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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

STRUCTURE AND RADIATION DEFECTS IN Bi_2Te_3, Bi_2Se_3, Sb_2Te_3 COMPOUNDS, THEIR EFFECT ON THERMODYNAMIC PROPERTIES

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GENERAL DESCRIPTION OF THE WORK

Relevance and development of the work. The dissertation is devoted to the synthesis of double semiconductor compounds with various interesting physical properties, the study of thermodynamic properties of the obtained research samples and the effect of heavy ions on these properties. Modern semiconductor compounds Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 are functional materials widely used in electronics. The recent observation of topological isolation in these compounds creates new opportunities for new technological applications. It is known that under external influences (electric field, magnetic field, pressure, temperature, etc.) various changes are observed in the physical properties of semiconductors. Therefore, the study of various physical properties under external influences determines the applicability of these materials.

For the application of inverters based on $A_2^{V}B_3^{VI}$ binary compounds in space technologies, nuclear reactors, accelerators, it is important to study these compounds under the influence of radiation. Recently, the study of the effect of high-energy heavy ions on functional materials with different properties is considered one of the main areas of research not only in semiconductor physics, but in materials science in general. It has been established that significant changes occur not only in the surface properties of compounds implanted with heavy ions, but also in other physical properties, depending on the depth of penetration. Therefore, the study of changes in the physical properties of samples irradiated with heavy ions depending on the radiation dose creates new applications for these compounds.

Among the studies of the various properties of heavy ions and semiconductor materials, the effect of 167 MeV Xe^{+26} ionizing radiation has a special place. These high-energy ions cause the formation of non-uniform radiation defects along the thickness of the samples. These defects affect not only the structural properties, but also the thermodynamic properties of the compounds. In the presented dissertation the effect of Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 semiconductor

binary compounds and 167 MeV Xe^{+26} ionizing radiation on the observed thermal transitions was studied. The mechanism of change of thermodynamic parameters under the influence of radiation has been determined. In order to study the structural defects in $A_2^{V}B_3^{VI}$ binary compounds in more detail, the $Bi_2Te_{2.7}Se_{0.3}$ compound was intercalated with Ni atoms, and the surface structure and crystal structure of the obtained material were studied.

Object and subject of research:

The object of research is the study of Bi_2Te_3, Bi_2Se_3, $Bi_2Te_{2.7}Se_{0.3}$ and Sb_2Te_3 compounds, and the subject is the study of the effect of defects in these compounds on thermodynamic properties and electrophysical properties of Ni ions $Bi_2Te_{2.7}Se_{0.3}$ compounds.

The purpose and objectives of the study:

The purpose of the dissertation is to determine the effect of defects on the thermodynamic properties of Ni_2Te_3, Bi_2Se_3, Sb_2Te_3 compounds in the $A_2^{V}B_3^{VI}$ group and on the electrophysical properties of Ni ions in $Bi_2Te_{2.7}Se_{0.3}$ compounds.

In accordance with the purpose of the dissertation, the following issues were resolved:

- Investigation of the compliance of thermodynamic parameters with the law of change of thermodynamic parameters in layered crystals after irradiation with heavy ions, depending on the composition of the substance;
- Investigation of thermodynamic properties of binary semiconductor compounds Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 in the wide temperature range, determination of thermodynamic parameters;
- Study of the effect of heavy ions on the thermodynamic properties of the compound Bi_2Se_3, determination of changes in thermodynamic properties and thermodynamic parameters of bismuth selenium irradiated with Xe^{+26} ions of 167 MeV at different doses;
- Investigation of thermodynamic properties of Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 compounds by the method of differential thermal analysis, calculation of free energy and enthalpy of processes occurring at melting temperature;

- Determination of free energy and enthalpy in bismuth tellurium during implantation with Xe^{+26} ions, determination of the mechanism of change of thermodynamic parameters in this compound under the influence of heavy ions;
- Study of thermodynamic properties of Sb_2Te_3, study of the effect of Xe^{+26} ions on these thermodynamic parameters, calculation of thermodynamic parameters at that temperature;
- Intercalation of $Bi_2Te_{2.7}Se_{0.3}$ with Ni atoms. Investigation of compounds formed by the action of Ni ions in the plane-crystal structure of the structure and in the layers of the crystal, in the surface structure of the Vander-Vaals.

Research methods:

The research objects were synthesized under vacuum conditions by the standard method. Structural phase analysis of the obtained compounds and determination of cage parameters were carried out on a D8 Advance (Bruker) X-ray diffractometer by X-ray diffraction method at room temperature and under normal conditions. The atomic dynamics of the compounds were studied at room temperature and under normal conditions by the Raman spectroscopy method on a Nanofinder 30 Raman spectrometer. The obtained Raman spectra were analyzed with the Gaussian function in the latest version of the Origin program. Thermodynamic parameters of research objects irradiated with heavy ions before irradiation and at different fluxes were performed on the STA 6000 device "Perkin Elmer" by the method of Differential Thermal Analysis. The SRIM analysis method was used to study the depth of diffusion of heavy ions into Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds. Heavy ion irradiation experiments were performed under vacuum conditions in the IC-100 cyclotron at the Flyorov Nuclear Reaction Laboratory of the Joint Institute for Nuclear Research (Dubna, Russia).

Atomic Force Microscope and Scanning Electron Microscope analysis methods were used to study changes in the surface and layers of the compounds.

