

**REPUBLIC OF AZERBAIJAN**

*On the rights of the manuscript*

**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**CRYSTAL STRUCTURES AND PHASE  
TRANSFORMATIONS IN COMPOUND AND SOLID  
SOLUTIONS OF  $\text{Cu}_4\text{X}_{2-m}\text{Y}_m$   
(X, Y = S, Se, Te, m = 0.0; 0.25; 0.50; 0.75)**

Speciality: **2223.01 – Crystallography, crystal physics**

Field of science: **Physics**

Applicant: **Nargiz Agami gizi Aliyeva**

**Baku – 2021**

The dissertation was carried out in the Laboratory of "Structure and Structure Transformation" at the Institute of Physics of the National Academy of Sciences of Azerbaijan.

Scientific supervisors:

Candidate of chemical sciences, associate professor

**Gahraman Huseyn oglu Huseynov**

Doctor of physical and mathematical sciences

**Talat Rzagulu oglu Mehdiyev**

Official opponents:

Correspondent member of ANAS,

Doctor of physics-mathematics sciences, professor

**Salima Ibrahim gizi Mehdiyeva**

Active member of ANAS,

Doctor of physical sciences, associate professor

**Anvar Pirverdi oglu Nahmadov**

Candidate of physical-mathematical sciences,  
associate professor

**Azar Sabir oglu Amirov**

ED 1.14 Dissertation Council of the Higher Attestation Commission  
under the President of Azerbaijan Republic

Chairman of the dissertation council:

Active member of ANAS,

Doctor of physics-mathematics sciences, professor

**Nazim Timur oglu Mammadov**

Scientific secretary of the Dissertation council

Doctor of physics sciences, associate professor

**Rafiga Zabil gizi Mehdiyeva**

Chairman of the scientific seminar:

Doctor of physics sciences, professor

**Imamaddin Rajabali oglu Amiraslanov**

## GENERAL DESCRIPTION OF WORK

**The actuality of work:** According to the progress of new technical-scientific methods it is necessary to overall study about them from the aspect of material science, chemistry and physics. In this way, we need to get new achievements in chemistry, physics, structural analysis, crystal chemistry, material science and cybernetic. In this way, we have to pay attention to items such as; synthesis of the chemical composition of the intended material, choice of suitable method to grow single crystal from the synthesized samples, study and specify physico-chemical properties and roentgen structure and choosing the suitable technology. Also, we have to consider the reasons for the importance of the previous works in this field.

It is clear that the numbers of semiconductor materials have a broad range. First of all, based on requirements, classic semiconductors such as elementary and intermetallic compounds were proposed. At Second step, binary and complex oxides and chalcogenides were studied. At the next step transitions elements (3d,4f) based new semiconductor materials have appeared. Contemporary times the scientists are interested in a study on composites and nanomaterials. Therefore it is very important to study the structural analyses of the compositions belong to Cu-Te, Cu-Se and Cu-S systems and production of material with new properties for our purposes based on crystal-chemistry knowledge. Also, we know that progressive industries need materials with new physico-chemical properties. It should be noted that the compounds and solid solutions in our study such as  $\text{Cu}_4\text{SSe}$ ,  $\text{Cu}_4\text{SeTe}$ ,  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ ,  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$ ,  $\text{Cu}_2\text{Te}_{2.3}$  and  $\text{Cu}_4(\text{SeTe})_{1.33}$  have different structural properties in room temperature. This means that the physical and structural properties of the crystal are affected by different polymorph phases of the compounds purposefully. It is imposible to compare the structure and properties of different compounds and find a relationship between the crystal structure and its physical properties (essential Relationships in Semiconductors) without analysis of such problems. It is important to remember that Copper can be seen as

several different valences such as  $\text{Cu}^{1+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$ . This kind of valence changeable atoms has difficulties during technological processes. Therefore, choosing heat treatment temperatures and mainly annealing process is very important in the study of this kind of atoms.

Because the research field of the above-mentioned  $\text{Cu}_{2-m}\text{S}(\text{Se}, \text{Te})$  ( $m < 1$ ) materials and their physico-chemical and structural properties are very important therefore the technology achieve research objects and structural properties and study of the structural phase transformation process is the main scientific path of the dissertation. Then the importance of the dissertation subject is evident.

### **Aims and purpose of the research:**

This to get the related regulations with achievement of compound of  $\text{Cu-X}$  ( $\text{X}=\text{S}, \text{Se}, \text{Te}$ ) from systems and the effect of  $\text{Cu}_4\text{X}_{2-m}\text{Y}_m$  ( $\text{X}, \text{Y}=\text{S}, \text{Se}, \text{Te}; m=0.0; 0.25; 0.50; 0.75$ ) the substitution of chalcogen-chalcogen in its solid solution crystals, the structural properties of the obtained polymorph modifications and the structural phase transformations.

It needs to solve the following problems for obtaining the above-mentioned aim.

