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PHASE FORMATION AND STRUCTURAL PHASE TRANSFORMATIONS IN CHALCOGENIDE SYSTEMS BASED ON Ag, Cu

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Applicant: **Yusif Imrayil oghlu Aliyev**

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Scientific consultant: Dr.Physics and Math.Sciences, professor

Yusif Gazanphar Asadov

Official opponents: Corresponding member of ANAS,
Dr.Physics and Math.Sciences, professor
Salima Ibrahim Mehdiyeva
Corresponding member of ANAS,
Dr.Physics and Math.Sciences, professor
Ogtay Abil Samedov
Dr.Physics and Math.Sciences, professor
Mahammadali Mazahir Zarbaliyev
Dr.Physics and Math.Sciences, professor
Hamza Samad Seyidli

ED 1.14 Dissertation Council of the Higher Attestation Commission under the President of the Republic of Azerbaijan operating under the Institute of Physics of the Azerbaijan National Academy of Sciences

Chairman of the Dissertation Council:
Full member of ANAS,
Dr.Physics and Math.Sciences, professor
Nazim Timur oghlu Mammadov

Scientific Secretary of the Dissertation Council:
Doctor of Physical Sciences, associate professor
Rafiga Zabil gizi Mehdiyeva

Chairman of the scientific seminar:
Doctor of Physical Sciences, professor
Imameddin Rajabali oghlu Amiraslanov

GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and the degree of elaboration. Crystallography - one of the most important directions in the physics of modern solids and its most important directions, studies the physics of crystals, changes in the various properties of substances, their structure and physicochemical analysis. In order to create the functional materials needed for modern technology, it is important to know how solids that have important physical properties under normal conditions and at room temperature will behave under external influences, such as high temperature, pressure, radiation, and so on. This information not only increases the applicability of crystalline compounds in various fields, but also plays an important role in the production of new composite materials based on them.

It is known that depending on external influences, polymorphic transformations, phase transitions, amorphization, recrystallization, solid solution fragmentation, thermal destruction, regulation, disorganization and various other physicochemical processes can occur in crystalline solids. Under normal conditions, these processes cause a radical change in the physical and chemical properties of solids with a stable chemical composition. Among the problems of crystallography and crystal physics, polymorphism has a special place, as during this process a crystallographic structure is broken and a new modified crystal, an embryo with a completely new crystal structure is formed in the place of that crystal. In this case, despite the fact that the chemical composition of the compound does not change, the physical and mechanical properties of the newly formed modification are completely different from the properties of the parent crystal. In some cases, this process is more complicated. The newly obtained crystal structure can consist of several phases, not one.

X-ray studies carried out under special conditions allow to obtain basic information about the crystal structure of a substance under external influences (changes in temperature, pressure, electric and magnetic fields, exposure to ionizing radiation, etc.). The study of polymorphic transformations on crystals with stoichiometric and non-stoichiometric composition is of more scientific and practical interest.

A complete study of the presence of high temperature modifications of crystals and the mechanism of phase transitions is not possible without the application of high-temperature X-ray method. Obtaining X-ray diffraction spectra at different temperatures allows to study different crystallographic quantities, thermal expansion. For this purpose and to detect structural changes in the crystal, the parameters of the crystal lattice from room temperature to melting temperature were studied.

When studying the mechanism of polymorphic transformation, in addition to information about the structure, it is important to obtain information about the thermodynamic parameters for each modification. Since copper and silver chalcogenides are rich in polymorphic transformations in terms of studying the mechanism of polymorphic transformations in opaque crystals, these systems were taken as the object of research in the presented dissertation. Therefore, Cu and Ag chalcogenide systems were taken as the object of research in the presented dissertation. To determine the nature of polymorphic transformations, it is important to accurately determine the temperature dependence of the crystal lattice parameters, volume and density, as well as the parameters of the elemental core. Accurate determination of these parameters has always been one of the current problems of solid state physics. Because the stability of the structure of the crystal is very important for the perfection of its physical and mechanical properties.

X-ray structural studies carried out under special conditions allow to obtain basic information about the substance (effects) in the field of external forces (changes in temperature, pressure, electric and magnetic fields). It is known that in order to plan in advance the working area of any converter to be prepared from the substance under study, it is necessary to study that substance under external influences. The results obtained from structural studies in studies conducted for this purpose are considered the most reliable data. This is because structural information obtained at the atomic level is the basis for explaining any physical property.

Semiconductor compounds are widely used in many areas of modern electronics. Chalcogenides have a special place among the materials with semiconducting properties. As a result of recent

research conducted in prestigious international research centers, the discovery of topological isolation[1] in these materials has further increased their interest. Therefore, both the study of the structure and the study of the various physical properties of these compounds have entered a new phase. The dissertation is devoted to the structural studies of both silver and copper known chalcogenide semiconductors, as well as new compounds obtained as a result of various substitutions of these elements with metal atoms such as zinc and cadmium. Phase formation and structural phase transformations in Ag, Cu-based chalcogenide systems have been studied. It was found that during the partial replacement of not only metal atoms, but also chalcogen atoms, it is possible to obtain various compounds with a new crystal structure. The results of the study of new modifications obtained during anion-anion and cation-cation substitutions are very important for the production of new functional materials using these substances in the future.

The study of polymorphic transformations on crystals with stoichiometric and non-stoichiometric composition is of more scientific and practical interest. A complete study of the presence of high temperature modifications of crystals and the mechanism of phase transitions is not possible without the application of high-temperature X-ray method.

Copper chalcogenides, which are rich in polymorphic transformations are more suitable for studying the mechanism of polymorphic transformations in optically opaque crystals[2]. The favorable adaptation of the basic physical parameters of copper and silver chalcogenides allows them to be used to create a number of new converters. Copper, silver, double, triple and non-stoichiometric

[1] Eremeev S.V., Landolt G., Aliyev Z.S., Babanly M.B., Amiraslanov I.R. et al. Atom- specifik spin mapping and buried topological states in a homologous series of topolifical insulators // Nature Commun.2012, v.3, p.635- 644.

[2] Sahib H., Puja A., Khagendra B., Wai-Yim C. Conspicuous interatomic bonding in chalcogenide crystals and implications on electronic, optical, and elastic properties // AIP Advances V. 10, 2020, p.075216-(1-17).

chalcogenide compounds are strongly self-alloying with specific defects of the crystal lattice, such as semiconductor materials.

In the crystal structures of compounds of the Cu-S, Cu-Se and Cu-Te systems, copper atoms are distributed in two different valence states. The inclusion of Cu^{1+} and Cu^{2+} cations in the crystal structure of the compounds of this system of copper atoms is one of the main reasons for the existence of a number of non-stoichiometric compounds between stoichiometric compounds. Study of the main regularities of the physicochemical properties of nonstoichiometric compounds of the Cu-S, Cu-Se, Cu-Te system and the study of the effect on the real structure with partial isomorphic substitution of atoms of other elements that satisfy the condition of isomorphic substitution of copper atoms - stabilization of individual structures, elucidation of the crystallographic aspects of these processes is of scientific and practical interest.

Phase formation of structural transformations of Ag^{+1} and Cu^{1+} cations, as well as S^{2-}, Se^{2-} and Te^{2-} anions, as well as stabilization of individual modifications, Ag_2S(Se, Te), Cu_2S(Se, Te), AgCuS(Se, Te) and their great interest is the study of the effect of mutual isomorphic substitution in nonstoichiometric compositions[3].

The solution of these problems sheds light on the problems of improving the technology of semiconductors with polymorphic transformations, the control of the crystal structure and important physical properties. These are one of the current scientific problems in solid state physics and semiconductor materials technology.

The dissertation work was carried out in accordance with the scientific research plan of the Laboratory of Structure and Structural Transformation of the Institute of Physics of the Azerbaijan National Academy of Sciences.

[3] Stijn O. M., Anne C. B., Mert K., Marc-Etienne M. et al. Tailoring Cu+ for Ga3+ Cation Exchange in Cu2–xS and CuInS2 Nanocrystals by Controlling the Ga Precursor Chemistry // ACS Nano 2019, 13, 11, 12880–12893

Object and subject of research:

Ag and Cu-based binary and triple chalcogenide compounds with different phase transitions in the high temperature region were selected as research objects:

$Ag_2S(Se,Te)$, AgCuS, $AgCu_{1-x}Fe_xS$, $Cu_2S(Se,Te)$, $CuFeS_2$, $Ag_{2-x}Cu_xS$, AgCuSe, $Ag_{1.5}Cu_{0.5}Se$, $AgCuS_{0.5}(Se,Te)_{0.5}$, $AgCuSe_{0.5}Te_{0.5}$, $Cu_{1.80}Te$, $Cu_{1.50}Zn_{0.30}Te$, $Cu_{1.75}Cd_{0.05}Te$, $Cu_{1.75}Te$, $Cu_{1.70}Zn_{0.05}Te$, $Cu_{1.70}Cd_{0.05}Te$ compounds.

Research goals and objectives:

The main purpose of the dissertation is to study the regularities of the process of phase formation in chalcogenide systems based on silver and copper, the acquisition of new compounds in these chalcogenides by anion-anion and cation-cation substitutions, the study of structural-phase transformations at high temperatures and determining the role of crystallographic parameters for each phase.

– Synthesis of new silver and copper-based chalcogenide compounds and cultivation of their single crystals.

– Structure and X-ray phase analysis of $Ag_2S(Se,Te)$, $Cu_2S(Se,Te)$, $CuFeS_2$, AgCuS, $Ag_{2-x}Cu_xS$ (x=1.07; 0.8; 0.45), $AgCuS_{0.5}(Se,Te)_{0.5}$, AgCuSe, $Ag_{1.5}Cu_{0.5}Se$, $AgCuSe_{0.5}Te_{0.5}$, $Cu_{1.80}Te$, $Cu_{1.50}Zn_{0.30}Te$, $Cu_{1.75}Cd_{0.05}Te$, $Cu_{1.75}Te$, $Cu_{1.70}Zn_{0.05}Te$, $Cu_{1.70}Cd_{0.05}Te$ and $AgCu_{1-x}Fe_xS$.

– Recording of possible polymorphic transformations in new silver and copper-containing chalcogenides at high temperatures by X-ray diffractometric method, determination of equilibrium temperature between polymorphic phases, calculation of crystallographic parameters for different modifications, density of compounds and temperature dependence of thermal expansion coefficients for each phase.

– Investigation of changes in the crystal structure during the partial replacement of Cu atoms with Cd and Zn atoms in $Cu_{1.75}Te$ and chalcogenides based on it. Structural phase transitions that occur in these compounds in the region of high temperatures.

– Calculation of the coefficient of thermal expansion in the crystal

$Cu_{1.70}Zn_{0.05}Te$ based on the temperature dependence of the lattice parameters.

– Structural phase transitions in AgCuX (X = S, Se, Te) chalcogenide semiconductors at high temperatures. Investigation of structural properties of AgCuX compounds during anion-anion substitution.

– Determination of structural phase transitions and crystallographic parameters of different phases in the combination of $AgCuS_{0.5}Se_{0.5}$ at high temperatures..

– Determination of structural phase transitions and crystallographic parameters of different phases in the combination of $AgCuSe_{0.5}Te_{0.5}$ at high temperatures.

– Calculation of thermal expansion coefficients for $AgCuS_{0.5}Se_{0.5}$ and $AgCuSe_{0.5}Te_{0.5}$ compounds.

– The effect of cation-cation substitutions on the crystal structure and phase transitions of $Ag_{2-x}Cu_xS(Se)$ compounds obtained at different concentrations of Ag and Cu atoms.

– Synthesis of $Cu_{1.50}Zn_{0.30}Te$ compound with Cu → Zn substitutions in $Cu_{1.8}Te$ compound. Phase transitions of $Cu_{1.50}Zn_{0.30}Te$ compound at high temperatures.

– Synthesis of $Cu_{1.75}Cd_{0.05}Te$ with Cu → Cd substitutions in $Cu_{1.8}Te$. Phase transitions of $Cu_{1.75}Cd_{0.05}Te$ compound at high temperatures.

Research methods:

Modern research methods, latest generation devices were used in the study of phase formation and structural phase transformations in Ag, Cu-based chalcogenide systems, the obtained results were analyzed by modern analysis methods and software.