Defensive provisions:

1. Investigation of the thermodynamic properties of Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 crystals in the temperature range 500°C ≤ T ≤ 720°C as a result of ionization of heavy Xe^{+26} at 167Mev.
2. During irradiation with heavy Xe^{+26} ions of 167 MeV to 3.83×10^{14} cm^{-2} fluxes, various changes occurred in the values of thermodynamic parameters due to the occurrence of structural defects in Bi_2Se_3. Melting temperature T=705°C to T=636°C, peak energy corresponding to melting temperature, activation energy was determined.
3. The value of Vigner's enthalpy, temodynamic parameters: free energy, activation energy in the temperature range 85°C≤T≤556°C in Bi_2Te_3 compound were determined.
4. Melting temperature due to defects in bismuth tellurium during irradiation with Xe^{+26} ions of 167 MeV to 3.83×10^{14} cm^{-2} flux, the corresponding peak energy, activation energy were calculated.
5. The penetration depth of 167 MeV Xe^{+26} ions into the bismuth selenium compound was calculated. The depth of penetration depends on the energy of the heavy ions.
6. Melting temperature, corresponding energy, activation energy were determined due to defects in Sb_2Te_3 compound during irradiation with Xe^{+26} ions of 167 MeV to 3.83×10^{14} cm^{-2} flux.
7. During the intercalation of $Bi_2Te_{2.7}Se_{0.3}$ with Ni ions, the formation of a two-phase system and the formation of nanostructures in the surface structure of Vander-Vaals was shown.

Scientific novelty of the research:

-Defects occur during irradiation of Bi_2Se3, Bi_2Te_3, Sb_2Te_3 crystals with heavy Xe^{+26} ions of 167 MeV. In the temperature range of 500°C ≤T≤ 720 °C, the melting temperature decreases.

- During irradiation with heavy Xe^{+26} ions of 167 MeV to 3.83×10^{14} cm^{-2} fluxes, various changes occurred in the values of thermodynamic parameters due to the occurrence of structural defects in Bi_2Se_3.Melting temperature T = 705 °C to T = 636 °C, heat energy used for melting: E_s = 7.87 μC to 5.66 μC, and activation energy E_{Akt}=0.086 C / mol to 0.042 C / mol decreases to.

- The value of Wigner's enthalpy in the temperature range 85 °C $\leq T \leq$ 556 °C in Bi_2Te_3 compound V_E = 16.7 C / q, peak temodynamic parameters corresponding to temperature T = 585 °C: free energy - E_s=7.25 μC, activation energy - E_{Akt} = 0.092 C / is equal to mol.

- Due to defects in bismuth tellurium during irradiation with Xe^{+26} ions of 167 MeV to 3.83 × 10^{14} cm^{-2} fluxes, the melting temperature decreases from T = 585 °C to T = 555 °C, the peak energy accordingly: E_s = 7.25 μC from 4.4 μC, and the activation energy decreases from E_{Akt} = 0.092 C / mol to 0.041 C / mol.

- Heavy Xe^{+26} at -167 MeV calculated the penetration depth of their bismuth selenium compound.

- Melting point: T = 626° C to T = 528 °C, corresponding energy: from E_s = 7.26 μC To 3.8 μC, and the activation energy decreased from E_{Akt} = 0.07 C / mol to 0.036 C / mol.

- During the intercalation of the compound -$Bi_2Te_{2.7}Se_{0.3}$ with Ni ions, nanocrystalline particles (grains) and nanofibers were formed on the surface of Van-Vaals.

Theoretical and practical significance of the research:

Bi_2Te_3, Bi_2Se_3, $Bi_2Te_{2.7}Se_{0.3}$ and Sb_2Te_3 have a special place among semiconductor compounds. The discovery of topological isolation in these compounds has created new applications in modern electronics. Therefore, they are of great scientific and practical importance for the study of various physical properties of compounds, their application in various fields and the synthesis of new functional composite materials based on them.

Research in the field of high temperatures is important. Thus, overheating occurs during use in various applications, including electronics. In this case, depending on the heating temperature, the working materials may not perform their function. Therefore, it is very important to study each material under the influence of temperature and determine the working area.

The study of the effect of heavy ions on the various physical properties of functional materials increases the field of application of these materials. It is known that semiconductor compounds are widely studied in various fields of electronics. They can also be used in

accelerators, aviation technology, spacecraft. It is known that various external influences occur in these areas, and as a result of these influences, the semiconductor material can change its working area. Therefore, the irradiation of Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 compounds with heavy ions is very important to study the effect of radiation on their phase transitions.

Although the results obtained in this study are of an applied nature, they are also important in terms of fundamental physics. Determining the phase transitions corresponding to the melting temperature, the change in the state of the system and finding the thermodynamic parameters of these phase transitions, the calculation of the energy stored in the crystal structure - Vigner's enthalpy are very important for theoretical calculations on these systems.

Approbation and application:

The main research results obtained in the dissertation were discussed at national and international conferences:

- 15^{th} International Confrance on "Texnical and Physical Problems of Electrical Engineering" (ICTPE), 14-15 october 2019, Istanbul, Turkey;
- International scientific-practical conference "Prospects for the application of magnetic alloys in information technology and military industry." Azerbaijan Architecture and Construction University. October 9-11, 2019, Baku, Azerbaijan;
- Second International Scientific Conference of Young Scientists and Specialists Multidisciplinary approaches in solving modern problems of fundamental and applied sciences (Natural sciences), 3-6 march 2020, Baku, Azerbaijan;
- 9^{th} Rostocker International Conference: "Technical Thermodynamics: Thermophysical Properties and Energy Systems", October, 2020, Rostock, Germany.
- "Amorphous and microcrystalline semiconductors.Proceedings of the International Conference", 05-07-July 2021, Saint -Petersburg, Russia.

The results of the dissertation were published in 15 scientific papers, including 10 articles (including 3 foreign journals included in the Web of Sciences) and 5 conference theses.

Name of the organization where the dissertation work is carried out:

Dissertation work, performed in the "Acoustoptics" laboratory of the Institute of Physics named after academician of the Azerbaijan National Academy of Sciences.

The structure and scope of the study:

The dissertation consists of an introduction, five chapters, main results, 2 tables, 17 figures, 22 graphs and a total of 241058 characters, including 123 references.

CONTENT OF THE WORK

The introduction reflects the relevance and prospects of the topic of the dissertation, the purpose of the work, scientific innovations, scientific and practical significance, the purpose and the main provisions for the defense.