- Collecting of the related literature with the subject and aim of the dissertation, analyze and specify the importance of the subject.
- Choosing the technology to get crystals of  $\text{Cu}_4\text{SSe}$ ,  $\text{Cu}_4\text{SeTe}$ ,  $\text{Cu}_4(\text{SeTe})_{1.33}$ ,  $\text{Cu}_4\text{Te}_{2.3}$  compounds and  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  and  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  solid solutions.
- Roentgen Analyses of the synthesized crystals of compositions and solid solutions, crystal-chemical analysis of the results and determine the lattice parameters.
- Determine accurately crystal structures of the resulted compounds and solid solutions crystals.
- Study of the structural phase transitions of the samples in the wide temperature range.

### **Research methods:**

For the purpose of the dissertation, using the capabilities of D8 ADVANCE diffractometer and differential scanning calorimeters and differential scanning calorimeters the lattice parameters, crystal structures, and temperature-dependent structures of the study samples were investigated.

### **Main provisions to the defence:**

1. The reasons of structural diversity in  $\text{Cu}_4\text{X}_{2-m}\text{Y}_m$  ( $\text{X}, \text{Y}=\text{S}, \text{Se}, \text{Te}; m=0.0, 0.5, 0.25, 0.75$ ) type compounds and solid solutions Crystals.
2. The influence of the changing metal-chalcogen atom percentage ratio on the phase production process due to the substitution of chalcogen-chalcogen in the  $\text{Cu-X}$  ( $\text{X} = \text{S}, \text{Se}, \text{Te}$ ) systems.
3. The reason for the diversity of the structural phase transitions process observed in the selected samples of the  $\text{Cu}_4\text{X}_{2-m}\text{Y}_m$  ( $\text{X}, \text{Y}=\text{S}, \text{Se}, \text{Te}; m=0.0, 0.5, 0.25, 0.75$ ) under the experimental condition and methods of the investigation in the temperature range of  $0 < T < 1250\text{K}$ .
4. The role of covalent banded (Cu-Cu) hybrid group in the transition to the bulk type structures of different packet polytypes phases in  $\text{Cu}_4\text{X}_{2-m}\text{Y}_m$  ( $\text{X}, \text{Y}=\text{S}, \text{Se}, \text{Te}; m=0.0, 0.5, 0.25, 0.75$ ) composition crystals.

### **The scientific novelty of the research:**

1. To complete understanding of the related problems with dissertation subject and aim, The  $\text{Cu}_4\text{SSe}$ ,  $\text{Cu}_4\text{SeTe}$ ,  $\text{Cu}_4\text{Te}_{2.3}$ ,  $\text{Cu}_4(\text{SeTe})_{1.33}$ ,  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ ,  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  compounds and solid solutions were synthesized and lattice parameters and structure types of them were obtained using the rentgen- phase analysis at the room temperature. It was found that in the research samples, the ratio of the substitution of chalcogen-chalcogen has resulted from the structural changing.
2. Based on the powder roentgen-diffraction data of the  $\text{Cu}_4\text{SSe}$  and  $\text{Cu}_4\text{Te}_{2.3}$  polycrystals, the crystal structures were recognized and structure of the  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  crystal specified.
4. The Structural phase transformations of the  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ ,  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$ ,  $\text{Cu}_4\text{SeTe}$  and  $\text{Cu}_4(\text{SeTe})_{1.33}$  samples were studied in

the temperature range  $300 < T < 1250 \text{ K}$  and the following results obtained:

a) Directly, the rhombohedral phase of the  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  with lattice parameters of  $a_h=4.162$ ,  $c_h=20.66$  in an aspect of hexagonal is changed to cubic phase with antiferite type structure at  $T \approx 573 \text{ K}$  temperature.

b) Based on the study at the same experimental condition, it has resulted that in the wide range temperature the room temperature phase of  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  solid solution crystals (is different from the  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ ) with lattice parameters as shown on table 1, is transformed at  $T = 770 \text{ K}$  to two mixed phases:  $\text{Cu}_2(\text{SeTe})_{0.5}$  with hexagonal structure,  $a = 4.231 \text{ \AA}$ ,  $c = 7.223 \text{ \AA}$ ; s.gr.  $P6_3/mmc$  and  $\text{Cu}_2\text{Te}$  with cubic structure,  $a = 6.061 \text{ \AA}$ . Then these two mixed phases are changed to cubic phase with  $a = 6.061 \text{ \AA}$  at about  $T = 850 \text{ K}$ .

c) Based on the study of the  $\text{Cu}_4\text{SeTe}$  composition sample by high-temperature roentgen-diffraction method in the  $\sim 300 < T < 1250 \text{ K}$  range temperature, it is obtained that the room temperature hexagonal phase (s.gr.  $P6_1$ ) with parameters of  $a = 4.1880 \text{ \AA}$ ,  $c = 41.8531 \text{ \AA}$  is changed to two super and sub cubic mixed phases with  $a_1 = 6.050 \text{ \AA}$  and  $a_2 = 11.83 \text{ \AA}$  parameters at  $T = 673 \text{ K}$ . These two phases are changed to a single cubic phase with  $a = 6.067 \text{ \AA}$  (s.gr.  $Pa-3$ ) at  $T = 773 \text{ K}$ .