The research objects were synthesized in high-temperature stoves under high vacuum conditions, and single crystals were grown from the obtained compounds by the Bricman method.

Crystal structures and phase transitions of the studied samples of different compositions were studied by X-ray diffraction method. The studies were performed on Bruker Advance D8 and DRON-3M X-ray diffractometers. These diffractometers allow the phase structure

analysis of crystals. By analyzing the obtained X-ray diffraction spectra, it is possible to determine the crystal structures of the components, determine the lattice parameters, the symmetry of the crystal structure and the spatial groups. If the synthesized composition consists of several phases, then it is possible to determine the crystallographic parameters of the phases as a result of the analysis by determining the diffraction maxima corresponding to each phase. X-ray diffractometers DRON-3M used the URVT-2000 unit to obtain high temperatures in structural studies.

Modern analysis methods, "FullProf", "DIAMOND 3.2" and "Origin 9" programs were used in the analysis of diffraction spectra obtained by X-ray diffraction at room temperature and high temperatures.

The main provisions of the defense:

1. Crystal structure of new compounds obtained by substituting Cu atoms with Zn and Cd atoms with a concentration of $x = 0.05$ in the $Cu_{1.75}Te$ chalcogenide semiconductor compound.
2. Structural phase transitions in $Cu_{1.8}Te$, $Cu_{1.50}Zn_{0.30}Te$, $Cu_{1.75}Cd_{0.05}Te$, $Cu_{1.75}Te$, $Cu_{1.70}Zn_{0.05}Te$, $Cu_{1.7}Cd_{0.05}Te$ compounds at high temperatures.
3. Structural transformations in the triple semiconductor compound AgCuS in the high temperature region.
4. Obtaining new structures during the anion-anion exchange of S atoms with Se atoms in AgCuS crystals and the study of phase transitions at high temperatures.
5. Crystal structure of $Ag_{1.55}Cu_{0.45}S$ compound synthesized by cation-cation substitutions, tetragonal-cubic structure phase transition occurring in the high temperature region.
6. Crystal structure and structural transformations of $Ag_{1.2}Cu_{0.8}S$ in the high temperature region.
7. Orthorombic-hexagonal and hexagonal-cubic phase transitions in the combination of $Ag_{0.93}Cu_{1.07}S$ in the high temperature region.
8. Crystal structure of $Ag_{1.5}Cu_{0.5}Se$ and orthorombic-cubic phase transition at high temperatures.

9. Influence of Ag → Cu substitutions on the crystal structure of $Ag_{0.4}Cu_{1.6}Se$ synthesized by cation-cation substitutions, orthorombic-cubic phase transition in the high temperature region.
10. Structural aspects of phase formation and phase transitions in silver and copper-based chalcogenide semiconductors.

Scientific novelty of the research:

1. It was determined that the crystal structure of the $Cu_{1.75}Te$ chalcogenide semiconductor compound under normal conditions and at room temperature corresponds to the hexagonal symmetry of the P-6m2 (187) space group. A two-phase system was obtained when Cu atoms were replaced by Zn atoms with a concentration of $x = 0.05$, and a three-phase system was obtained when they were replaced by Cd atoms. Phase transition temperatures at high temperatures were determined for each compound.
2. Fm-3m symmetrical crystal structure was observed in each of the compounds $Cu_{1.75}Te$, $Cu_{1.7}Zn_{0.05}Te$ and $Cu_{1.75}Cd_{0.05}Te$ at high temperatures $T > 750$ K. Crystallographic parameters were determined for different phases and temperature dependences of cage parameters were obtained. Coefficients of thermal expansion were calculated for$Cu_{1.75}Te$, $Cu_{1.7}Zn_{0.05}Te$ and $Cu_{1.75}Cd_{0.05}Te$.
3. It was found that the crystal structure of the AgCuS compound at room temperature corresponds to the orthorombic symmetry of the *Cmcm* space group. Orthorombic-hexagonal phase transition at $T \approx 400$ K and hexagonal-cubic phase transition at $T \approx 770$ K was detected under the influence of high temperature. Crystallographic parameters were determined for orthorombic, hexagonal and cubic phases.
4. A two-phase system consisting of $Cu_{1.96}S$ and AgCuS compounds was observed in AgCuS crystals at equal concentrations of S atoms with Se atoms ($AgCuS_{0.5}Se_{0.5}$). It was determined that a single-phase highly symmetrical structure at $T \approx 700$ K was obtained under the influence of high temperature. The structural features of different phases were studied.
5. The effect of high temperature on the crystal structure of $Ag_{1.55}Cu_{0.45}S$ was studied and it was determined that a tetragonal-

cubic phase transition occurred at T = 400 K. Crystallographic parameters were determined for tetragonal and cubic phases, coefficients of thermal expansion were calculated according to these parameters.

6. As a result of structural studies, it was found that the crystal structure of $Ag_{1.2}Cu_{0.8}S$ consists of two different monoclinic phases. In the region of high temperatures a highly symmetrical single-phase crystal structure was formed in this composition and a structural phase transition occurred at a temperature of T = 420 K.
7. Structural phase transitions in the combination of $Ag_{0.93}Cu_{1.07}S$ in the region of high temperatures have been studied. It was found that the symmetry of the crystal structure increased under the influence of temperature. Orthorombic-hexagonal phase transitions were observed at T = 370 K and hexagonal-cubic phase transitions at T = 450 K.
8. Structural studies of $Ag_{1.5}Cu_{0.5}Se$ have shown that under normal conditions and at room temperature, the crystal structure of this compound consists of two phases: orthorombic Ag_2Se and orthorombic AgCuSe. At a temperature of T = 500 K an orthorhombic-cubic phase transition took place and a single-phase highly symmetrical crystal structure was obtained.
9. Structural studies of $Ag_{0.4}Cu_{1.6}Se$ have shown that under normal conditions and at room temperature, the crystal structure of this compound consists of two phases: orthorombic Cu_2Se and orthorombic AgCuSe. Orthorombic-cubic phase transition occurred at T = 500 K and a single-phase highly symmetrical crystal structure was obtained.
10. As a result of the study of phase formation and structural phase transformations in Ag, Cu-based chalcogenide systems, it was found that at high temperatures these compounds form a highly symmetrical cubic crystal structure of the Fm-3m space group.

Scientific and practical significance of the research:

The results of the research can be widely used in synthesis technology and bleaching of single crystals in combinations of stoichiometric and non-stoichiometric and other semiconductor substances of copper, silver chalcogenides. It also has valuable

experimental results for understanding the mechanism of structural transformations and is of great importance for the solution of practical problems in a deeper explanation of their physical properties.

Given the above, it can be said that the study of phase formation and structural phase transformations in Ag and Cu-based chalcogenide systems is of great scientific and practical importance. The results obtained in these studies are important both for use as a model object in theoretical research and for the production of converters based on these materials.

Approbation and application:

The main results obtained during the dissertation work were reported at the following national and international scientific events:

- ✓ XIV National Conference on Crystal Growth (NCCG-2010), Moscow, Kurchatov Institute, December 6-10, 2010,
- ✓ 3rd International Conference on Superconductivity and Magnetism – ICSM-2012, 29 April – 4 May 2012, Istanbul, Turkey,
- ✓ XLVII School of the FSBI "PIYF" on Condensed Matter Physics "FKS - 2013", March 11–16, 2013, St. Petersburg,
- ✓ International conference dedicated to the 70th anniversary of the Physics and Technology Institute NPO "Physics-Sun", November 14-15, 2013, Tashkent, Uzbekistan,
- ✓ International Youth Scientific School "Modern Neutronography", October 28 - November 1, 2013, Dubna, Russia,
- ✓ XLIX PIYF School of Condensed Matter Physics (FKS-2015), March 16-21, 2015, St. Petersburg, Russia,
- ✓ Seminar, Structural phase transitions in chalcogenides, Baku Higher Oil School, October 16, Baku, Azerbaijan,
- ✓ 50th School of FGBI "PIYF" on Condensed Matter Physics FKS – 2016, March 14–19, 2016, St. Petersburg, Russia,
- ✓ LI PIYF School of Condensed Matter Physics (FKS-2017), March 11-16, 2017, St. Petersburg, Russia,

- ✓ XVIII All-Russian School-Seminar on Problems of Physics of Condensed Matter, November 16-23, 2017, Yekaterinburg, Russia,
- ✓ International Conference "Radiation processes and their application" dedicated to the 70th anniversary of academician M.K. Karimov, November 13-14, 2018, Baku, Azerbaijan.
- ✓ 7th Rostocker International Conference: "Thermophysical Properties for Technical Thermodynamics" (THERMAM 2018) Institute of Technical Thermodynamics University of Rostock, 26–27 July, 2018, Rostock, Germany,
- ✓ LIII PIYF School on Condensed Matter Physics FKS-2019, March 11–16, 2019, St. Petersburg, Russia,
- ✓ 54th PIYF School on Condensed Matter Physics FKS-2020, March 16 - 21, 2020, St. Petersburg, Russia,
- ✓ 9th Rostocker International Conference: "Thermophysical Properties for Technical Thermodynamics" (THERMAM 2020) Institute of Technical Thermodynamics University of Rostock, 15 October 2020, Rostock, Germany,
- ✓ Seminar, Scientific seminar of the Physics faculty of the Azerbaijan State Pedagogical University, May 4, 2021, Baku, Azerbaijan.
- ✓ 10th Rostocker International Conference: "Thermophysical Properties for Technical Thermodynamics" (THERMAM 2021) Institute of Technical Thermodynamics University of Rostock, 9 September 2021, Rostock, Germany,
- ✓ International Conference "Phase Transitions, Critical and Nonlinear Phenomena in Condensed Matter", September 12 - 17, 2021, Makhachkala, Russia.

The main materials of the dissertation were published in 48 scientific works. 32 of these materials are articles (including 18 are foreign journals with an impact factor included in the "Web of Sciences" platform and 14 are periodicals recommended by the Supreme Attestation Commission under the President of the Republic of Azerbaijan) and 16 are international and national conference materials.

The results were published in 5 reports of scientific research of the Institute of Physics of the Azerbaijan National Academy of Sciences.

The degree of participation of the author:

The topic of the dissertation, scientific idea and the main direction of research are defined by the author. The main purpose of the research and the issues that need to be addressed were identified by the author. He was directly involved in the selection of research objects, the synthesis of samples, the cultivation of single crystals and structural research. He played a key role in writing and publishing articles and theses, preparing reports for conferences. He has published the results of structural research in high-ranking journals included in the international summary and indexing databases, reported at international and national scientific events.

The reliability of the main results obtained in the dissertation was determined by the choice of the topic relevant to modern crystallography, the synthesis of important scientific and experimental components in this field, the use of modern research methods, the use of modern programs in the analysis of X-ray diffraction spectra. The main results were adopted by peer-reviewed journals included in such prestigious international databases as “Web of Sciences”, “Scopus”, discussed at international scientific events..

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

The dissertation work was carried out in the laboratory "Structure and structural transformations" of the Institute of Physics of the Azerbaijan National Academy of Sciences.

Volume, structure and main content of the dissertation:

The dissertation consists of an introduction, six chapters, main results and a list of 268 references. The dissertation consists of a total of 444.500 characters, 55 tables and 34 figures.

CONTENT OF THE WORK

In the introduction, the relevance and degree of development of the topic of the dissertation, the main purpose of the dissertation, the received scientific innovations, the scientific and practical significance of the work, the purpose and the main provisions of the defense are substantiated.

The first chapter of the dissertation is devoted to the literature review of the results obtained during previous structural studies of binary systems Ag - S, Ag - Se, Ag - Te, Cu - S, Cu - Se, Cu-Te, copper and silver triple chalcogenide compounds. The analysis of the results showed that these compounds have been studied for many years. Although they have been studied for a long time, many of their properties have not been sufficiently studied. In particular, there is very little literature on the phase transitions that occur in these compounds. It is known from the course of crystallography and crystal physics that many physical properties of solids with a crystalline structure depend on their crystal structure. In particular, during anion-anion, cation-cation substitutions, significant changes in the physical properties of compounds can occur due to the difference between the ionic radius of the elements.