The first chapter of the dissertation is devoted to a review of the literature on the results of previous research on the objects of research Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 binary semiconductor compounds. The crystal structures of these compounds are given: lattice parameters, symmetries, atomic coordinates. The structural transformations and phase transitions corresponding to the melting temperature were analyzed for each composition, and the structural properties of the different phases were shown. The results of the research obtained by various diffraction methods were investigated. Cage parameters, atomic coordinates, lengths of interatomic bonds and angles between bonds are shown. This chapter also examines the thermodynamic properties and thermodynamic parameters of double semiconductors. Thermodynamic processes occurring in these compounds, changes in thermodynamic parameters during phase transitions, the importance of Differential Thermal Analysis in semiconductors, theoretical analysis of the obtained experimental

results are shown. Differential Thermal Analysis and Thermographimetric Analysis methods are used to determine the phase transitions that occur in solids, including semiconductors, and to calculate the thermodynamic parameters of solid-liquid phase transitions.

The effect of radiation on semiconductors and especially on $A_2^{V}B_3^{VI}$ binary semiconductor compounds has been studied, and changes in semiconductors under the influence of ionizing radiation have been studied. Radiation with heavy ions in solids and their effect on various physical properties are explained. Previous studies in semiconductors have provided extensive information on the formation of defects under the influence of 167 MeV Xe^{+26} ions and the effect of these defects on various physical properties.

Thesecond chapter is devoted to the experimental methods designed to achieve the goal of the dissertation, the various analysis methods used to analyze the research results, software and devices. X-ray diffraction, Raman spectroscopy, Differential Thermal Analysis, ion implantation, SRIM analysis methods were used during the researches.

Synthesis of Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 compounds in high temperature furnaces, obtaining crystals of these compounds by standard method, selection of optimal mode during the synthesis process and research process in high temperature furnaces are shown. Structure data were determined by analyzing the obtained X-ray diffraction spectra[1] .

Atomic dynamics studies were performed by Raman spectroscopy to determine the differences in the crystal structure of the objects, and the thermodynamic properties of objects irradiated with heavy ions before irradiation and at different fluxes were studied by the method of Differential Thermal Analysis. It was irradiated at the Flyorov Nuclear Reactions Laboratory.

[1]Heiker D.M. X-ray diffractometry / -M: Phys. 1963. - 380 p.

Thethird chapter presents the results of research using X-ray diffraction, Raman spectroscopy and Differential Thermal Analysis methods[2]

The results of research on the crystal structure, atomic dynamics, thermal properties and thermodynamic parameters of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds are given.

It was found that each of these compounds crystallizes in a highly symmetrical rhombohedral syngonium.

The small differences in the lattice parameters are explained by the difference between the ionic radii of the elements included in the compounds.

Structural phase analyzes were performed for each of the different components by X-ray diffraction at room temperature and under normal conditions. It was found that the crystal structures of the research objects have a rhombohedral symmetry with high symmetry. The differences in the crystal structure are explained by the difference between the ionic radii of the Bi-Sb and Se-Te atoms. This diversity has been observed not only in structural studies, but also in atomic dynamics studies using the Raman spectroscopy method.

There are 3 main dance modes in the Raman spectrum of Bi_2Se_3. ν_1=56.22 cm^{-1}, ν_2=98.73 cm^{-1} and ν_3=133.84 cm^{-1} were determined. It has been established that these dance modes, which can be observed experimentally by the Raman spectroscopy method, correspond to the Bi-Se and Se-Se bonds. Dance fashions corresponding to Bi-Bi bonds have not been observed experimentally.

The Raman spectrum of the bismuth telluride compound also corresponds to the dance modes observed in the Raman spectrum of the bismuth selenide compound. 3 Raman mode: ν_1 = 59.19 cm^{-1}, ν_2=100.52 cm^{-1} and ν_3 = 135.34 cm^{-1} It was observed that these dance modes fall into the low frequency range corresponding to Bi-Te and Te-Te bonds.

The atomic dynamics of the Sb_2Te_3 compound is more complex than the atomic dynamics of the Bi_2Se_3 and Bi_2Te_3 compounds. Four

[2]Smykatz-Kloss, W. Differential Thermal Analysis /- Berlin: Springer, 1974.- 185 p.

dance modes were observed in the Raman spectrum obtained under normal conditions: ν_1 = 43.31 cm^{-1}, ν_2 = 66.32 cm^{-1}, ν_3 = 97.27 cm^{-1} and ν_4 = 131.08 cm^{-1}, which is consistent with the results of previous studies. These dance modes correspond to the dances of Sb - Te and Te - Te bonds.

Thus, the structural properties of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 crystals at room temperature and under normal conditions were studied comprehensively by X-ray diffraction and Raman spectroscopy methods. It has been found that small differences in the ionic radii of the Bi → Sb and Se → Te atoms cause significant differences both in the crystal structure and in the atomic dynamics of the crystals. This difference is more pronounced during Bi → Sb cation substitutions. Thus, the crystal structures and atomic dynamics of Bi_2Se_3 and Bi_2Te_3 compounds are more similar. Bi_2Te_3 and Sb_2Te_3 compounds differed in both the number of Raman modes and the interpretation of the crystal structure.

It has been found that when the ionic radii of the atoms in the composition are large, the frequencies of the Raman modes decrease, which is explained by the increase in the length of the interatomic bonds. When the ionic radii of atoms are small, however, the lengths of the interatomic bonds decrease, resulting in an increase in the frequencies of the Raman modes.

Studies conducted by the method of Differential Thermal Analysis have shown that Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds have several thermal regions in the temperature range $30ºC \leq T \leq 800ºC$. These thermal regions are explained by the breaking of weak bonds in the compounds and the occurrence of melting. Thermodynamic parameters of the phase transition corresponding to the melting temperature at wide temperatures: free energy, enthalpy were calculated.