5. By the high-temperature study of the compound of  $\text{Cu}_4(\text{SeTe})_{1.33}$ , it was shown that the room temperature having cubic structure sample with  $a = 7.3062 \text{ \AA}$  and space group  $P-43m$  is changed to another cubic phase with  $a = 5.8439 \text{ \AA}$  and space group  $F-43n$  at  $693 \text{ K}$ .

6. The Roentgen-diffraction and Differential scanning calorimetry methods were used for research objects at the same time in the temperature range of  $300-873 \text{ K}$  at and the results anal arqon environment ysed and compared.

**The theoretical and practical significance of the research:**

1. According to a thorough analysis of the experimental results obtained in this dissertation, the crystals of  $\text{Cu}_4\text{X}_{2-m}\text{Y}_m$  ( $\text{X}, \text{Y}=\text{S}, \text{Se}, \text{Te}; m=0.0-; 0.25; 0.50; 0.75$ ) type compounds and solid solutions can be used as an active element for thermoelectric converters as they have ionic conductivity. Based on the crystal structures, structure transformations and their physico-chemical properties of the investigated compounds and solid solutions, they can be used in chemical current sources, electrochemical sensors and various optical-ion devices such as ionic conductors.
2. The results of the dissertation work can be useful as a reliable source of research for a study on the structure and physico-chemical properties of materials of different types of structure.

#### **Approbation and implementation:**

- The main results of the dissertation work were discussed at the following international conferences: International Conference of "Advances in applied physics & materials science congress" (Antalya-2011),

- "Fundamental and Applied Problems of Physics" Proceedings of the international conference dedicated to the 70th anniversary of the Physicotechnical Institute of NPO, "Physics-Sun" (Tashkent-2013)

- At the VII Republic Conference on "Modern Problems of Physics", Institute of Physics Problems of BDU, (Baku-2013)

- International Conference on Physics Problems of BDU, "Dedicated to the 10th anniversary of the Institute of Physics Problems of BDU" (Baku-2015).

The main conclusions reflecting the content of the dissertation work were published in 8 articles (four of them were published in the SCI list journals with impact factor and 4 published as conference materials).

#### **Name of the organization the Dissertation has been performed:**

The dissertation was carried out in the Laboratory of "Structure and Structure Transformation" at the Institute of Physics named after H.M. Abdullayev of the National Academy of Sciences of Azerbaijan.

**Volume and Structure of the Dissertation:** The dissertation consists of 232881 symbols, including introduction, four chapters, key results, 17 tables, 32 pictures and 114 references.

## CONTENT OF WORK

**In the introduction** the importance of the dissertation subject was substantiated, the purpose of the work and main claims in the defence, and the scientific novelty and practical significance of the results were explained.

**First chapter:** In the first chapter of the dissertation, literature data on the crystalline structure of compounds in the Cu-S (Se, Te) systems and the structural changes by changes in temperature were analyzed crystal chemically and the importance of the subject was substantiated. The base of this chapter is the review of the literature data relevant to the topic of the dissertation, the structural properties of Cu chalcogenides and the analysis of the experimental results reflecting their physical and chemical properties. The coordination properties of under analysing compounds structures were considered and the general characteristics of the only quaternary (tetrahedral), trio (triangle) and hexa (octahedral) coordinate phases were analyzed on the basis of crystallochemical considerations. The structure and crystallochemical properties of  $\text{Cu}_{2-m}\text{S}$  (Se, Te) compounds, which are the basis of this chapter, were analyzed analytically.

**Second chapter:** This chapter mainly focuses on the description of existing and available techniques for producing of research objects and roentgen phase and roentgen structure analysis of the obtained samples as well as the rules for performing experiments on high-temperature X-ray diffraction.<sup>1</sup> This chapter also broadly explains the lattice parameters data and their computational methods (Table 1).

**Third chapter:** This chapter was dedicated to determining the crystal structures of the first time obtained  $\text{Cu}_4\text{SSe}$ ,  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  and  $\text{Cu}_4\text{Te}_{2.3}$  compounds by Rietveld method.

<sup>1</sup> Козлова, О.Г. Рост и морфология кристаллов /– М.: Изд.-ва. МГУ, 1980. - 368 с.



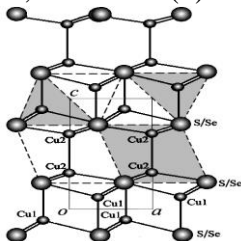
The third chapter of the dissertation work is totally dedicated to specifying of the crystal structures of the research objects and study of the structural phase transitions of them as a function of temperature by different methods.<sup>2</sup>

**Determination of the crystal structure of Cu<sub>4</sub>SSe compound:** Cu<sub>4</sub>SSe compound is crystallized in trigonal structure. Molecular weight M=365.204, a<sub>h</sub>=4.0210(1) Å, c<sub>h</sub>=6.8381(1) Å, V=95.75(4) Å<sup>3</sup>, ρ<sub>x</sub>=6.333(3) gr/cm<sup>3</sup>, s.gr. P-3m1, Z=1. The crystal structure of Cu<sub>4</sub>SSe was determined based on the diffraction data by the Rietveld method with the TOPAS-4.2 calculation program. The obtained model of crystal structure for the Cu<sub>4</sub>Sse compound is shown in Figure 1. In this structure, the Cu<sub>1</sub> atoms are distributed in the 2d, Cu<sub>2</sub> atoms in the 2c, and the (S, Se) atoms in the 2a positions. Their coordinates are as follows:

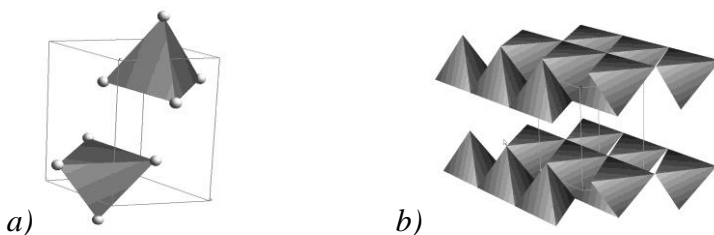
S/Se 2d x=2/3, y=1/3, z=0.242(3)

Cu(1) 2d x=1/3, y=2/3, z=0.091(3)

Cu(2) 2c x=0, y=0, z=0.311(4)



**Figure 1. The model of Cu<sub>4</sub>SSe crystal structure**



**Figure 2. a) the tetrahedral of Cu<sub>4</sub>SSe b) their two-dimensional layer**

<sup>1</sup>Браут Р.Фазовые переходы /-М.: Мир, 1967.-288 с.

The Cu1 atoms are located in the cavities formed from chalcogenide atoms and Cu2 atoms are located in the slightly deformed octahedral polyhedron with [Cu-Cu]+ dumb-bells form. It should be note that the structure of Cu<sub>4</sub>SSe can be considered as an anti-covalent CuS structure. The difference is that the sulfur atoms in CuS are participated as covalently bonded dumb-bells, while the copper atoms participated as dumb-bells in the Cu<sub>4</sub>SSe structure. Other structural similarity of Cu<sub>4</sub>SSe crystal is the Cu<sub>2</sub>S-chalcocite with GaSe structure. The arrangement of atoms that are perpendicular to the "c" axis of the crystal lattice in all three structures is like –metal-metal-chalcogenide-metal-metal-chalcogenide-...

In the Cu Dumbbells Cu<sub>1</sub>-Cu<sub>2</sub>=2.77(2) Å; Cu<sub>2</sub>-Cu<sub>2</sub>=2.58(6) Å; Cu-chalcogen distances: Cu<sub>1</sub>-(SSe)=2.28(3) Å, Cu<sub>1</sub>-(SSe)<sub>3</sub>=2.54(1) Å.

**Crystal structure determination of the Cu<sub>4</sub>Te<sub>2.3</sub> compound:** Most of these phases are removed from the Novotny structure of the Cu<sub>2</sub>Te crystal, based on an analysis of the crystal structure of the crystalline phases in the various structures formed in the Cu-X (X = S, Se, Te) systems. However, there are a number of serious facts in this structure that need to be clarified. Cu<sub>2</sub>Te was synthesized and annealed at 770K for clarifying this kind of problems. The mass containing several filiform monocrystals was observed in the upper zone of the sample after annealing. As a result of chemical analysis, these monocrystals were identified as copper. The weight of copper wires obtained at the analytical scales was approximately 0.106 mg. In the Cu<sub>2</sub>Te combination, it was determined that the mass of the copper atoms falling out of the mass of copper, when the amount of copper separated, was approximately equal to that of Cu<sub>1.75</sub>Te. Due to the dissertation subject, the general formula for the selected objects was chosen as Cu<sub>4</sub>X<sub>2-m</sub> (X = S, Se, Te) so according to this rule, Cu<sub>1.75</sub>Te should be given as Cu<sub>4</sub>Te<sub>2.285</sub> = Cu<sub>4</sub>Te<sub>2.3</sub>. According to the results of the analyses of rentgen-phase diffraction of Cu<sub>4</sub>Te<sub>2.3</sub> it was determined that the researched sample is crystallized in the trigonal structure with lattice parameters:

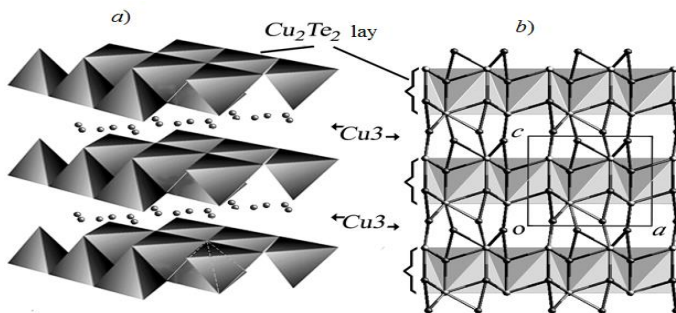
$a_h=8.328(1) \text{ \AA}$ ,  $c_h=7.196(1) \text{ \AA}$ ,  $V=432,2(1) \text{ \AA}^3$ , s.gr.P-3m1,  $Z=4$  and molecular weight  $M=547.664$ .