It is clear from the literature review of the research objects that during the research, compounds with different crystallographic symmetry were selected by selecting different types of compounds. Extensive information is given about the crystal structures of compounds with monoclinic, orthorhombic, tetragonal, hexagonal and cubic syngony and the phase transitions observed in these structures.

Crystallographic data obtained from the study of silver and copper-containing chalcogenide compounds by X-ray, neutron and electron diffraction methods are given, estimates of crystallographic parameters for different structures are presented. 3D images of interesting crystal structures obtained in "DIAMOND 3.2" program are presented. It has been found that in the crystal structures of these compounds, different cation ions can stand in the same crystallographic positions. Because copper and silver ions have the same valence, they can more easily replace each other.

At the end of the chapter, extensive information is given on the methods of studying the crystal structure, mainly the radiographic method. It has been shown that the most suitable method for the study of crystalline compounds in the laboratory is the X-ray diffraction method. The mechanism of scattering of X-rays from crystals is given, the Wolf-Bragg formula is presented. Methods for determining the crystallographic parameters by analyzing the obtained X-ray diffraction spectra are shown. Information on the Ritveld method for the analysis of radiographs obtained from polycrystals is presented. Methodology for calculating thermodynamic parameters, mainly coefficients of thermal expansion is given on the basis of crystallographic data.

For these compounds, the crystallographic data obtained in previous studies were collected and classified, the possibility of obtaining new structures with anion-anion and cation-cation substitutions in these compounds was shown. Based on the results of the literature, the importance, scientific and practical significance of the dissertation is substantiated. Information was provided on the importance of new properties expected in the crystal structure during the production of new compounds due to valence variability in copper and silver-containing chalcogenides.

At the end of the literature review, the purpose, relevance and importance of the research work are substantiated. It has been shown that the results obtained will serve as a basis for future scientific research on these materials.

The second chapter presents the results of studies on the combination of $Cu_{1.75}Te$ and polymorphic transformations in chalcogenides based on it. Synthesis conditions of $Cu_{1.75}Te$ compound in high temperature furnaces and $Cu_{1.7}Zn_{0.05}Te$, $Cu_{1.7}Cd_{0.05}Te$ compounds obtained by cation-cation substitutions in this compound are given. The Bricman method is widely described and substantiated as a suitable method for obtaining single crystals of semiconductor compounds. Information on the device and parameters for conducting research by X-ray diffraction method of crystal structures of research objects is shown. The Wolf-Bragg formula is given, the mechanism of

X-ray diffraction from crystals and methods for determining the structural parameters of crystals are given. The advantages and disadvantages of X-ray diffraction over other diffraction methods are shown.

X-ray analysis of the $Cu_{1.75}Te$ chalcogenide semiconductor compound under normal conditions and at room temperature revealed that the crystal structure of this compound has a fairly high symmetry and corresponds to the hexagonal symmetry of the P-6m2 (187) space group.

The X-ray diffraction spectra of the $Cu_{1.75}Te$ chalcogenide semiconductor compound obtained at room temperature and at high temperatures are given in Figure 1.

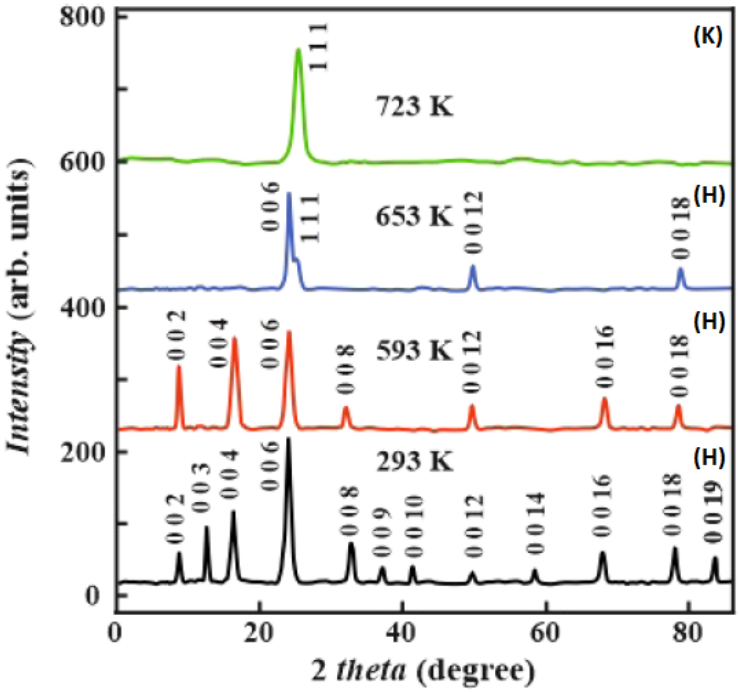

Figure 1. X-ray diffraction pattern of $Cu_{1.75}Te$ compound at room temperature and high temperatures.

Analysis of the X-ray diffraction pattern obtained at room temperature revealed that the crystal structure of the double chalcogenide compound $Cu_{1.75}Te$ consists of one phase, and this phase corresponds to the hexagonal syngonium crystal structure of the P-6m2 (187) space group. The values of the parameters of the elementary nucleus with respect to the d_{hkl} distances between the atomic planes are the values of the parameters of the calculated elementary nucleus: $a = b = 4.17$ Å and $c = 21.65$ Å were determined. As can be seen from the diffraction pattern, a maximum of 12 is observed in the range of $0 \leq 2\theta \leq 90°$ diffraction angle at room temperature. These diffraction maxima are: (0 0 2), (0 0 3), (0 0 4), (0 0 6), (0 0 8), (0 0 9), (0 0 10), (0 0 12), (0 0 14), (0 0 16), (0 0 18) and (0 0 19) correspond to the atomic planes.

Based on the obtained crystallographic parameters, the crystal structure of the $Cu_{1.75}Te$ compound was obtained in the Diamond 3.2 program. It is derived from the crystal structure that copper atoms stand on the tins of an elementary core composed of Cu-metal and Te - chalcogen atoms. Tellurium atoms form covalent bonds with copper atoms throughout the crystal lattice. It is known that although copper atoms have a constant valence in the CuTe and Cu_2Te binary compounds, the copper atoms in the $Cu_{1.75}Te$ compound enter both monovalent and divalent states. Because of the greater number of copper atoms entering the monovalent state, tellurium atoms form bonds with two copper atoms. The valence change affects not only the number of bonds formed by atoms, but also the length of the bonds between atoms. This is because the ionic radius of copper atoms in the monovalent and divalent states are different.

As a result of cation-cation substitution by partial replacement of Cu atoms with Zn atoms, $Cu_{1.70}Zn_{0.05}Te$ compound was synthesized on the basis of $Cu_{1.75}Te$ chalcogenide semiconductor. It was found that the crystal structure of the $Cu_{1.70}Zn_{0.05}Te$ compound is somewhat more complex than that of the $Cu_{1.75}Te$ compound. Under normal conditions and at room temperature, the crystal structure of this compound consists of two phases. The analysis revealed that one of these phases

corresponds to the orthorombic symmetry of the space group Pnma (62) and the other to the hexagonal symmetry of the space group P3m1 (156).

As can be seen, despite the small substitutions, significant changes in the crystal structure were observed due to the difference in the ionic radius of the Cu and Zn atoms. It is known that the Cu and Zn atoms included in the $Cu_{1.70}Zn_{0.05}Te$ compound can be both monovalent and divalent when forming covalent bonds in the compounds. If the Cu atoms are monovalent, the ionic radius is $R_{Cu+1} = 0.95$ Å, if it is binary, $R_{Cu+2} = 0.75$ Å, if the Zn atoms are monovalent, the ionic radius is $R_{Zn+1} = 0.97$ Å, and if it is binary, $R_{Zn+2} = 0.76$ Å. As can be seen, the difference between the ionic radii of Cu and Zn metals is very close ($\Delta R \approx 0.01$ Å). However, this small difference also has an effect on the crystal structure.

In order to further study the effect of cation-cation substitutions on the crystal structure in the $Cu_{1.75}Te$ compound, partial substitutions of Cu atoms with Cd atoms were carried out. Structural studies of synthesized $Cu_{1.70}Cd_{0.05}Te$ have shown that partial substitutions of Cu→ Cd have a greater effect on the crystal structure than Cu → Zn substitutions. The results of X-ray studies of the compound $Cu_{1.70}Cd_{0.05}Te$ show that the crystal structure of this compound consists of three phases. These phases correspond to the orthorombic syngony of the Pnma (62) space group, the hexagonal syngony of the P6/mmm (191) space group, and the cubic syngony of the Fm-3m (225) space group.

As can be seen, the crystal structure of the $Cu_{1.70}Cd_{0.05}Te$ compound is more complex than that of the $Cu_{1.70}Zn_{0.05}Te$ compound. This is because the difference between the ionic radius of the Cu and Zn atoms is greater than the difference between the ionic radius of the Cu and Cd atoms. In the case of monovalence, the ionic radius of Cd atoms is $R_{Cd+1} = 1.52$ Å and in the case of duality, $R_{Cd+2} = 0.95$ Å. It can be seen that the difference between the ionic radius of Cu and Cd metals is quite large ($\Delta R \approx 0.24$ Å). This difference has led to differences in the crystal structure, even at low concentrations of substitutions. This is because the difference in ionic radius has a

serious effect not only on the number of bonds formed by atoms, but also on the lengths of the bonds between atoms.

Crystal structures and phase transitions of $Cu_{1.75}Te$, $Cu_{1.70}Zn_{0.05}Te$ and $Cu_{1.70}Cd_{0.05}Te$ compounds in the high temperature region have been studied. It was found that the symmetry of the crystal structure in each of these compounds increased under the influence of high temperatures. As the temperature rose, the orthorhombic and hexagonal phases disappeared and a cubic syngony phase with the Fm-3m (225) space group was formed.

It was found that the complexity of the crystal structure during cation-cation substitution also affected the phase transition temperature. The transition to the cubic phase in $Cu_{1.75}Te$ occurred at $T_{H\rightarrow K} \approx 700$ K, in $Cu_{1.70}Zn_{0.05}Te$ at $T_{O,H\rightarrow K} \approx 800$ K, and in $Cu_{1.70}Cd_{0.05}Te$ at $T_{O,H,K\rightarrow K} \approx 850$ K temperature. These results are due to the fact that all the thermal energy supplied to the system in the $Cu_{1.75}Te$ compound was used to increase the symmetry of the crystal structure. In the combination of $Cu_{1.70}Zn_{0.05}Te$, part of the heat energy supplied to the system was used to form a single phase in the crystal structure, and part to increase the symmetry of the crystal structure. In the combination of $Cu_{1.70}Cd_{0.05}Te$, the thermal energy transferred to the system was used to increase the symmetry of the crystal structures of the orthorhombic and hexagonal phases to crystallization in a single cubic symmetry.

At the end of the chapter, the research results are summarized and the main information obtained during the structural research is presented. The values of crystallographic parameters and the values of phase transition temperatures are presented for each research object.

In the third chapter, structural phase transitions at high temperatures in $Cu_{1.80}Te$ and chalcogenides based on it were studied. Structural studies by X-ray diffraction have shown that at room temperature and under normal conditions, the crystal structure of this compound corresponds to the tetragonal structure of the P3m1 (156) space group. It has been found that copper atoms enter the $Cu_{1.80}Te$ compound both bilaterally and monovalently. Therefore, the lengths of the covalent bonds formed by copper atoms in different

crystallographic positions with chalcogen Te atoms also vary. In the monovalent case, the ionic radius of copper atoms is R_{Cu1+} = 0.95 Å, in the binary case they are R_{Cu2+} = 0.75 Å. The difference between the ionic radii of copper atoms during valence variability ($\Delta R_{Cu1+-Cu2+}$= 0.2 Å) was also observed in the lengths of covalent bonds formed by copper and tellurium atoms.