The mechanism of reactions over a wide range of temperatures depends on the kinetics of the interatomic interactions and the energy stored in the crystal structure. There is a certain temperature range in which no phase transition occurs in the crystals, only energy accumulation occurs. This energy is called Vigner's enthalpy in

thermodynamics. Determining the Vigner's enthalpy when studying each system is important for understanding that system. In this chapter, the Vigner enthalpy of the system for binary semiconductors Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 in a wide temperature range is determined. At the end of the chapter, the main results obtained are shown and explained.

Thefourth chapter examines the effect of heavy ions on the thermodynamic parameters and thermodynamic properties of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds.

Changes in these compounds under the influence of xenon ions were studied by SRIM analysis[3], the effect of heavy ions on thermodynamic properties by Differential Thermal Analysis. The results of the analysis in the SRIM Code program showed that Xe^{+26} ions can penetrate to Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 binary semiconductors to a depth of $d \approx 16$ μm when irradiated with 167 MeV heavy Xe^{+26} heavy ions in the IC100 cyclotron (Dubna, Russia). (Figure 1.)

Calculations were performed using the SRIM Code program to study the penetration of high-energy xenon ions into Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds. During the calculations, Bi and Se atoms, density of bismuth selenide compound: $\rho = 6.82$ g/cm^3, Bi and Te atoms forming bismuth telluride, density of bismuth telluride compound: $\rho = 7.71$ g/cm^3 of Sb and Te atoms forming stibium telluride and density of stibium telluride compound: $\rho = 6.50$ g/cm^3 included.It was found that with xenon ions with energy E = 167 MeV, $\Phi_1 = 5.0\times10^{12}$ ion/cm^2, $\Phi_2 = 5.0\times10^{13}$ ion/cm^2 and $\Phi_3 = 3.83 \times 10^{14}$ ion/cm^2, the nature of the penetration of ions into all three compounds during fluorescence. it happens almost the same way.

From the depth dependence of the energy lost by the ions at each nm depth (*dE/dx*) during the calculations (Figure 1.a), it was determined that xenon ions in double binary semiconductors (Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3) completely lose their energy at a depth of $l \approx 16$ μm $E = 0$ they take. As shown in Figure 1.*b*, DPA (Displacement Per Atom) - the energy required to dislodge an atom, the value of this

[3]Ziegler, J.F. The Stopping and Range of Ions in Matter / -New York: Pergamon Press, 1985. -375 p.

energy is very small for ions scattered on the surface. This means that the atoms on the surface either slip easily from their ideal crystallographic positions, or only scatter from the surface. As high-energy ions penetrate deeper, they are more likely to collide with atoms, and the value of the energy required to move the atoms increases. This effect begins to be observed after a depth of $l \approx 10$ μm.

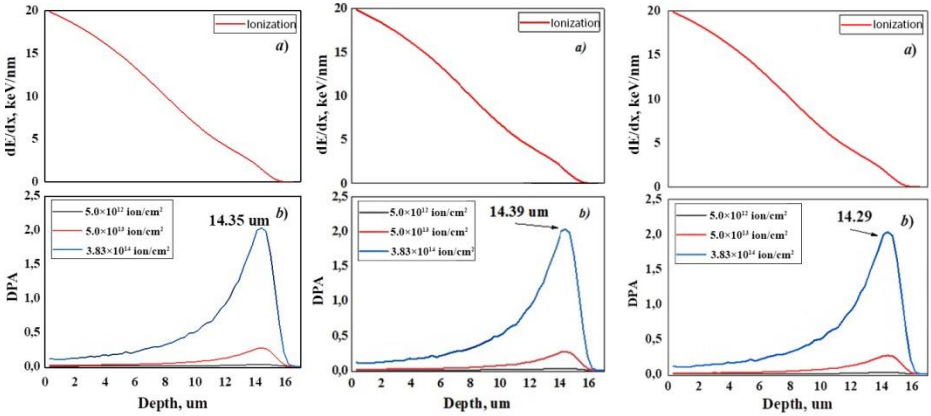


Figure 1. Distribution curve of Xe^{+26} ions in Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 compounds at different fluxes ($\Phi_1 = 5.0\times10^{12}$ ion/cm^2, $\Phi_2 = 5.0\times10^{13}$ ion/cm^2 and $\Phi_3 = 3.83\times10^{14}$ ion/cm^2) based on the results of SRIM analysis.

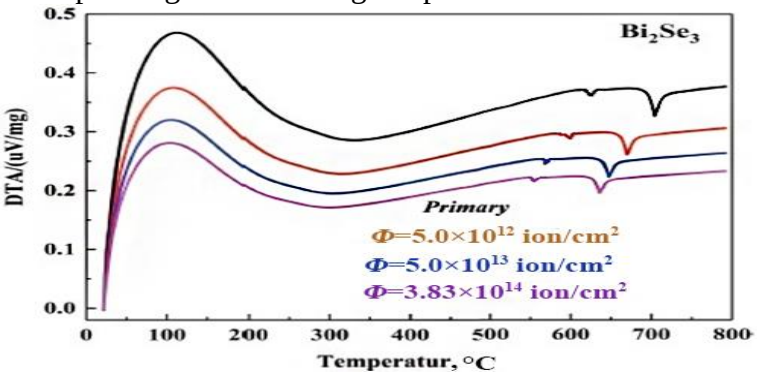
At a depth of $l \approx 14.35$ μm, the maximum energy required was observed (Figure 1.*b*). After a depth of $l \approx 16$ μm, $E_{DPA} = 0$. This means that atoms cannot be moved from their positions after a given value of depth. Therefore, a depth of $l \approx 16$ μm is considered to be the maximum penetration depth of 167 MeV heavy Xe^{+26} heavy ions in all three compounds.

This chapter also examines the effect of heavy ions on the thermodynamic properties of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds. Research samples of these compounds were irradiated with xenon ions with energy E = 167 MeV $\Phi_1 = 5.0\times10^{12}$ ion/cm^2, $\Phi_2 = 5.0\times10^{13}$ ion/cm^2 and $\Phi_3 = 3.83\times10^{14}$ ion/cm^2 fluxes, and after irradiation the

samples were Differential Thermal Analysis. (Figure 2.) It has been found that the effects of high-energy ions on these systems are different.