Therefore, it is necessary to repeat a study of the  $\text{Cu}_4\text{Te}_{2.3}$  crystal structure. The crystal structure of the  $\text{Cu}_4\text{Te}_{2.3}$  sample was carried out by the Rietveld method as in the  $\text{Cu}_4\text{SSe}$  described above (Figure 3a, b). The structure calculations of  $\text{Cu}_4\text{Te}_{2.3}$ , namely the coordinates of the free atoms and the inter-atomic distances, were determined respectively. The coordinates of the atoms in the structure are as follows:

Te(1)	6i	$x=0.337(5)$ , $y=0.169(2)$ , $z=0.275(2)$
Te(2)	2d	$x=2/3$ , $y=1/3$ , $z=0.745(5)$
Cu(1)	2d	$x=2/3$ , $y=1/3$ , $z=0.390(3)$
Cu(2)	6i	$x=0.340(10)$ , $y=0.170(5)$ , $z=0.610(3)$
Cu(3)	6i	$x=0.400(4)$ , $y=0.200(2)$ , $z=0.947(5)$

In the structure, the existence of three kinds of copper atoms is determined because of the variety of polyhedrons generated by the Cu atoms, which are located in 6 positions of Cu (1) -2d; Cu (2) and Cu (3). In the structure, Cu (1) atoms are located in the centre of the tetrahedrons created by Te Atoms. The distance of Cu (1) -Te = 2.52 (3) from the fourth Te is 2.55 (4)  $\text{\AA}$ . In the structure, Cu (2) atoms are located in the five coordinates (4Te Cu). The distances between atoms are: Cu (2) -4Te = 2.521 (3) -2.55 (4)  $\text{\AA}$ ; Cu (2) -Cu (3) = 2.47 (4)  $\text{\AA}$ . The Coordination number of Cu (3) atoms is 3. The distance of Cu (3) atoms from the 2Te were approximately 2.40 (4)  $\text{\AA}$ , and from the Cu (2) atoms was about 2.47 (4)  $\text{\AA}$ . AS can be seen from Figure 3 (a, b), the structure consists of infinite tetrahedral layers of  $\text{Cu}_2\text{X}_2$  composition. The obtained infinite tetrahedral layers of  $(\text{Cu}_2\text{X}_2)_n$  from the  $\text{Cu}_4\text{Te}_{2.3}$  crystal and projection of (a c) plane of this crystal are respectively given in (a) and (b).

It seems that the specified  $(\text{Cu}_2\text{X}_2)_\infty$  layers in the above described  $\text{Cu}_4\text{SSe}$  and  $\text{Cu}_4\text{Te}_{2.3}$  crystal structures can be accepted as obtained stable structure fragments for different compositional of  $\text{Cu}_{2-x}\text{X}$  compounds. It is also interesting that the tetrahedral isolated layers in the structure form covalent bonds with Cu atoms locating between the layers.

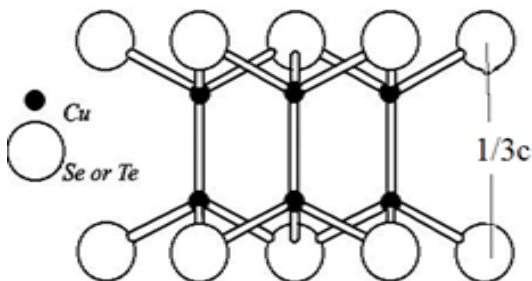


**Figure 3. The observed infinite tetrahedral layers of  $(\text{Cu}_2\text{X}_2)_n$  in the structure of  $\text{Cu}_4\text{Te}_{2.3}$  crystal (a) and projection of (a c) plane of this crystal (b).**

**The crystal structure of  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  solid solution.** In this work, all of the X-ray-diffraction experiments for the  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  sample were performed by the D8 ADVANCE diffractometer. Experiment mode:  $10 < 2\theta < 80^\circ$ , 40kb, 40mA,  $\text{CuK}\alpha$ -radiation  $\lambda = 1.5406 \text{ \AA}$ . Based on the above-mentioned X-ray-diffraction information gained by contemporary calculation program TOPAS, it has been determined that the researched  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  solid solution crystals are crystallized in the rhombic cell and its constants from aspect of the hexagonal lattice are:  $M = 436.424\text{g}$ ,  $a_h = 4.162 \text{ \AA}$ ,  $c_h = 20.66 \text{ \AA}$ ,  $V = 309.9 \text{ \AA}^3$ , space group R-3m,  $\rho_x = 7.0543\text{q / cm}^3$ , and  $Z = 3$ .

Comparing the obtained lattice parameters of  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  with  $\text{Cu}_2\text{Te}$  indicates that the structure of these both material is the same, and the  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ , which we are investigating, is a three-packet polytype form of  $\text{Cu}_2\text{Te}$  (picture 4).

From the results of the specimens of the crystal structures, it is clear that the basis of the structures formed in the copper-chalcogenide systems is regular-irregular structured, where the models of room-temperature phase are often stable and easily form different variants under the influence of external factors. Now, let's look at the dissertation objects from the aspect of structural Transition process with temperature.