In order to study the effect of cation-cation substitutions on the crystal structure of the $Cu_{1.80}Te$ compound, the $Cu_{1.50}Zn_{0.30}Te$ compound was synthesized and its crystal structure was studied in the high temperature region. As a result of the analysis of the X-ray diffraction pattern obtained at room temperature, it was determined that the crystal structure of the $Cu_{1.50}Zn_{0.30}Te$ compound cannot crystallize in a single phase and consists of two different phases. The analysis revealed that the crystal structures of each of these phases have different crystallographic parameters. The crystal structure of phase I has a slightly higher symmetry and corresponds to the tetragonal syngonium of the P3m1 space group. The crystal structure of phase II has low symmetry compared to phase I, and Pnma corresponds to orthorombic syngony of the space group. As can be seen from the diffraction patterns obtained at room temperature, a maximum of 9 diffraction was observed in the angular range of $10^o \leq 2\theta \leq 100^o$. These diffraction maxima correspond to the rhombohedric symmetric phase: (1 0 0), (1 0 4), (2 0 0), (3 0 1), (3 1 5), (3 1 9), (4 1 3), (5 0 5) and according to the phase with orthorhombic symmetry: (1 5 3), (0 0 10), (1 5 5), (3 1 2), (3 0 8), (4 0 1), (4 6 8), (5 0 9) consists of atomic planes. Based on the values of the distances between the atomic planes, the values of the crystallographic parameters of the elemental nucleus of the $Cu_{1.50}Zn_{0.30}Te$ compound were calculated. It was determined that the cage parameters of the rhombohedral phase under normal conditions and at room temperature are: $a = b$ = 8.374 Å, c = 21.598 Å, and the cage parameters of the orthorhombic phase are: a = 7.290 Å, b = 22.325 Å, c = 36.244 Å. Different estimates were obtained for the densities of these phases. It was found that the density of the crystal in the rhombohedral phase with a higher symmetry: $\rho_{rom.}$= 7.347 g/cm^3, and in the orthorombic phase with relatively low

symmetry $\rho_{ort.}$ = 7.095 g/cm^3. As can be seen, a higher density was observed in the highly symmetrical phase in the $Cu_{1.50}Zn_{0.30}Te$ compound, a process that is better explained by crystallization. As can be seen, a higher density was observed in the highly symmetrical phase in the $Cu_{1.50}Zn_{0.30}Te$ compound, a process that is better explained by crystallization.

Both phases observed in the X-ray diffraction spectrum obtained at room temperature were observed up to $T \approx 800$ K in the high temperature region. At higher temperatures, a cubic syngonium crystal structure with high symmetry is formed.

During the analysis of the X-ray diffraction pattern obtained at a temperature of T = 773 K, in addition to the diffraction maxima corresponding to the two-phase system: rhombohedric and orthorhombic symmetrical phases, 4 different new diffraction maxima were observed. It has been determined that these diffraction maxima: (1 1 1), (2 0 0), (2 2 0) and (3 1 1) correspond to atomic planes. The parameters of the elementary nucleus were calculated according to the formula $\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$ for the values of the distances between these planes: $a = b = c$ = 6.120 Å. Significant changes were observed in the X-ray diffraction pattern obtained at a temperature of T = 800 K. The diffraction maxima corresponding to the rhombohedric and orthorhombic symmetry phases observed with the previous spectra disappeared, and only the planes corresponding to the cubic symmetric phase: (1 1 1), (2 0 0), (2 2 0), (3 1 1) were observed.

As a result of the analysis of the X-ray diffraction pattern of the compound $Cu_{1.50}Zn_{0.30}Te$, it was determined that a rhombohedral, orthorhombic → cubic phase transition occurred at a temperature of

T = 800 K. After the phase transition, an ideal high-temperature cubic structure characteristic of copper and silver chalcogenide semiconductors was formed. Figure 2 shows the temperature dependences of the parameters of the elemental core of the compound $Cu_{1.50}Zn_{0.30}Te$.

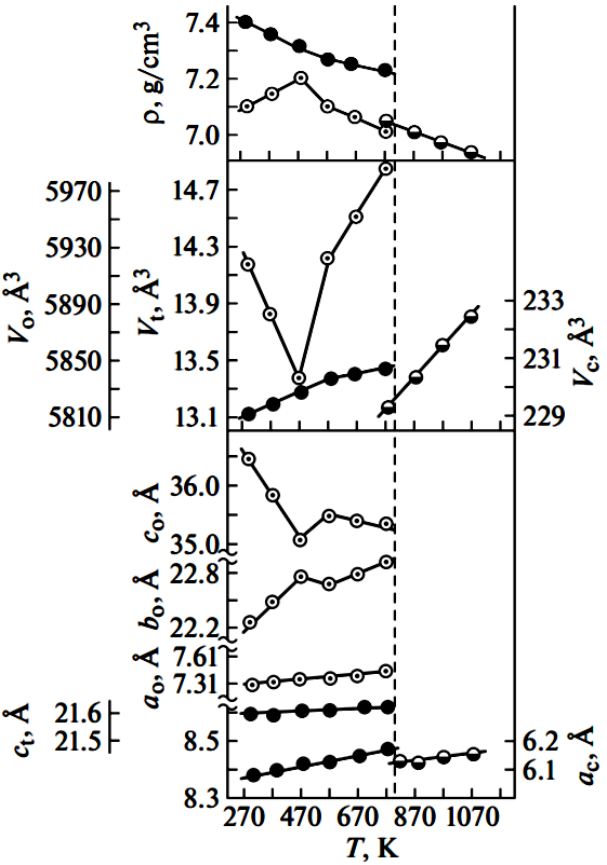

Figure 2. Temperature dependences of the parameters of the elementary core of the compound $Cu_{1.50}Zn_{0.30}Te$.

As can be seen from the dependence, an increase in the values of the parameters of the elemental core was observed as the temperature value increased. This increase continued until the temperature T = 800 K, and a structural transformation took place from a two-phase system to a single-phase system. As can be seen, this phase transition was not only observed with the transformation of the structure, but also with the process of phase formation.

The temperature dependence of the parameters of the elemental core of the compound $Cu_{1.50}Zn_{0.30}Te$ shows that a sudden change in

temperature $T \approx 500$ K was observed and there was a difference in the mechanism of change of many parameters depending on the temperature. It is known from crystallophysics that as the value of temperature increases, the length of the bonds expands due to the increase in the energy of the interatomic bonds, resulting in an increase in the values of the lattice parameters. From the values given in Figure 2, it can be seen that an increase in the orthorombic phase was observed with a sharp jump in parameter b, and an anomalous decrease was observed in parameter c. This phenomenon is called an anomaly and lasts up to $T = 500$ K. Such events in the crystal structure can be caused by fluctuations due to thermal energy as the temperature rises, or by defects in the crystal structure during the synthesis process.

It is important to visualize the processes occurring in the crystal structure under the influence of temperature and to be able to compare the effects of temperature on different phases, to find the values of the coefficients of thermal expansion. For this purpose, the values of thermal expansion coefficients were calculated for each phase of the $Cu_{1.50}Zn_{0.30}Te$ compound. The anomaly observed in the temperature dependence of the cage parameters was characterized by negative values obtained in the values of thermal expansion coefficients. Most enlargements occurred in the orthorhombic phase. In this phase, the change in the coefficients of linear expansion does not occur by the same mechanism. However, the values of some coefficients were observed in the range: $\alpha > 100\times10^{-6}$ K^{-1}. In rhombohedral symmetry, slightly lower coefficients were observed for thermal expansion coefficients than for the orthorombic phase. For these coefficients, the values for the range: $\alpha < 100\times10^{-6}$ K^{-1} were obtained. Smaller values were observed for the coefficients of thermal expansion in cubic symmetry. It was found that in a cubic phase with high symmetry: $\alpha \approx 15\times10^{-6}$ K^{-1} coefficients are obtained. As the symmetry in the crystal structure of the $Cu_{1.50}Zn_{0.30}Te$ compound increases, a more temperature-resistant system is formed, and the values of the crystallographic parameters: linear and volume expansion coefficients change less with the subsequent increase in temperature (Table 1).

Table 1. Coefficients of thermal expansion ($\times 10^{-6}$, K^{-1}).for orthorombic, trigonal and cubic phases in the $Cu_{1.50}Zn_{0.30}Te$ combination.

Phase	*T*, K	$\alpha_{[100]}$	$\alpha_{[100]}$	$\alpha_{[100]}$	$\bar{\alpha}$	$\bar{\beta}$
Orthorombic	293-373	70.302	121.485	-353.734	-53.982	-65.33
	373-473	2.728	120.761	-206.976	-27.829	-72.32
	473–573	39.547	-26.858	136.806	49.832	4.88
	573–673	52.975	40.175	-40.573	17.526	18.01
	673–773	29.726	5.567	-26.876	2.806	25.78
Trigonal	293-373	32.855	-	2.316	22.675	67.27
	373-473	26.215	-	1.389	17.940	59.22
	473–573	30.901	-	16.667	26.156	66.30
	573–673	3.555	-	1.387	2.832	51.04
	673–773	21.319	-	0.924	14.521	49.98
Cubic	773–873	16.340	-	-	16.340	49.020
	873–973	14.682	-	-	14.682	44.046
	973–1073	14.660	-	-	14.660	43.980

In order to study the structural aspects of cation-cation substitutions in the $Cu_{1.80}Te$ compound and to clarify the results obtained for the $Cu_{1.50}Zn_{0.30}Te$ compound, the $Cu_{1.75}Cd_{0.05}Te$ compound was synthesized and its crystal structure was studied in the high temperature region. It has been determined that the crystal structure of the $Cu_{1.75}Cd_{0.05}Te$ compound at room temperature and under normal conditions also consists of two different phases according to the crystal structure of the $Cu_{1.50}Zn_{0.30}Te$ compound. A two-phase system was observed in the $Cu_{1.80}Te$ compound during the partial replacement of Cu atoms with Cd atoms, as well as the partial replacement of Cu atoms with Zn atoms. The first of these phases corresponds to the orthorombic phase of the Pnma space group, and the second to the tetragonal phase of the P3m1 space group. An anomaly was observed in the values of cage parameters obtained at temperatures above T = 673 K. At a temperature of T = 773 K, a cubic phase with the Fm-3m space group began to form. It was determined that the rhombohedric and orthorhombic phases disappeared at T = 850

K, and a single-phase system consisting only of cubic symmetry was observed.

As can be seen, significant changes in the crystal structure of the $Cu_{1.80}Te$ compound were observed during substitution, even at very low concentrations ($Cu_{1.70}Cd_{0.05}Te$ və $Cu_{1.50}Zn_{0.30}Te$). This is due to the fact that the nature of the bonds formed by the elements Zn and Cd with the Te atoms is completely different from the nature of the bonds formed by the Cu and Te atoms. The difference in the lengths of the bonds affects not only the values of the lattice parameters, but also the symmetry of the crystal lattice. Therefore, during these substitutions, the crystal structure became complex, and a structure consisting of several phases $Cu_{1.50}Zn_{0.30}Te$ and $Cu_{1.75}Cd_{0.05}Te$ was observed.

At the end of the chapter, the results obtained during X-ray structural studies for compounds based on the $Cu_{1.80}Te$ binary compound are summarized. Crystallographic parameters and phase transition temperature values for different compositions are presented.

In the fourth chapter, the crystal structures of AgCuS, $AgCuS_{0.5}Se_{0.5}$ and $AgCuSe_{0.5}Te_{0.5}$ compounds and structural phase transitions in the high temperature region are determined. Changes in the structure of anion-anion substitutions in these compounds have been identified. Depending on the stoichiometric amount of elements, the conditions for the synthesis of compounds are given. Information about the device and their parameters were shown during X-ray structural studies.

Analysis of the X-ray diffraction pattern obtained at room temperature revealed that the crystal structure of the AgCuS compound consists of a single phase, which corresponds to an orthorombic syngonium crystal structure of the Cmcm (63) space group. From the analysis of spectra, it was obtained that a maximum of 15 is observed at room temperature in the range of $10 \leq 2\theta \leq 100°$. These maxima correspond to the planes: (1 1 0), (0 2 0), (0 2 1), (1 1 2), (0 2 2), (2 0 0), (4 0 0), (1 3 1), (2 2 0), (2 0 4), (3 1 2), (1 3 5), (2 0 6), (1 3 6) and (0 2 7). The values of the parameters of the elementary nucleus were calculated with respect to the d_{hkl} distances between the atomic planes,

and the values a = 4.0600 Å, b = 6.6600 Å, c = 7.9908 Å were determined.