As can be seen from Figure 2, as the radiation dose increases, the phase transition corresponding to the melting temperature in the irradiated compounds occurs at a lower temperature. The phase transition temperature at the melting point in the Bi_2Se_3 compound is from T = 705 °C to T = 636 °C (ΔT = 69 °C), and in the Bi_2Te_3 compound from T = 585 °C to T = 555 °C (ΔT = 30 °C), while in the Sb_2Te_3 compound it decreased from T = 626 °C to T = 528 °C (ΔT = 98 °C).As a result of ionozation of heavy Xe^{+26} ionization at 167 MeV in thetemperature range of 30 °C ≤ T ≤ 800 °C, a decrease in themelting temperature was determined, which is one of the thermodynamic properties of Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 crystals.As can be seen from Figure 2. the large peak corresponds to the melting temperature of Bi_2Se_3 and the small peak to BiSe. Depending on the radiation at fluxes $\Phi = 5\times10^{12}$, 5×10^{13} and 3.83×10^{14} ion/cm^2, it melts in the temperature range of 520 °C - 606 °C for BiSe, 620 °C-705 °C for Bi_2Se_3 crystal. Depending on the radiation, a symmetrical-linear decrease in the melting temperatures of Bi_2Se_3 and BiSe crystals was observed.

The various effects of radiation on Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds were not observed only at the phase transition temperature corresponding to the melting temperature.



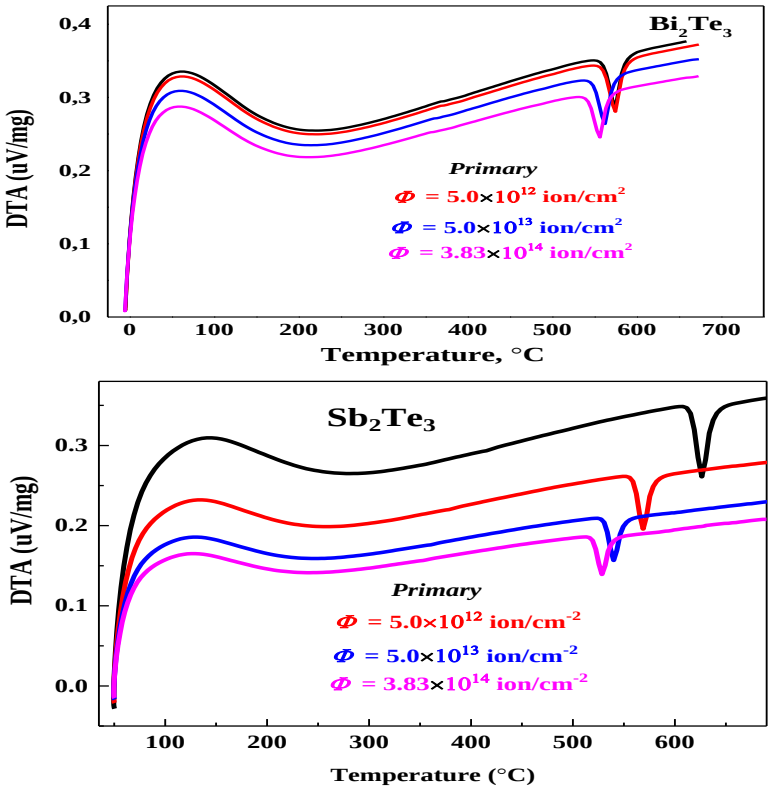


Figure 2. DTA spectra of samples of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 compounds irradiated before irradiation and at different fluxes.

The analysis of DTA spectra revealed that there are significant differences in the energy of the stable region observed before the melting temperature - the value of the Wigner's enthalpy, as well as in thermodynamic parameters at the melting temperature. In high-flux irradiation of compounds, the area between the DTA curve and the temperature axis decreases during the phase transition corresponding to the melting temperature.

This effect is an indication that a decrease in the free energy and enthalpy of the phase transition is observed under the influence of heavy ions. This effect was more pronounced during flux radiation with Xe ions $\Phi = 5\times10^{13}$ ion/cm^2 and $\Phi = 3.83\times10^{14}$ ion/cm^2. It has

been found that the energy of a crystal also depends on radiation in stable regions.

It is known that many defects in the crystal structure occur during irradiation with heavy ions.

In the crystal structure of the Sb_2Te_3 compound, under the influence of heavy ions, chemical bonds break down and various defects form between the bonds. Due to the energetic nature of each defect, it can be called an "energy-gathering center". The heat flux function under the influence of temperature was analyzed to assess the energy value of these centers.

Under the influence of temperature, defects in the crystal structure migrate to different energy levels due to the activation energy. The mobility of some defects in the crystal structure occurs over a wide temperature range. However, there are certain types of defects, the migration of which in the crystal structure varies in a specific temperature range. The process of recombination of defects under the influence of heavy ions is quite high. The value of the Wigner enthalpy after a temperature of T> 500 ºC is directly related to the activation energy of the process. Experimentally, with increasing ion intensity, there is a decrease in the value of the Wigner enthalpy in the crystal structure of the Sb_2Te_3 compound. During implantation, Xe ions form various types of surface defects in the crystal structure. In addition, as the flux of the radiation increases, the amount of activation energy in the crystal structure decreases. In non-irradiated samples, the amount of Wigner's enthalpy due to maternal defects decreases from 5×10^{13} to $3.84\cdot10^{14}$ ion/cm² during fluorescence irradiation. The dependence of the field kinetics and activation energy of the Wigner enthalpy of the Sb_2Te_3 compound irradiated with ^{132}Xe ions with an energy of 167 MeV on the radiation intensity is shown in Figure 4.

The results of the analysis of the function characterizing the temperature dependence of the heat flux show that in the crystal structure of the Sb_2Te_3 compound, volume-specific defects are formed depending on the synthesis conditions and external influencing factors. Depending on the mechanism of formation of defects and their migration, the Vigner enthalpy slides into different temperature ranges.