**Figure 4. Crystal structure model of  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$**

**Determination of the structural phase transformations in  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  crystal.** To study the temperature-dependencies of the structural transitions in  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ , the prepared powder from the sample after mixing with alcohol is spread on a plate over the thermocouples in the high-temperature camera of the diffractometer. Then the camera is closed and after evacuating to  $\sim 10^{-3}$  torr, the X-ray diffraction pattern is recorded every 100k to 680k temperature (figure 5).

An analysis of the diffraction patterns at the different temperatures shows that there is no significant change in the crystal diffraction spectrum up to 273-400K except that only about  $2\theta \approx 12.9^\circ$  the intensity of the peak is reduced by half. In addition to decreasing the intensity of the peak of  $2\theta \approx 12.9^\circ$  at 473k temperature, also a significant change is observed in the range of  $2\theta \approx 23-28^\circ$ , and a new intensive peak is created that has corresponded to the mix of rhombohedral (hexagonal) and cubic phases at that temperature. At 573 K, the diffraction pattern is simplified and the phase-transition occurs. As a result of the auto-indexing process carried out by TOPAS program, it was determined that this phase is cubic, its parameter is  $a = 5.899 \text{ \AA}$ , the space group is Fm-3m,  $Z = 4$ , and the structure is  $\text{CaF}_2$ .

Thus, it was found that the  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  solid solutions crystals with a rhombohedral (hexagonal) structure change to a cubic phase at  $\sim 573 \text{ K}$ , which causes the phase transition temperatures to be significantly slower than binary organizers.

**Determination of the structural phase transformations in Cu<sub>4</sub>SeTe compound.** Determining the cell parameters of the room temperature phase Cu<sub>4</sub>SeTe sample was important before to study the temperature-dependence of its structural transformations. For this purpose, the obtained X-ray-diffraction data from Cu<sub>4</sub>SeTe compound at 300K were used. Detailed studies conducted with the TOPAS computing program have shown that Cu<sub>4</sub>SeTe compound crystallizes in the hexagonal structure and it is like a β-Cu<sub>2</sub>Te based polytype phase having layered and ordered structure. It was found that the room temperature phase of this compound has a hexagonal structure and its cell specifications are: Molecular weight M=460.744, a= 4.1880 Å, c= 41.8531 Å, V = 636.71Å<sup>3</sup>, s.g. P6<sub>1</sub>, ρ<sub>x</sub> = 7.2622g/cm<sup>3</sup>, Z= 6.

According to the procedure for Cu<sub>4</sub>Se<sub>1.5</sub>Te<sub>0.5</sub>, from the analysis of the obtained roentgen-diffraction data between 300-1150K (Figure 6), it is observed that there is a significant change in the sample at temperatures of 573, 673, 723 and 773K. In other words, there is no change in the structure of the sample between 300-573K temperatures. By accurate-Looking at the diffraction pattern at that figure (573K), it becomes obvious that the intensity is considerably changed at 2θ= 412.714° and 2θ= 25.959°, and some new peaks appeared at 2θ= 25.5870° and 2θ= 26.750, and also some low-intensity scatterings disappeared.

According to Figure 6, the difference in the diffraction pattern at 673K is quite large. Because at this temperature, all the scattering reflections on the room temperature phase are extinguished and the system becomes a completely new X-ray diffraction phenomenon. As a result of the indexing process of the diffraction data at these temperatures, it was found that the system corresponds to the mechanical mixture of the two phases super and sub cubic with cell parameters a≈11.83Å and a≈6.05Å. This result can be seen in the recorded diffraction pattern at 773K. As a result of the final analysis and indexing process, it was found that the structural transformation is complete at this temperature, and the low-temperature Cu<sub>4</sub>SeTe phase is changed to another phase with parameters a= 6.067 Å, V= 223,339 Å<sup>3</sup>, space group Pa-3, ρ<sub>x</sub>= 6.949 gr/cm<sup>3</sup> and Z= 4.

**Determination of the structural phase transformations in  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  solid solution crystal.** The  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  crystals crystallize at room temperature in trigonal structure and its cell parameters are:  $M= 485.064$ ,  $a_h= 8.2319\text{\AA}$ ,  $c_h= 21.4145\text{\AA}$ ,  $V = 1256.68 \text{\AA}^3$ , space group  $P3m1$ ,  $Z = 12$ ,  $\rho_x= 7.33 \text{ gr/cm}^3$ . Comparison of the cell parameters with values obtained for the previous two samples showed that they have different structures. Then diffraction patterns of the  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  powder were obtained at different temperatures.

These X-ray-diffraction patterns were compared with each other and analyzed, then it was found that in the range of  $300 < T < 850\text{K}$  the changes of X-ray-diffraction in the  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  are observed at about 770 and 850K. By comparing the diffraction spectra obtained for the  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  sample with  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  and  $\text{Cu}_4\text{SeTe}$  compounds, it was clear that without considering the temperature values in the changes, the results were consistent with the  $\text{Cu}_4\text{SeTe}$ . As a result of the presented structural reports, the diffraction change observed at 770 K for  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  corresponds to the splitting of the sample into two different phases at that temperature. These phases consist of the cubic phase  $\text{Cu}_2\text{Te}$  and hexagonal phase  $\text{Cu}_2(\text{SeTe})_{0.5}$ . The cell parameters of these phases are:  $a= 6.061 \text{\AA}$ , space group  $Pa-3$  and  $a= 4.231 \text{\AA}$ ,  $c= 7.223 \text{\AA}$ , and space group  $P63/mmc$  (Figure 7).