Based on the obtained crystallographic parameters, the crystal structure of the AgCuS compound obtained in the "Diamond 3.2" program was constructed and it was determined that monovalent metal-silver atoms stand on the tins of the elemental nucleus of AgCuS crystals. Other metal atoms - monovalent copper atoms - are distributed throughout the volume of the crystal lattice. Equivalent chalcogen - sulfur atoms form covalent bonds with sulfur and copper atoms throughout the crystal lattice.

It is known that Ag atoms stand at the nodes of the crystal structure, and therefore the coordinates of these atoms are: $x = 0$, $y = 0$, $z = 0$. Cu atoms are located in different coordinates than Ag atoms. Their coordinates are $x = 0$, $y = 0.46$, $z = 0.25$. The coordinates of the S halogen atoms are $x = 0$, $y = 0.8$, $z = 0.25$. The bonds formed by Ag atoms with Cu atoms are $d_{(Ag\text{-}Cu)1}$ = 2.8604 Å and $d_{(Ag\text{-}Cu)2}$ = 3.6575 Å, and the bonds formed by S atoms are $d_{(Ag\text{-}S)1}$ = 3.4787 Å and $d_{(Ag\text{-}S)2}$ = 3.9949 Å. The bonds formed by Cu atoms with S atoms are $d_{Ag\text{-}Cu}$ = 3.8999 Å. As can be seen, the lengths of the bonds formed by the Ag, Cu and S atoms are different. This difference depends on the coordinates of the atoms, the ionic radius and the type of bond. It is known that in the monovalent case the ionic radius of copper atoms is R_{Cu1+} = 0.95 Å, in the monovalent case the ionic radius of silver atoms is R_{Ag1+} = 1.10 Å, in the binary case the ionic radius of sulfur atoms is R_{S2-} = 1.86 Å. As can be seen, the ionic radii of the S atoms are larger than the ionic radii of the Cu and Ag atoms. If $\Delta R_{Ag\text{-}Cu}$ = 0.15 Å, then $\Delta R_{S\text{-}Cu}$ = 0.91 Å, $\Delta R_{S\text{-}Ag}$ = 0.76 Å. Therefore, this difference manifests itself in the formation of inter-atomic bonds, and the bonds formed by the S atoms are larger than the others.

15 diffraction reflexes observed in the X-ray diffraction spectrum of the AgCuS compound obtained at room temperature were also present in the high temperature region and were observed up to $T < 370$ K. Significant changes were observed in the X-ray diffraction pattern obtained at a temperature of T = 400 K. It was found that only 7 of the 15 diffraction reflexes observed at room temperature were

observed. These reflexes correspond to the planes: (0 1 1), (0 1 2), (0 1 3), (1 1 2), (0 2 1), (0 1 4) and (1 1 4). It was found that the new structure obtained in the combination of AgCuS is single-phase. The crystal structure of this new phase also corresponds to the hexagonal syngonium of the $P6_3/mmc$ (194) space group. Based on the d_{hkl} distances between the *hkl* atomic planes, the values of the core parameters were calculated and the values of $a = b = 3.9590$ Å, $c = 6.7884$ Å were determined.

As the temperature increased, another structural change was observed in the AgCuS compound. It was found that re-changes are observed in the X-ray diffraction pattern obtained at a temperature of $T = 770$ K. The values of the parameters of the elementary nucleus with respect to these planes were calculated and set a = b = c = 5.7288 Å. 6 reflexes were observed in the X-ray diffraction pattern. These reflexes corresponded to the atomic planes: (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), and (4 0 0). It has been determined that the crystal structure of this new phase also belongs to the highly symmetrical cubic syngony of the space group $Fm\bar{3}m$ (225).

The values obtained for the crystallographic parameters show that there are differences not only in the positions but also in the intensities of the diffraction maxima. It is known that the positions of the diffraction maxima characterize the distances between the atoms and the lattice parameters accordingly. This process can also be observed during thermal expansion within the same phase. The intensities of the diffraction maxima characterize the atomic coordinates. Their sharp difference is a sign that the atoms are in different crystallographic positions.

Analysis of X-ray diffraction patterns obtained at higher temperatures showed that a cubic symmetrical crystal structure was observed at temperatures up to $T = 990$ K and no polymorphic structure transformation took place. As a result of structural studies conducted in the region of high temperatures by the method of X-ray diffraction, it was observed that in the combination of AgCuS in the temperature range of $290\ K \leq T \leq 990\ K$ occurs orthorombic → hexagonal → cubic phase transitions. The temperature dependences of

the cage parameters according to the temperatures T = 293, 400 and 770 K are given in Figure 3. Dependencies show that as the temperature value increases, there is a linear expansion in the values of the cage parameters.

It was found that in the triple AgCuS triple semiconductor junction, as in the $Cu_{1.75}Te$ binary semiconductor junction, a crystalline structure of the Fm-3m space group with ideal cubic symmetry is obtained under the influence of high temperatures. It can be concluded that high-temperature Fm-3m cubic crystal structure is characteristic for copper and silver chalcogenides.

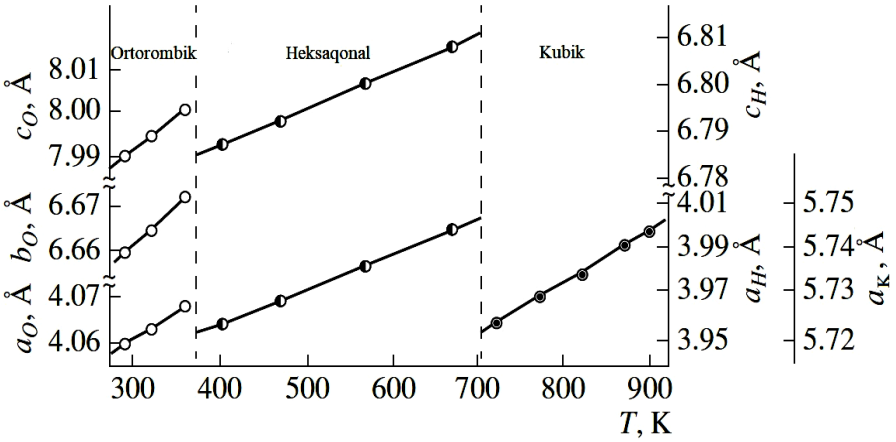

Figure 3. Temperature dependences of the parameters of the elemental core of the AgCuS compound.

It was found that in the triple AgCuS triple semiconductor compound, as in the $Cu_{1.75}Te$ binary semiconductor compound, a cubic crystal structure with a highly symmetrical Fm-3m space group is obtained under the influence of high temperatures. It can be concluded that high-temperature Fm-3m cubic crystal structure is characteristic for copper and silver chalcogenides.

In order to study the effect of anion-anion substitutions on the crystal structure in triple copper and silver-containing chalcogenide semiconductors, the compound $AgCuS_{0.5}Se_{0.5}$ was synthesized, the crystal structure and phase transitions of the obtained composition were studied. It was found that at room temperature and under normal conditions, this composition crystallizes in a two-phase state. One of these phases corresponds to a $Cu_{1.96}S$ compound with a monoclinic symmetry of the $P2_1/n$ space group, and the other to an AgCuSe compound with an orthorombic symmetry of the P4/nmm space group. When studying the crystal structure of this composition under the influence of high temperature, it was determined that the structural phase transition occurs at a temperature of T = 770 K. After the phase transition, a phase with high symmetry with cubic syngony is formed. Fm m space group has a fairly high symmetry. This phase is observed at high temperatures in chalcogenide semiconductors. The compound $AgCuS_{0.5}Se_{0.5}$ also crystallizes in this symmetry. At the nodes of the cube, the equivalent S or Se atoms settle in the coordinates x = 0, y = 0, z = 0. Monovalent Ag or Cu atoms are distributed throughout the volume of the crystal lattice (cube). Their coordinates are x = 0.25, y = 0.25, z = 0.25 or x = 0.3807, y = 0.3807, z = 0.3807. The crystal structure of the $AgCuS_{0.5}Se_{0.5}$ compound is shown in Figure 4.

As can be seen from Figure 4, the Ag and Cu atoms in the crystal structure alternate in the same way as the S and Se atoms. S (Se) atoms form various covalent bonds with Ag (Cu) atoms. When these bonds are formed with close atoms, the lengths of the interatomic distances are $d_{S(Se)\text{-}Ag(Cu)}$ = 2.5524 Å, and when these bonds are formed with relatively distant atoms, the lengths of the interatomic distances are $d_{S(Se)\text{-}Ag(Cu)}$ = 3.9343 Å. The Ag and Cu atoms form smaller bonds with each other. The lengths of these bonds can even be up to dAg (Cu) -Ag (Cu) = 1.3876 Å. The metal atoms that form a covalent bond with the halogen atoms at the nodes and faces of the cube form a highly symmetrical stable system. This crystalline structure is maintained at a temperature of T = 973 K.

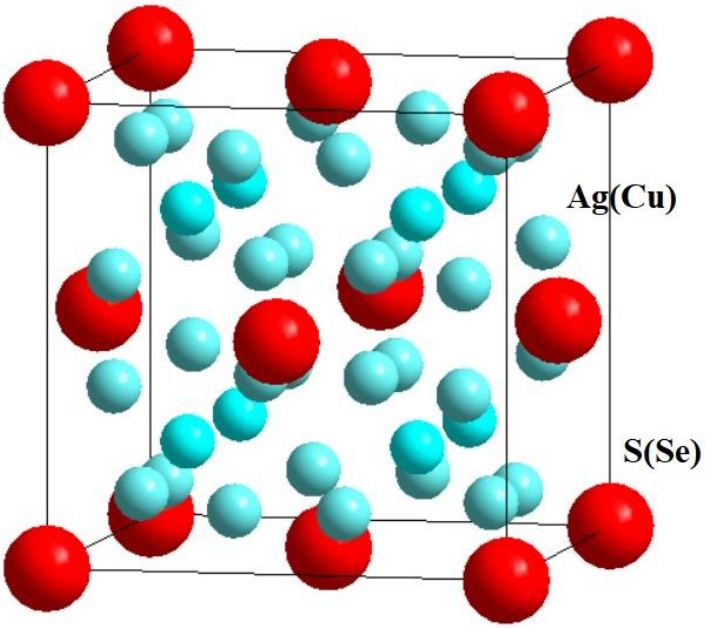

Figure 4. Crystal structure of $AgCuS_{0.5}Se_{0.5}$ at temperature T = 773 K.

As can be seen, in AgCuS crystals, when the S atoms are partially replaced by Se atoms, fundamental changes in the crystal structure occur. It is not possible to obtain a stable system under normal conditions and at room temperature. A system of phases with two different symmetries is obtained, and the symmetry of these phases is quite low. In the combination of $AgCuS_{0.5}Se_{0.5}$ a single-phase system is obtained only at high temperatures, which occurs in accordance with the crystals of AgCuS. As can be seen, the difference between the ionic radii of the Se and S chalcogens in the dual state creates differences not only in the values of the lattice parameters, but also in the symmetry of the crystal structure. However, under the influence of high temperatures, this difference is removed from the black and a stable thermodynamic system with a sufficiently high symmetry is formed.

Temperature dependences of cage parameters for different phases of $AgCuS_{0.5}Se_{0.5}$ composition were obtained, the mechanism of change of cage parameters in the region of high temperatures was determined. The density of the crystal was determined for each phase. It was found that the volume of the crystal lattice increases due to the increase in the distance between the atoms under the influence of temperature, and therefore there is a decrease in the density value. According to this mechanism, the values of the coefficients of thermal expansion for the phases were also calculated. It was found that the values of the coefficients of thermal expansion in different planes in the orthorhombic and monoclinic phases also vary.