The change in the Wigner effect depends on the experimental conditions. Given that the radiation conditions are performed in a vacuum, the value of Vigner's energy from all experimental studies is close to the minimum, which minimizes external influences. Experimental results show that as the value of the radiation dose increases, the amount of Vigner energy in the Sb_2Te_3 compound decreases and the formation of defects in the crystal structure decreases exponentially.

These differences show that the differences in the lengths of the interatomic distances due to differences in the ionic radii of the Bi – Sb and Se – Te atoms affect not only the crystallographic parameters of the crystal structure and atomic dynamics, but the system as a whole.

When these compounds are treated as a thermodynamic system, both the energy of the system's ability to work - the free energy, and the energy accumulated by the heat flux in a stable region - the Vigner's enthalpy, are different. Therefore, the nature of the change in thermodynamic parameters of these systems during implantation with high-energy xenon ions is also different.

In **thefifth chapter**, the crystal and surface structure of the object of study obtained during the intercalation of the compound $Bi_2Te_{2.7}Se_{0.3}$ with Ni atoms are studied in a complex way. The crystal $Bi_2Te_{2.7}Se_{0.3}$ was electrochemically intercalated with Ni atoms. During the intercalation process, a $1\times2\times0.05$ cm^3 sample of $Bi_2Te_{2.7}Se_{0.3}$ was carried out by electrolysis in a 0.5% solution in a beaker with Ni V = 1 dm^3.

The crystal structure and morphology of the obtained research object were studied at room temperature in X-ray diffractometer and scanning electron microscope, respectively. Analysis of the diffraction patterns of $Bi_2Te_{2.7}Se_{0.3}$ layered crystals intercalated with nickel metal revealed that the obtained spectra consist of two different phases, in addition to the diffraction maxima corresponding to the $Bi_2Te_{2.7}Se_{0.3}$ crystals. One of these phases corresponded to the $Ni_{1.297}Te$ compound formed by the nickel atoms, and the second phase to the NiSeTe compound.

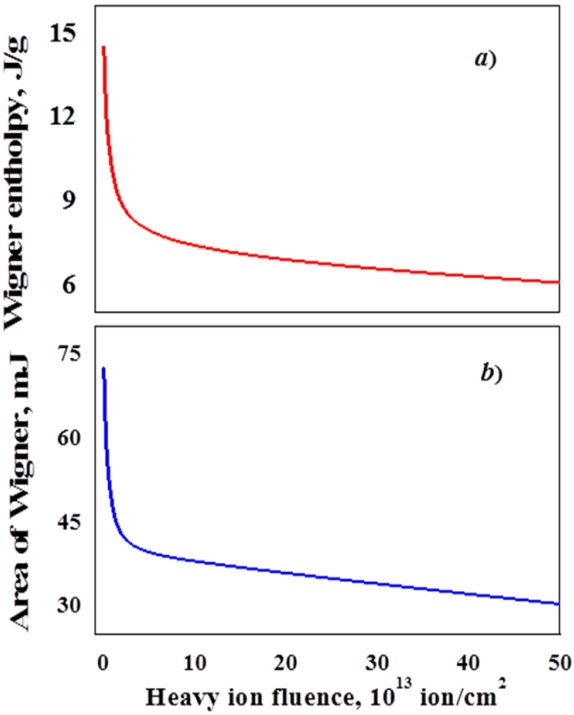


Figure 4. Field kinetics of Wigner's enthalpy in Sb_2Te_3 irradiated with ^{132}Xe ions with 167 MeV energy and dependence of activation energy on radiation intensity.

Structural analysis has shown that when intercalated with nickel atoms, the atoms do not remain suspended inside the $Bi_2Te_{2.7}Se_{0.3}$ layered crystals, but form covalent bonds with tellurium and selenium atoms. Intercalation of the $Bi_2Te_{2.7}Se_{0.3}$ compound with Ni results in the formation of a 1.17% $Ni_{1.29}Te$ semiconductor compound in the structure.

The crystal structure of the $Ni_{1.29}Te$ compound was also analyzed in X-ray diffraction patterns.

After intercalation, the surface structure of $Bi_2Te_{2.7}Se_{0.3}$ layered crystals was photographed with the help of AFM-BUNKER Nano N8

Neos atomic force microscope (AGM) and NC-AFM electron microscope. The surface structure of the $Bi_2Te_{2.7}Se_{0.3}$ crystal intercalated with Ni obtained at different scales under an atomic force microscope is shown in Figure 5.The formation of $Ni_{1.297}Te$ cores with dimensions of 35 ± 5 nm is associated with the filling of holes of linear defects with a radius of 20 nm inherent in the structure. The structure of the nuclei is formed as a result of the self-formation of intercalated atoms in defects close to the planes of the $Bi_2Te_{2.7}Se_{0.3}$ layers, where the interaction of magnetic exchange between nickel atoms plays an important role. As a result, the growth process is limited.The presence of spherical $Ni_{1.297}Te$ crystallites with a maximum size of 0.5-0.6 μm on the surfaces of $Bi_2Te_{2.7}Se_{0.3}$ <Ni> was studied by scanning electron microscopy (Figure 6). The growth of nuclei in the stratified layers of $Bi_2Te_{2.7}Se_{0.3}$ crystals occurs through two main processes. Thus, nickel ions are transported by the electric field from the solution to the layers of the crystal, and the cores are formed in defects by the process of coalescence.

Atomic force microscopy has shown that the formation of a structure in the $Ni_2Te_{2.7}Se_{0.3}$ compound intercalated with Ni combines with Te ions in the Van-der-Vaals surface structure, resulting in semiconductor $Ni_{1.29}Te$ quantum dots and nanoparticles measuring 35±5 nm. forms. (Figure 5.) During the interpretation, it was determined that this compound forms an orthorhombic crystal structure. It was found that corresponds to a ≈ 3.9 Å, b ≈ 6.8 Å and c ≈ 12.3 Å. The structure shows that Ni and Te atoms form different bonds. This is due to the fact that the Ni atoms that make up the crystal structure stand in 6 different positions. The Te atoms, which form covalent bonds with Ni atoms, stand in four different positions. The lengths of the covalent bonds formed by atoms in different positions also vary.