Also, the structure of the last above mentioned transformation at  $T \sim 850\text{K}$  was identified as cubic structure. The cell parameters of that phase are the following:  $M= 485.064$ ,  $a= 6.061 \text{\AA}$ , s.g.  $Pa-3$ ,  $V= 223.653\text{\AA}^3$ ,  $Z= 4$ ,  $\rho_x= 7.2801 \text{ gr/cm}^3$ .

**Study of the structural phase transition in the compound  $\text{Cu}_4(\text{SeTe})_{1.33}$ .** The investigated compound  $\text{Cu}_4(\text{SeTe})_{1.33}$  crystallizes at room temperature in a cubic lattice and its cell parameters are as follow: molecular weight  $M= 397.198$ ,  $a= 7.3062 \text{\AA}$ ,  $V= 402.02 \text{\AA}^3$ , s.g.  $P-43m$ ,  $\rho_x= 6.5999 \text{ gr/cm}^3$  and for compound  $\text{Cu}_4(\text{SeTe})_{1.33}$   $Z= 4$ , the volume containing the anions  $50.25 \text{\AA}^3$ .

Figure 8 shows the structural phase transition process in  $\text{Cu}_4(\text{TeSe})_{1.33}$  at different temperatures. By analyzing the X-ray-diffraction patterns the figure, it is clear that no structural changes

are observed at  $T = 293\text{-}620\text{K}$ . However a significant change is observed at  $T = 620\text{K}$ . Thus, at the points  $2\theta \approx 27.8^\circ, 43.7^\circ, 51.9^\circ$  etc., new normal intensities are reflected, some peaks are turned off, and some peaks are reduced. Some peaks disappeared and the intensity of some peaks decrease. To obtain the start point temperature of these changes, by increasing temperature from  $570\text{K}$ , every  $100\text{K}$  the diffraction spectrum of the sample is recorded. Analyzing these spectra showed that the beginning of the observed diffraction changes is about  $590 \pm 3\text{K}$ . Next, the temperature of the sample was increased as before, and it was found that the observed diffraction change was completed only at  $T = 690\text{K}$ , indicating the continuation of the phase transition process from  $590$  to  $690\text{K}$ . The calculations based on the obtained diffraction data indicate that the obtained structure at  $693\text{K}$  is a small-scale of the cubic of room temperature phase of  $\text{Cu}_4(\text{SeTe})_{1.33}$  with crystallographic parameters:  $a = 5.8439 \text{ \AA}$ ,  $V = 199.631 \text{ \AA}^3$ , s.g.  $F\text{-}43n$ ,  $Z = 4$

#### **Determination of the structural phase transformations in $\text{Cu}_4(\text{SeTe})_{1.33}$ , $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ , $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$ and $\text{Cu}_4\text{SeTe}$ crystals by the DSC method.**

It should be noted that due to the influence of external factors (mainly temperature, pressure, radiation, vacuum, tension, etc.), the rapid change in the crystalline structure, as well as the physico-chemical and mechanical properties, is a very interesting event and an important issue. are made. It is known that the study of changes in the crystal structure of chemicals under the influence of external factors (conditions), as well as the physical and chemical properties of them, is studied by DTA, RFA, STA and various physical devices. Of these methods, the high-temperature diffraction method is considered the most favorable, given the study of this method, the quantitative content of structural changes, i.e. the structure.

In addition to the X-ray diffraction method to monitor the studied phase transition temperatures, this process was also investigated by Calorimetric method. For this purpose, the fine powder prepared from  $\text{Cu}_4(\text{SeTe})_{1.33}$  compound was used for obtaining the temperature dependence spectrum at  $300\text{-}873\text{K}$ . The experimental results were obtained using the Differential Scanning



calorimetry (DSC). Figure 9 shows the DSC spectrum from  $\text{Cu}_4(\text{SeTe})_{1.33}$ . It is clear from the figure that only one endothermic effect ( $T = 629 \text{ K}$ ) is observed in the 300-873K range. This also means that the mentioned temperature accurately is the structural transition temperature of  $\text{Cu}_4(\text{SeTe})_{1.33}$  compound and the room temperature simple cubic phase is changed to FCC structure at this temperature. Figure 10 shows the structural transformations of the other compounds samples mentioning above by calorimetric method. Finally, it should be noted that the compliance of the comparative analysis of studies conducted by both methods (RFA, SSC) is related to the performance of experiments under different conditions (vacuum and argon environment).

1. In  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  sample two endo effect:  $T_1 = 413.5\text{K}$ ,  $T_2 = 801.3\text{K}$  and one exo effect:  $T = 725.2\text{K}$  were observed.