In order to study in more detail the effect of anion-anion substitutions on triple chalcogenides, the composition $AgCuSe_{0.5}Te_{0.5}$ was synthesized, the structural phase transitions in the region of high temperatures were studied. It was found that at room temperature and under normal conditions, this composition is more complex than AgCuS and $AgCuS_{0.5}Se_{0.5}$. Analysis of X-ray diffraction spectra at room temperature revealed that $AgCuSe_{0.5}Te_{0.5}$ crystallizes in a three-phase state. The first of these phases corresponds to the Cu_2Te compound with orthorombic symmetry of the P6/nmm space group, the second to the AgCuSe compound with the P4/nmm spatial group orthorhombic symmetry, and the third to the FC-3m $AgCuSe_5$ with high symmetrical cubic symmetry of the space group. Under the influence of high temperatures, the crystal structure of this composition crystallizes in a single-phase cubic symmetry, and at a temperature of T = 570 K, a structural phase transition occurs. It was determined that the high-temperature phase is a cubic symmetry of the Fd-3m space group corresponding to the $AgCuSe_{0.5}Te_{0.5}$ combination. Temperature dependences of cage parameters at different phases were obtained for $AgCuSe_{0.5}Te_{0.5}$ composition, the mechanism of change of cage parameters in the region of high temperatures was determined. According to this mechanism, the values of the coefficients of thermal expansion for the phases were also calculated. It was found that the values of the coefficients of thermal expansion in different planes in the orthorhombic and monoclinic phases also vary. Thus, the largest

value of thermal expansion (70.268×10^{-6} K^{-1}) occurred on the plane [010] for the Cu_2Te compound, which corresponds to parameter b in the temperature dependence of the lattice parameters. The volume also corresponds to the largest value of the coefficient of expansion (111.951×10^{-6} K^{-1}) in the combination of Cu_2Te, the main part of which is the parameter b.

Structural studies of AgCuS, $AgCuS_{0.5}Se_{0.5}$ and $AgCuSe_{0.5}Te_{0.5}$ have shown that element atoms with different ionic radius can not occupy the same position during anion-anion substitution. Therefore, a two-phase system was obtained when S atoms were partially replaced by Se atoms, and a three-phase system was obtained when they were completely replaced by Se and Te atoms. These differences are explained by the difference between the ionic radius of the sulfur, selenium and tellurium atoms.

Analysis of the experimental results showed that under the influence of high temperatures, a cubic phase with high symmetry was formed in each of these compounds. At the end of the chapter, the results of X-ray diffraction studies were summarized and the data obtained were presented. It is shown that the values of crystallographic parameters and the values of phase transition temperatures were determined for each research object.

In the fifth chapter, the effect of cation-cation substitutions on the crystal structure and phase transitions of $Ag_{2-x}Cu_xS(Se)$ compounds is studied. During the research, various compounds synthesized at different concentrations of silver and copper atoms were taken. Structural studies of the $Ag_{1.55}Cu_{0.45}S$ compound have shown that the crystal structure of this compound has tetragonal symmetry with the I4/mcm space group. Under the influence of high temperatures, a tetragonal-cubic phase transition occurs at this compound at a temperature of T = 420 K, and a cubic symmetrical crystal structure of the Im-3m space group is formed. It was found that as the temperature value increases, a restructuring phase transition occurs at T = 870 K, and a cubic symmetrical crystal structure with the Fm-3m space group is formed.

The densities of the $Ag_{1.55}Cu_{0.45}S$ compound for different

phases were calculated according to the experimental parameters. It was found that the density of the crystal decreases during the transition from the tetragonal symmetry of the I4/mcm space group to the cubic phase of the Im-3m space group. This is explained by the expansion of the crystal under the influence of temperature. During the transition to the cubic phase of the Fm-3m space group, the density of the crystal increases, which occurs as the symmetry of the crystal structure increases.

Structural studies of the $Ag_{1.2}Cu_{0.8}S$ compound synthesized at different concentrations of Ag and Cu atoms have shown that the crystal structure of this compound is somewhat complex. During the analysis of diffractograms obtained at room temperature, it was determined that this composition crystallizes in the two-phase state. The first phase has monoclinic symmetry with $P2_1/c$ space group, and the second phase has monoclinic symmetry with $P2_1/n$ space group. Analysis of diffractograms obtained at high temperatures showed that each of these phases is observed in the temperature range T <400 K. At higher temperatures, a phase transition of the monoclinic-monoclinic structure occurs, and a cubic symmetrical crystalline structure of the Fm-3m space group is formed in the $Ag_{1.2}Cu_{0.8}S$ combination.

In the $Ag_{2-x}Cu_xS$ system, the $Ag_{0.93}Cu_{1.07}S$ compound was synthesized to study the phase transitions occurring in the compounds obtained at higher concentrations of Cu atoms, the crystal structure and structural phase transitions were studied. It was found that the crystal structure of this compound at room temperature has orthorombic symmetry with the Cmcm space group. However, at T = 370 K, significant changes are observed in the radiographs. This is explained by the increase in the symmetry of the crystal structure and the occurrence of an orthorombic-hexagonal phase transition. As a result of spectral analysis, it was determined that the newly obtained hexagonal phase corresponds to the $P6_3/mmc$ space group. At higher temperatures, another structural phase transition was observed. As a result of the analysis of diffractograms, it was determined that at a temperature of T = 460 K, a hexagonal-cubic phase transition occurs

and a cubic phase of the Fm-3m space group is formed.

The results of the structural studies showed that in each of the compounds included in the system $Ag_{2-x}Cu_xS$: in each of the compounds $Ag_{1.55}Cu_{0.45}S$, $Ag_{1.2}Cu_{0.8}S$ və $Ag_{0.93}Cu_{1.07}S$, the structure of Fm-3m is formed under the influence of high temperatures, which leads to the formation of AgCuS is the ideal crystal structure to match. As can be seen from the results of X-ray studies for $Ag_{2-x}C_xuS$ compounds, defects caused by the difference between ionic radius at room temperature are eliminated by thermal energy in the high temperature range and therefore the transition to the ideal structure phase occurs. The crystallographic parameters of the phases observed in the high temperature region in the $Ag_{1.55}Cu_{0.45}S$ combination: symmetry, space group, lattice parameters and density are given in Table 2.

Table 2. Crystallographic parameters of $Ag_{1.55}Cu_{0.45}S$ in the high temperature region

***T*, K**	**Phase**	**Cage parameters**			***z***	***ρ*, g/cm^3**
		***a*, Å**	***c*, Å**	***V*, Å^3**		
293	Tetragonal, I4/mcm	8.647	11.576	865.5	16	6.981
385	Tetragonal, I4/mcm	8.667	11.778	884.7	16	6.981
425	Cubic, Im-3m	4.833	-	112.9	2	6.704
573	Cubic, Im-3m	4.876	-	115.8	2	6.520
673	Cubic, Fm-3m	5.951	-	210.7	4	7.179
873	Cubic, Fm-3m	5.982	-	214.1	4	7.179

Structural studies for the $Ag_{2-x}Cu_xS$ system have also been performed for the $Ag_{2-x}Cu_xSe$ system. The $Ag_{1.5}Cu_{0.5}Se$ compound was synthesized under the condition that the concentration of Ag atoms was higher than that of Cu atoms. As a result of the analysis of the X-ray diffraction pattern, it was determined that a maximum of 36 is observed in the range of $1 \leq d_{hkl} \leq 3.5$ at room temperature. During the interpretation of these maxima, it was obtained that the crystal structure of the $Ag_{1.55}Cu_{0.45}S$ compound can not form a single phase. Ag_2Se - AgCuSe solid solution is obtained and a two-phase system is formed. One of these phases corresponds to the Ag_2Se compound and 13 of the diffraction maxima observed on the radiograph belong to this phase. The crystal structure of this phase corresponds to the space group $P2_12_12_1$ (19) with orthorhombic symmetry. The second phase corresponds to the AgCuSe compound, and 23 of the diffraction maxima observed on the radiograph belong to this phase. The crystal structure of this phase corresponds to the orthorombic symmetric P4/nmm (129) space group. The values of the parameters of the elementary nucleus are determined with respect to the d_{hkl} distances between the atomic planes. For the Ag_2Se phase: a = 4.333 Å, b = 7.062 Å and c = 7.764 Å, for the AgCuSe: a = 4.105 Å, b = 20.350 Å and c = 6.310 Å were appointed.

The diffraction pattern obtained at T = 373 K was similar to the X-ray diffraction pattern obtained at room temperature. All reflexes were observed at room temperature. Few reflexes were observed in the diffraction patterns obtained at T = 423 and 473 K relative to room temperature. It was found that these spectra also correspond to a two-phase structure consisting of Ag_2Se and AgCuSe crystals. 4 reflexes were observed in the spectra obtained at T = 523 and 573 K temperatures. As a result of the analysis, it was determined that the new phase corresponds to a single-phase crystal structure. These reflexes correspond to the cubic symmetrical crystal structure of the Fm-3m (225) space group. The parameters of the elementary nucleus were calculated according to the distances between the atomic planes. It was determined that T = 523 K has the values $a = b = c$ = 6.107 Å at temperature. Various modifications of $Ag_{1.5}Cu_{0.5}Se$ in the high

temperature range, crystallographic parameters for these modifications are given in Table 3.

Table 3. Crystallographic parameters of $Ag_{1.5}Cu_{0.5}Se$ in the high temperature region.

***T*, K**	**Modification**	**Cage parameters**			***Z***	**Space group**
		a	***b***	***c***		
293	Ag_2Se- orthorombic	4.333	7.062	7.764	4	$P2_12_12_1$
	AgCuSe-orthorombic	4.105	20.350	6.310	10	P4/nmm
373	Ag_2Se- orthorombic	4.340	7.084	7.787	4	$P2_12_12_1$
	AgCuSe-orthorombic	4.110	20.481	6.307	10	P4/nmm
423	Ag_2Se- orthorombic	4.354	7.068	7.869	4	$P2_12_12_1$
	AgCuSe-orthorombic	4.085	20.797	6.317	10	P4/nmm
473	Ag_2Se- orthorombic	4.364	7.078	7.900	4	$P2_12_12_1$
	AgCuSe-orthorombic	4.090	20.793	6.330	10	P4/nmm
523	$Ag_{1.5}Cu_{0.5}Se$- cubic	6.107	-	-	4	Fm-3m
573	$Ag_{1.5}Cu_{0.5}Se$- cubic	6.118	-	-	4	Fm-3m

As can be seen from the values given in the table, the $Ag_{1.5}Cu_{0.5}Se$ composition at room temperature can not form as a single-phase crystal structure. Ag_2Se – AgCuSe solid solution is formed. Ag_2Se and AgCuSe compounds in the solid solution keep their structural properties. It can be seen that the difference in the ionic radii of the Ag and Cu atoms does not allow the formation of a single-phase system during synthesis. Therefore, no single-phase crystal structure is formed and a two-phase solid solution is formed. At a temperature of T= 523 K, the composition of $Ag_{1.5}Cu_{0.5}Se$ forms a single-phase crystal structure and this crystal structure has a fairly high symmetry and corresponds to a cubic crystal structure. Some of the Ag atoms are in the same position with the Cu atoms. Se chalcogen atoms combine with the metal atoms Ag and Cu to form covalent bonds. These covalent bonds form a cubic crystal structure with high symmetry. This crystalline structure with high symmetry can not form at low temperatures.

In order to describe the effect of high temperature $Ag_{1.5}Cu_{0.5}Se$ on the crystal structure, temperature dependences of the parameters and density of the elemental core (cage) for different phases were obtained. It is derived from the dependencies that an anomaly occurred in the mechanism of change of cage parameters at a temperature of $T \approx 400$ K. This phenomenon is mainly due to defects in the crystal structure. After the restoration of defects due to thermal energy, all the energy transferred to the crystal lattice is used for expansion and accumulation of Vigner's potential in the system. Such defects are possible due to the violation of homogeneity during the partial replacement of Cu atoms with Ag atoms. However, after the recovery of defects, the system changes by the same mechanism.

The $Ag_{0.4}Cu_{1.6}Se$ compound was synthesized in order to study in more detail the structural phase transitions that occur in the compounds included in the $Ag_{2-x}Cu_xSe$ system. As a result of research, it was found that the structural properties of $Ag_{0.4}Cu_{1.6}Se$ are similar to the structural properties of $Ag_{1.5}Cu_{0.5}Se$. A two-phase system at room temperature was also observed in this combination. The main difference is that since the concentration of Cu atoms in $Ag_{0.4}Cu_{1.6}Se$ is higher than the concentration of Ag atoms, the Ag_2Se phase has been replaced by the Cu_2Se phase. It was found that the crystal structure of this composition is two-phase at room temperature, consisting of $P222_1$ spatial group orthorombic symmetry corresponding to Cu_2Se compound and P4/nmm spatial group orthorombic symmetry corresponding to AgCuSe compound. Analysis of radiographs obtained at high temperatures showed that at T = 570 K an orthorombic-cubic phase transition occurs and a cubic phase of the Fm-3m space group is formed.