It has been found that the valences of Ni atoms in different positions in the $Ni_{1.29}Te$ compound are also different. Therefore, the ionic radii of divalent Ni atoms are smaller than the ionic radii of monovalent Ni atoms. This effect affects not only the atomic coordinates in which the atoms are located in the crystal structures, but

also the distances between the atoms and the crystallographic parameters of the structure in general. The surface structure of the $Bi_2Te_{2.7}Se_{0.3}$ compound intercalated with Ni atoms was investigated using a JEOL JSM-661OLV SEM (scanning electron microscope) (Analyzer brand: OXFORD INSTRUMENTS X-Max). The obtained surface morphology is given in Figure 6. During the interpretation of the obtained surface structure, it was determined that parallel layers of different sizes were observed on the surface in a given structure at a scale of d = 200 μm. This is due to the purity and crystallization rate of the structural surfaces.

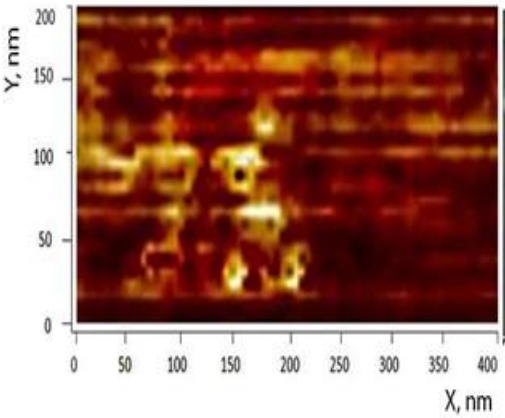


Fig.5.

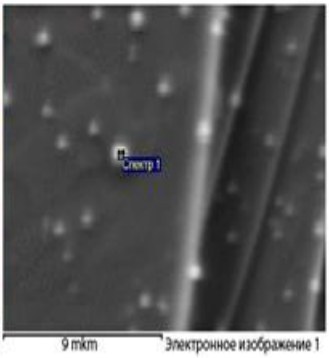


Fig.6.

The formation of these quantum dots in the surface structure expands the field of application of these materials. It is known that the physics of nanofibers and quantum dots are different from other parts of the material, and different properties are observed at these dots. Therefore, the observation of quantum dots and nanowires in $Bi_2Te_{2.7}Se_{0.3}$ crystals intercalated with Ni is important not only for the study of structural defects, but also for the future application of these materials in various fields.

RESULTS

The following main results were obtained during the dissertation work.

1. In a wide temperature range (30 ° C ≤ T ≤ 800 ° C) in Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 compounds the value of Wigner's enthalpy for a stable thermal region, temodynamic parameters were calculated, the values of free energies and activation energies were determined:

a) Wigner's enthalpy value for Bi_2Se_3 layered crystal - V_E= 17.84 C/q, peak temodynamic parameters corresponding to temperature T = 706 °C: free energy - E_s = 7.87 μC, activation energy - E_{Akt} = 0.086 C / mol;

b) For Bi_2Te_3 compound in the temperature range of 85°C≤ T≤556°C V_E=16.7 C / q, free energy corresponding to temperature T = 585 °C -E_s=7.25 μC, activation energy - E_{Akt}= 0.092 C / mol;

c) For the Sb_2Te_3 compound, V_E = 14.52 C / q, Es = 6.51 μC, the activation energy was determined to be E_{Akt} = 0.07 C/mol.

2. Defects were formed in Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 compounds by irradiation with 167 MeV Xe^{+26} ions to a dose of 3.83×10^{14} cm^{-2}, and the melting temperature from T = 705 °C to T = 636 °C in the Bi_2Se_3 compound due to the defects (Δ T = 69 °C), in the Bi_2Te_3 compound from T = 585 °C to T = 555 °C (Δ T = 30 °C), in the Sb_2Te_3 compound from T = 626 °C to T = 528 °C (Δ T = 98 °C) decrease was determined.

3. In the values of Vigner's enthalpy and thermodynamic parameters in Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 compounds due to defects caused by irradiation to a dose of 3.83×10^{14} cm^{-2} with increasing intensity of 167 MeV Xe^{+26} ions: a decrease in the amount of free energy, activation energy has been identified:

a) The free energy of the peak corresponding to the melting temperature of Bi_2Se_3 from E_s = 7.87 μC to 5.66 μC; activation energy prices E_{Akt} = 0.086 C/ mol to 0.042 C / mol;

b) In Bi_2Te_3, E_s = 7.25 μC to 4.4 μC, and the activation energy E_{Akt}=0.092 C / mol to 0.041 C / mol;

c) In Sb_2Te_3, E_s = 7.26 μC to 3.8 μC, and the activation energy decreased from E_{Akt} = 0.07 C / mol to 0.036 C / mol.

4. The penetration of 167 MeV high-energy Xe $^{+26}$ ions into all three compounds (Bi_2Se_3, Bi_2Te_3, Sb_2Te_3) was found to occur in the same way. The penetration of ions into the depth was determined by the amount of ion energy released into the electronic subsystem of the crystals, and a maximum energy was observed at a depth of 14 μm. It was found that the maximum penetration depth corresponding to the tracks formed in the crystal was 16 μm, with the value of the energy lost at each nm depth decreasing to a depth of 16 μm.

5. Based on X-ray structural studies, the spatial group $Pmc2_1$ of the nickel-containing compound $Bi_2Te_{2.7}Se_{0.3}$ was determined to have cage parameters a = 3.909 Å, b = 6.863 Å, c = 12.340 Å, α = β = γ = 90 °. With unsaturated atomic bonds and Ni ions forming covalent bonds, the formation of nuclei with an orthorombic structure of the semiconductor $Ni_{1.29}Te$ - 1.17% in the internal defects of the surface, Ni-Te-Se-1.33% chains is associated with the restoration of unsaturated free connections.

