concentration of mobile ions.
6) It was shown that the numerical price and relaxation time of the dielectric constant of the $TlGaSe_2$ crystal implanted with 150 keV He^{2+} ions decreased. This decrease is due to the increase in the concentration of mobile ions in the crystal structure as a result of implantation.
7) Studies of the Raman spectras of $TlInS_2$ crystals implanted with H^+ ions have shown a significant enlargement in the spectral properties of In and Tl ions and a decrease in the Tl content in the surface layer of the crystal. This is associated with amorphization in the crystal structure after implantation.

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