The results of structural studies conducted at high temperatures for the $Ag_{2-x}Cu_xS$ and $Ag_{2-x}Cu_xSe$ systems show that at high temperatures, these compounds also form an ideal cubic crystal structure with the Fm-3m space group, which belongs to the copper and silver chalcogenides. These correspondences, which exist in systems with different compositions are the difference between the ionic radius of silver and copper atoms in the monovalent state: ΔR_{Ag1+}

$_{-\ Cu1+}$ = 0.15 Å and the difference in the ionic radius of sulfur and selenium atoms in the binary state: $\Delta R_{Se2-\ -\ S2-}$ = 0.12 Å. Structural studies of systems based on AgCuSe and AgCuS show that although these systems have different crystal structures at low temperatures, they have an ideal and stable crystal structure at high temperatures. When the concentrations of silver and copper atoms are close, the transition to the cubic phase occurs more quickly. Temperature dependences of the lattice parameters were constructed for all the obtained phases, and the coefficients of expansion from the plane (linear) and volume from the heat were calculated according to these dependences.

At the end of the chapter, the research results for $Ag_{2-x}Cu_xS$ and $Ag_{2-x}Cu_xSe$ systems are summarized and the main data obtained during the structural studies are presented. Crystallographic parameters and phase transition temperature values are shown for each system.

In the sixth chapter for the study of cation-cation substitutions with element atoms with magnetic properties in chalcogenides the structural properties of chalcogenide semiconductors in which Fe atoms are substituted have been studied. The structure of chalcopyrite ($CuFeS_2$) crystal was studied by X-ray diffraction method. Diffraction spectra obtained by the X-ray diffraction method were analyzed by the Ritveld method. Information about the Ritveld method is given, the advantages of this method are shown. As a result of the analysis, it was determined that the crystal structure of the $CuFeS_2$ compound under normal conditions and at room temperature corresponds to the tetragonal symmetry with the spatial group I-42d.

The coordinates of the atoms in the $CuFeS_2$ crystals were determined using the "Fullprof" program. In the tetragonal crystal structure, it has been determined that the Cu atoms are located at the nodes of the cage. S - chalcogen atoms form FeS_4 tetrahedra around Fe atoms located along the volume of the cage. No structural changes were observed during the partial substitution of Fe atoms with 1% Ni atoms, which was explained by the proximity of the ionic radius of the iron and nickel elements in the dual state.

Analysis of X-ray diffraction spectra of $CuFe_{0.99}Ni_{0.01}S_2$ was

also performed by the Ritveld method. Analysis of the X-ray diffraction pattern obtained at room temperature revealed that the crystal structure of the $CuFe_{0.99}Ni_{0.01}S_2$ compound consists of a single phase, as in the crystal structure of the $CuFeS_2$ compound and this phase corresponds to the tetragonal syngonium crystal structure of the I-42d space group (Figure 4).

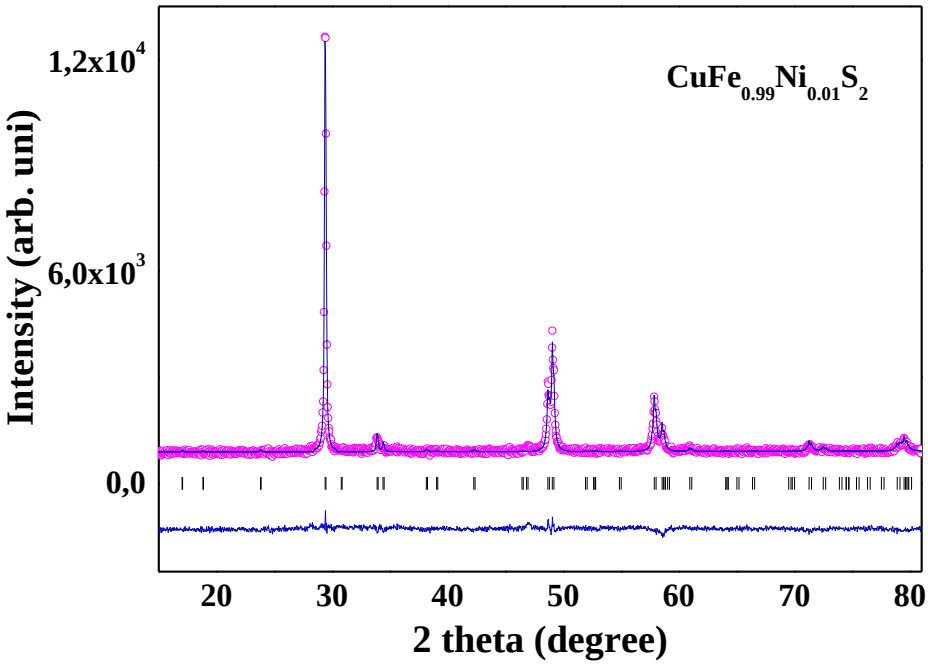

Figure 4. X-ray diffraction pattern of $CuFe_{0.99}Ni_{0.01}S_2$ compound at room temperature.

As can be seen from Figure 4, the given spectrum at room temperature in the range of $15 \leq 2\theta \leq 80°$ was analyzed in the Fullprof program. The values of the parameters of the elementary core are determined: $a = b = 5.2904(5)$ Å and $c = 10.4266(1)$ Å. It appears from these values that the lattice parameters of the $CuFe_{0.99}Ni_{0.01}S_2$ compound also fully correspond to the values of the lattice parameters

of the $CuFeS_2$ compound. Using the Ritveld method, the coordinates of the copper, iron and sulfur atoms in the elemental core of the $CuFe_{0.99}Ni_{0.01}S_2$ compound were determined. It was found that, as in the values of the cage parameters, the values of the atomic coordinates are also consistent. If we compare the radiographs of the compounds $CuFeS_2$ and $CuFe_{0.99}Ni_{0.01}S_2$, we see that indeed, no significant changes in the X-ray diffraction spectra of these compounds were observed. A comparison of the crystallographic parameters of these compounds showed that no change in the crystal structure was observed when Fe atoms were replaced by 1% Ni atoms. It is known from the course of inorganic chemistry that it is important to observe certain conditions during the partial replacement of the elements that make up the crystal structure. The main thing is that substitutes must have similar physical and chemical properties. They must show the same valence and have a close ionic radius. Otherwise, the added atoms will not be able to hold the position of the replaced atoms in the crystal structure. If we look closely, we see that in the trivalent case, the ionic radii of the iron and nickel atoms are the same: r_{Fe3+} =0.623 Å, r_{Ni3+} = 0.623 Å. Based on the crystallographic parameters obtained by analyzing the X-ray diffraction spectra of $CuFe_{0.99}Ni_{0.01}S_2$ and $CuFeS_2$ compounds by the Ritveld method, the crystal structures of these compounds were constructed in the DIAMOND 3.2 program.

As can be seen in Figure 5, copper atoms stand at the nodes of the crystal lattice. Iron and nickel atoms alternate in a crystal structure on certain planes. Sulfur atoms form $Fe(Ni)S_4$ tetrahedra around iron and nickel atoms. These polyesters, formed on the basis of metal-chalcogen covalent bonds, play an important role both in the formation of the crystal structure and in the formation of various physical properties.

The study of the crystal structure of the $CuFe_{0.99}Ni_{0.01}S_2$ compound obtained by partially replacing the $CuFeS_2$ chalcopyrite compound and Fe atoms in this compound with Ni atoms showed that, cation-cation substitutions at small concentrations with tetragonal symmetry do not significantly affect the crystal structures of these compounds. In order to study the effect of anion-anion substitution of

chalcogen atoms on these compounds and changes in the crystal structure, $CuFeS_2$ was synthesized, its crystal structure and structural phase transitions in the region of high temperatures were studied. The crystal structure of the $CuFeSe_2$ compound has also been studied in order to study the structural properties of these compounds in more depth.

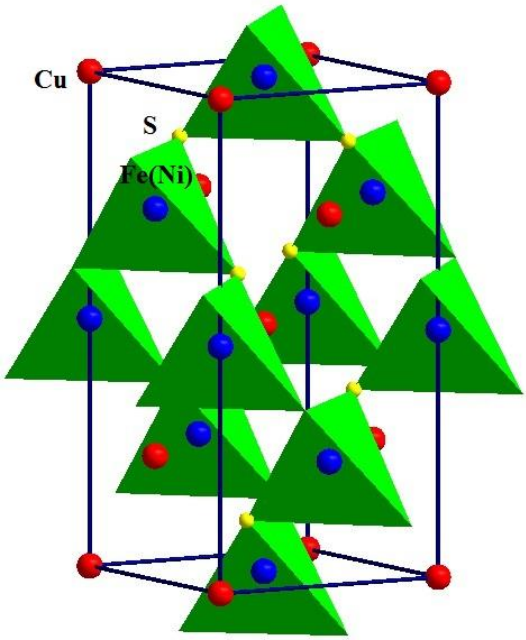

Figure 5. Crystal structure of $CuFe_{0.99}Ni_{0.01}S_2$ and $CuFeS_2$ compounds at room temperature.

The $CuFeSe_2$ compound was synthesized by the standard method in the form of a solid-phase system in a vacuum quartz ampoule in a high-temperature furnace. The synthesized polycrystalline substance was developed for structural studies. The crystal structure of the $CuFeSe_2$ chalcopyrite compound has been studied. Structural studies at room temperature and high temperatures up to T = 673 K were performed by X-ray diffraction. D8 Advance

(Bruker) X-ray diffractometer with 40 kV, 40 mA, Cu*K*α radiation, λ = 1.5406 Å parameter was used during the research. The object used for the experiments was crushed into a mortar and pestle. X-ray of $CuFeSe_2$ compound was obtained. The diffraction pattern was obtained in the angle range $10^o \leq 2\theta \leq 80^o$. Analysis of the X-ray diffraction pattern obtained at room temperature revealed that the crystal structure of the $CuFeSe_2$ compound consists of a single phase, which corresponds to the tetragonal syngonium crystal structure of the I-42c space group. The values of the parameters of the elementary core were determined: $a = b = 5.5210$ Å, $c = 11.0420$ Å, $V = 336.576$ Å^3 and $\rho = 5.4708$ g/cm^3. 10 reflexes were observed in the X-ray diffraction pattern at room temperature. It was determined that these reflexes are: (002), (112), (200), (104), (204), (214), (312), (400), (324), (316) and (218) correspond to atomic planes. Reflexes obtained at room temperature were also observed in the region of high temperatures, and no structural phase transition was observed. If we compare the crystallographic parameters obtained for the $CuFeSe_2$ compound with the parameters obtained for the $CuFeS_2$ compound, we see that the structural parameters of these compounds are very appropriate. It can be concluded that although the crystal structure of chalcopyrite has low symmetry, the anion-anion and cation-cation substitutions do not have much effect on its crystal structure and have a fairly stable crystalline structure.

The values of thermal expansion coefficients were calculated for the $CuFeSe_2$ compound. From the values of the coefficients obtained for different planes and volumes, it is clear that the coefficients α_a occurring in the plane (100) and α_b in the plane (010) change by almost the same mechanism. As the temperature rose, more expansion took place. However, in the α_c coefficient occurring on the plane (001), an anomaly occurred up to the temperature $T = 573$ K. Although the temperature rose, thermal expansion occurred at a slower rate. At higher temperatures, the mechanism continued normally and another anomaly was observed. This process was also observed in the values of the volume expansion coefficient.

$AgCu_{1-x}Fe_xS$ compounds were synthesized in AgCuS by partially replacing Cu atoms with Fe atoms. Studies in the field of high temperatures have shown that in hecagonal-cubic structure phase transition occurs in AgCuS crystals. Thermal analysis of $AgCu_{0.99}Fe_{0.01}S$ compound synthesized with a concentration of Fe atoms $x = 0.01$ in the high temperature range showed that the structural properties of this compound are similar to the structural properties of AgCuS compound. However, an anomaly was observed in the $AgCu_{0.97}Fe_{0.03}S$ compound synthesized at higher concentrations of Fe atoms. This process is explained by the fact that at higher concentrations Fe ions cannot replace Cu ions.