6. The formation of $Ni_{1.297}Te$ cores with dimensions of 35 ± 5 nm is associated with the filling of holes of linear defects with a radius of 20 nm inherent in the structure. The structure of the nuclei is formed as a result of the self-formation of intercalates atoms in defects close to the planes of the $Bi_2Te_{2.7}Se_{0.3}$ layers, where the interaction of magnetic exchange between nickel atoms plays an important role. As a result, the growth process is limited.

7. During the intercalation of $Bi_2Te_{2.7}Se_{0.3}$ <Ni> semiconductors by the AQM method, the formation of single, double, triple, quadruple $Ni_{1.297}Te$ cores and nanowires with dimensions d = 35 ± 5 nm was confirmed.

8. The presence of spherical $Ni_{1.297}Te$ nanocrystallites with a maximum size of 0.5-0.6 μm on the surfaces of $Bi_2Te_{2.7}Se_{0.3}$ <Ni> was confirmed by scanning electron microscopy. The growth of nuclei in the stepwise layers of $Bi_2Te_{2.7}Se_{0.3}$ crystals is determined by two main processes: the transport of nickel ions from the solution to the crystal layers by an electric field; formation of nuclei in defects by the process of coalescence.

SCIENTIFIC WORK PRINTED ON THESIS SUBJECT

1. Abdullayev, N.M. The formation of slip band in layerd crystal / N.M. Abdullayev, A.Sh. Kakhramanov, K.G. Khalilova, S.R.Azimova // AJP Fizika, - Bakı: -2018, Vol.XXIV,№4,c.3-6.
2. Азимова, С.Р. Формирование дефектов в тонких фольгах из слоистых кристаллов / С.Р.Азимова // Azərbaycan Texniki Universiteti Elmi Əsərlər jurnalı, - Bakı: - 2019, №2, c.33-37.
3. Gashimov, A.M., Azimova, S.R., Asadov, Y.G. Development of ther moelectricthin films based on new nanocrystalline structures // 15th International Confrance on "Texnical and Physical Problems of Elektrical Engineering" (ICTPE), -Turkey, Istanbul: - 2019. p.108-112.
4. Əzimova, S.R. Bi_2Se_3 birləşməsinin quruluş və diferensial termik analizi / S.R. Əzimova // Elmi Əsərlər Fundamental elmlər, AZTU, - Bakı: -2019, - №3, - s. 52-56.
5. Əzimova, S.R. Bismut selenin termik xassələri // "Maqnityumşaq Ərintilərin İnformasiya Texnologiyalarinda və Hərbi Sənayedə Tətbiqi Perspektivləri " Beynəlxalq Elmi-Praktik Konfrans , Memerlıq və İnşaat Universiteti , - Bakı: - 09-10 Oktyabr, - 2019. - s. 67-69.
6. Əzimova, S.R. $Bi_2Se_{0.5}Te_{2.5}$ birləşməsinin termik xassələri // Gənc Alim və Mütəxəssislərin İkinci Beynəlxalq Elmi Konfransı, AMEA,: Bakı: - 2019. -03- 06 mart ,- 2020, - s. 289-291.
7. Azimova, S.R. Effect of the Se → Te substitutions on thermal properties of binary Bi_2Se_3 semiconductor / S.R. Azimova, N.M. Abdullayev, Y.I. Aliyev [et al.] // Modern Physics Letters B, - 2020. Vol.34, №15,- p.1-10.
8. Azimova, S.R. Study on the Thermodynamic Behavior of Sb-Te Binary Systems with Swift Heavy-Ions Irradiation at the High Temperatures, / S.R. Azimova, N.M. Abdullayev, Y.I. Aliyev [et al.] // Journal of the Korean Physical Society, -2020. - Vol. 77, № 3, - P.240-246.

9. Azimova, S.R. The behavior of thermodynamic kinetic on Bi_2Se_3 compound by ^{131}Xe ion implantation / S.R. Azimova, Y.I. Aliyev, D.M. Mirzayeva [et al.] // Modern Physics Letters B, -2020. Vol.34, №36, -p.1-10.
10. Azimova, S.R., Alıyev, Y.I., Abdullayev, N.M., Jabarov, S.H. Study on the thermodinamic behavior of Sb-Te binary systems at the high temprratures // 9 th Rostocker International Conference "Thermophysical Properties for Technical Termodynamics", - Rostock, Germany: 15 October - 2020, -p. 69.
11. Əzimova, S.R. *$Bi_2Te_{2.7}Se_{0.3}$<Ni>* təbəqələrinin kristalik və səth quruluşu /S.R.Əzimova // AJP Fizika, - Bakı: -2020, Vol.XXIV, №4, s.3-5.
12. Azimova, S.R. Thermal Properties of Bi_2Se_3 and $Bi_2Se_{0.5}Te_{2.5}$ Semiconductor compounds // Министерство науки и высшего образования Российской Федерации, Физико-Технический Институт им. А.Ф.Иоффе Российской Академиии Наук, "Аморфные и микрокристаллические полупроводники, Сборник трудов Менждународной конференции", - Санкт-Петербург: 05-07 июля ,-2021, -с. 225-226.
13. Azimova, S.R. Structural and Vibrational properties of Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 / S.R. Azimova //Advanced Physical Research, - Bakı: - 2021.Vol.3, №1,- p.46-51.
14. Əzimova, S.R. Bi_2Te_3 birləşməsinin termodinamik xassələrinə ağır ionların təsiri. // Cənc Tədqiqatçı ,- Bakı, -2021. VII cild, №1, -s.25-28.
15. Əzimova, S.R., Abdullayev N.M. $Bi_2Te_{2.7}Se_{0.3}$ laylarında kristallik özəklərin və nanoməftillərin formalaşma xüsusiyyətləri./ S.R.Əzimova, N.M.Abdullayev // AJP Fizika, - Bakı, -2021. XXVII cild, №4, -s.46-55.

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