In order to compare the structural properties of copper and silver chalcogenides with the structural properties of other chalcogenides, the crystal structure of the semiconductor compound $Fe_{1.2}In_{1.87}Se_4$ was also studied. X-ray studies of the crystal structure of the $Fe_{1.2}In_{1.87}Se_4$ compound obtained as a result of partial replacement of In atoms with Fe atoms in the In_2Se_3 compound were carried out.

During the discussion of the results obtained from the structural studies, it was determined that the crystal structure of this compound corresponds to the rhombohedric syngonium of the highly symmetrical R-3m space group. As a result of the analysis, it was determined that the metal atoms Fe and In in the crystal structure are in the same crystallographic position. Se halogen atoms form covalent bonds with metal atoms to form polyhedra - $In(Fe)Se_4$ tetrahedra. It was found that the concentrations of iron and indium metal atoms in different crystallographic positions also vary. Figure 6 shows the structure model for the $\vec{c}\vec{a}$ planes. The structural model shows that the metal atoms Fe and In, standing in different crystallographic positions, form different polyhedrons by forming covalent bonds with the surrounding halogen atoms.

The crystal structure of the $Ga_{0.83}In_{0.83}Fe_{0.34}S_3$ compound was also studied in order to make a comparative analysis and study of the crystal structures of the chalcogenides in which the Fe atoms were included. Structural studies by X-ray diffraction have shown that the crystal structure of the $Ga_{0.83}In_{0.83}Fe_{0.34}S_3$ compound corresponds to a

tetragonal symmetry with the P3m1 space group. As a result of the analysis, it was determined that only In atoms stand in some crystallographic positions, Ga and In atoms alternate in some, and Ga and Fe atoms alternate in others.

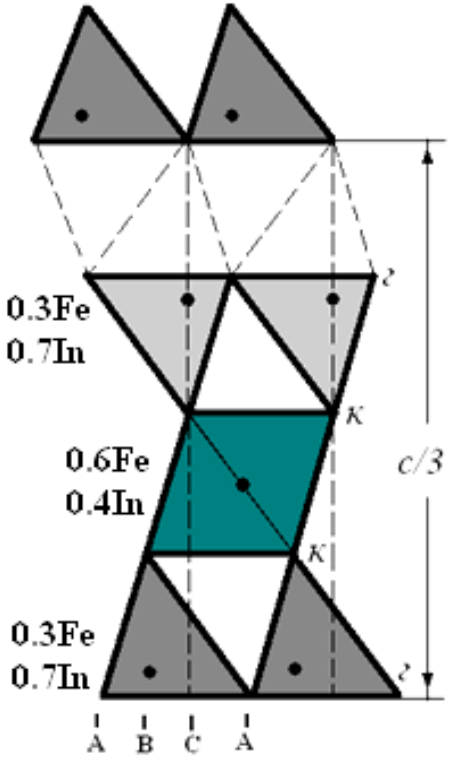

Figure 6. Structural model of $Fe_{1.2}In_{1.87}Se_4$ chalcogenide semiconductor compound on $\vec{c}\vec{a}$ planes.

Structural studies of chalcogenides containing Fe atoms have shown that the crystal structures of these compounds are generally highly symmetrical. It is known from the results obtained from the crystal structures of copper and silver chalcogenides that two-phase and three-phase structures are observed in the compounds obtained

during the cation-cation substitution of Cu or Ag atoms. However, in chalcogenides, in which iron atoms are included, single-phase structures exist.

At the end of the chapter, the results obtained during the X-ray examination were summarized. The results obtained during cation-cation substitution with atoms with magnetic properties in chalcogenide semiconductors were compared with the results obtained during cation-cation substitution with copper and silver atoms. It was found that along with copper and silver chalcogenides, iron chalcogenides crystallize in a structure with higher symmetry. The main reason for this is that iron atoms have magnetic properties. Thus, in the compounds formed from elements with magnetic properties, a distant magnetic order is formed. Therefore, the crystal structures of these compounds crystallize in a single-phase system. However, copper and silver chalcogenides do not have additional forces due to the lack of distant magnetic regularity. Comparing the structural properties of copper and silver chalcogenides with the structural properties of iron-containing chalcogenides means, in fact, comparing the structural properties of these compounds with the constituent atoms of elements with magnetic properties.

In the part of the main results of the dissertation, the main results obtained from the complex structural researches of copper and silver chalcogenides are summarized in 13 items.

CONCLUSIONS

1. It was found that the crystal structure of the $Cu_{1.75}Te$ chalcogenide semiconductor compound under normal conditions and at room temperature corresponds to the hexagonal symmetry of the P-6m2 (187) space group. A two-phase system was obtained when Cu atoms were replaced by Zn atoms with a concentration of $x = 0.05$ and a three-phase system when Cd atoms were replaced. It was determined that the crystal structure of the compound $Cu_{1.7}Zn_{0.05}Te$: Pnma (62) space group orthorombic syngony and P3m1 (156) space group hexagonal syngony crystals, the crystal structure of the compound $Cu_{1.7}Cd_{0.05}Te$: Pnma (62) in space group orthorombic syngony,

P6/mmm (191) space group hexagonal syngony, $Fm\bar{3}m$ (225) space group cubic syngony corresponds to the crystal structure of $Cu_{1.7}Zn_{0.05}Te$.

2. Fm-3m symmetrical crystal structure was observed in each of $Cu_{1.75}Te$, $Cu_{1.7}Zn_{0.05}Te$ and $Cu_{1.7}Cd_{0.05}Te$ compounds at high temperatures $T > 750$ K. Crystallographic parameters were determined for different phases and temperature dependences of cage parameters were obtained. Thermal expansion coefficients were calculated for $Cu_{1.75}Te$, $Cu_{1.7}Zn_{0.05}Te$ and $Cu_{1.7}Cd_{0.05}Te$.

3. In the Cu1.8Te double compound, the $Cu_{1.75}Cd_{0.05}Te$ composition was synthesized by partially replacing Cu atoms with Cd atoms. It was found that the crystal structure of this composition at room temperature consists of two phases: a tetragonal crystal structure of the P3m1 space group and an orthorhombic crystal structure of the Pnma space group. The values of the crystallographic parameters were determined for each phase. At a temperature of $T = 673$ K, a new hexagonal phase was formed and a three-phase system was formed. At $T = 773$ K, a system consisting of orthorhombic and cubic phases was observed. At a temperature of $T = 873$ K, a structural phase transition from a two-phase system to a single-phase system took place, and a single-phase cubic phase with the Fm-3m space group was formed.

4. It was found that the crystal structure of the AgCuS compound at room temperature corresponds to the orthorombic symmetry of the Cmcm space group. Orthorombic-hexagonal phase transitions at $T \approx 400$ K and hexagonal-cubic phase transitions at $T \approx 770$ K were detected under the influence of high temperature. Crystallographic parameters were determined for orthorombic, hexagonal and cubic phases.

5. $AgCuS_{0.5}Se_{0.5}$ was synthesized in AgCuS cryatals with anion-anion substitutions of S atoms with the same concentration as Se atoms. It was determined that the structure of the newly obtained composition consists of two phases consisting of compounds $Cu_{1.96}S$ and AgCuS. Under the influence of high temperatures, a structural phase transition occurred at $T \approx 700$ K in the $AgCuS_{0.5}Se_{0.5}$ compound. The crystal

structure of the newly acquired single-phase system corresponded to a highly symmetrical cubic structure. The structural features of the different phases were studied, and the values of the crystallographic parameters were determined for each phase.

6. The crystal structure and structural phase transitions of the Ag1.55Cu0.45S compound at high temperatures have been studied. It was determined that the crystal structure of this compound at room temperature corresponds to a tetragon of the space group I4/mcm (131). A tetragonal-cubic phase transition occurred at a temperature of T = 400 K. The crystal structure of the new phase was found to correspond to the cubic symmetry of the Im-3m space group. At T = 675 K, another structural phase transition occurred. The crystal structure of the new high-temperature phase corresponds to the cubic symmetry of the Fm-3m space group.

7. As a result of structural studies, it was found that the crystal structure of $Ag_{1.2}Cu_{0.8}S$ consists of two different monoclinic phases. It was determined that one of these phases corresponds to the monoclin monoclin phase of the $P2_1/c$ (14) space group according to the Cu_2S compound, and the other to the monoclin monoclin phase of the $P2_1/n$ (10) space group according to the Ag_2S compound. In the region of high temperatures, the structural phase transition occurred at a temperature of T = 420 K in the composition $Ag_{1.2}Cu_{0.8}S$ and a highly symmetrical single-phase crystal structure was formed. The crystal structure of the new phase corresponded to the cubic group synchrony of the Fm-3m (225) space group.

8. Structural phase transitions in the combination of $Ag_{0.93}Cu_{1.07}S$ in the region of high temperatures have been studied. It was determined that the crystal structure of this compound at room temperature corresponds to the orthorhombic syngonium crystal structure of the space group Cmcm (63). Under the influence of temperature, the symmetry of the crystal structure increased. Orthorombic-hexagonal phase transitions were observed at T = 370 K and hexagonal-cubic phase transitions at T = 450 K. It was determined that the crystal structure of the hexagonal phase corresponds to the space group

$P6_3/mmc$ (194), and the crystal structure of the cubic phase corresponds to the space group Fm-3m (225).

9. Structural studies of $Ag_{1.5}Cu_{0.5}Se$ synthesized by partial replacement of Ag atoms with Cu atoms have shown that under normal conditions and at room temperature, the crystal structure of this compound consists of two phases: the phases with orthorombic symmetry $P2_12_12_1$ space group corresponding to Ag_2Se combination and P4/nmm space group with orthorombic symmetry corresponding to AgCuSe combination. An orthorhombic-cubic phase transition occurred at T = 500 K and a single-phase highly symmetrical crystal structure with the Fm-3m space group was obtained. Crystallographic parameters were determined for each phase.

10. Structural studies of $Ag_{0.4}Cu_{1.6}Se$ synthesized with cation-cation substitutions have shown that under normal conditions and at room temperature, the crystal structure of this compound consists of two phases: $P222_1$ space group orthorhombic syngonium Cu_2Se and P4/nmm space group orthorombic syngonium AgCuSe. Under the influence of high temperature, an orthorhombic-cubic phase transition occurred at a temperature of T = 500 K, and a single-phase highly symmetrical crystal structure was obtained. The crystal structure of the phase obtained at high temperatures corresponded to the cubic symmetry of the Fm-3m space group.

11. In the $Cu_{1.8}Te$ double compound, the $Cu_{1.5}Zn_{0.3}Te$ composition was synthesized by partially replacing the Cu atoms with Zn atoms. It was found that the crystal structure of this composition at room temperature consists of two phases: a tetragonal crystal structure of the P3m1 space group and an orthorhombic crystal structure of the Pnma space group. The values of the crystallographic parameters were determined for each phase. At a temperature of T = 773 K, a new cubic phase with the Fm-3m space group was formed. At a temperature of T = 973 K, a structural phase transition from a three-phase system to a single-phase system took place, and a single-phase cubic phase with the Fm-3m space group was formed.

12. The crystal structure of the $CuFeSe_2$ compound was studied in the temperature range 300 K $\leq T \leq$ 673 K. It was determined that the

crystal structure of this compound at room temperature corresponds to the tetragonal syngonium crystal structure of the I-42c space group. The values of the parameters of the elementary core are determined: $a = b = 5.5210$ Å, $c = 11.0420$ Å. It was found that the structural phase transition does not occur in this compound in the specified temperature range. Coefficients of thermal expansion were calculated for different planes and volumes.

13. As a result of the study of phase formation and structural phase transformations in Ag, Cu-based chalcogenide systems, it was found that 2- and 3-phase structures are obtained in these compounds during cation-cation substitution. As a result of structural studies carried out at high temperatures, it was determined that the structural phase transition occurs under the influence of high temperatures in these compositions, and a highly symmetrical cubic crystal structure of the Fm-3m space group is formed.

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Address: Baku, H. Javid ave. 131, AZ-1143.

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