2. In  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  sample three endo effect:  $T_1 = 410\text{K}$ ,  $T_2 = 465\text{K}$ ,  $T_3 = 800.5\text{K}$  were observed.

3. In  $\text{Cu}_4\text{SeTe}$  sample two endo effect peaks:  $T_1 = 467.1\text{K}$ ,  $T_2 = 801.8\text{K}$  and one exo effect:  $T = 668.1\text{K}$  were observed.

If we comparatively analyzed the observed spectra with the results obtained by high-temperature vacuum diffraction method, we conclude the following. Earlier in the chapter, the results of that study were explained in detail.

**Chapter 4.** The fourth chapter of the dissertation is devoted to a comprehensive analysis of the results of extensive research, which is related to the purpose of the work and the direction of the research. It is also clear that the different results have been obtained for processes of the production of different phases specially in the chosen systems of Cu-S, Cu-Se, Cu-Te. It should be noted that the occurred structural changes in those systems and the causes of these changes are dependent on temperature, pressure and other external factors.<sup>3</sup> It is necessary to emphasis that in such a process, a number of features that occur in the crystal cell and their study are not so easy.

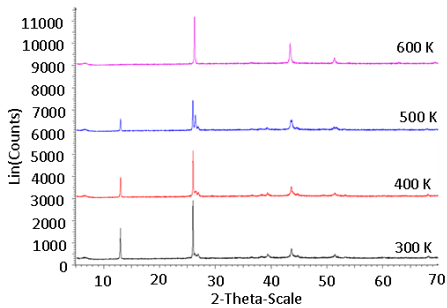
<sup>3</sup>Белов, Н.В. Структура ионных кристаллов и металлических фаз / М.:Л.Изд-во АН СССР, 1947, 238с.

Therefore it is impossible to achieve any new result without understanding the essence of the interesting events and related questions in this kind of process. All of the research results obtained in this chapter of the dissertation on such issues have been widely discussed and substantiated in the modern view. The main items discussed in this chapter of the dissertation are:

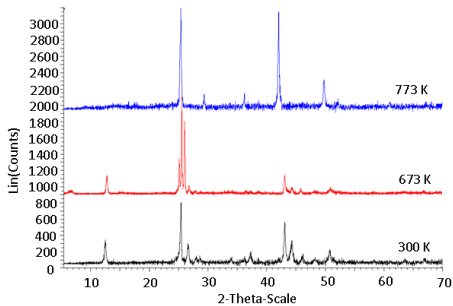
1. Determining the role of the regulatory factor in the process of formation the structure with the presence of metallic and non-metal atoms (Cu, C, Se, Te). This item should be controlled all of the time as the main subject of material science. Obviously, the Changing of valence ( $\text{Cu}^+$ ,  $\text{Cu}^{+2}$ ) show up easily its importance in synthesize process in the structure formation under the chemical reciprocal influence of Cu atoms. In other words, it allows to formation a large number of stoichiometric and non- stoichiometric phases in the systems.

2. The presence of S, Se, and Te with different electronic structures in the phase formation process may change the direction of the chemical reaction and cause the various structures in the formation of new phases.

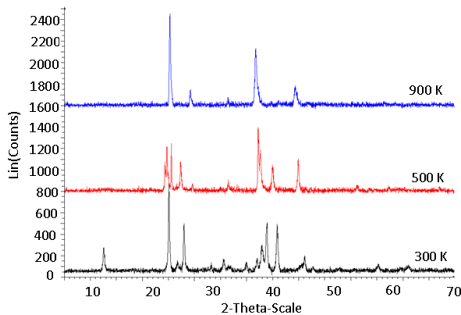
Beside the mentioned issues, one of the most important subjects is the production of new kind of structures by formation of the hybrid band between Cu and chalcogen atoms as well as a number of elements (Cu, Ga, In Ag, S, Se, Te) during the structure formation process. This is an interesting subject from crystallochemical aspect that has been extensively analyzed in this chapter of the dissertation.



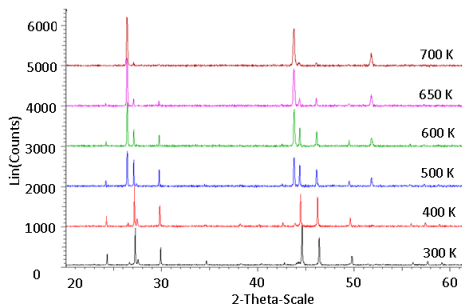
**Figure 5**



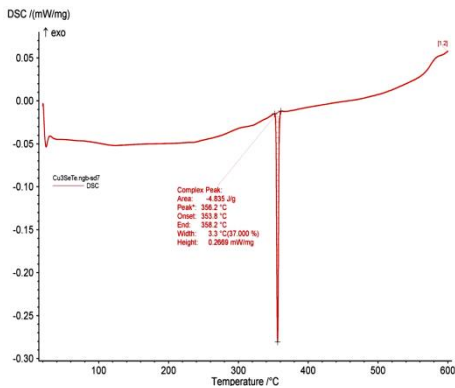
**Figure 6**



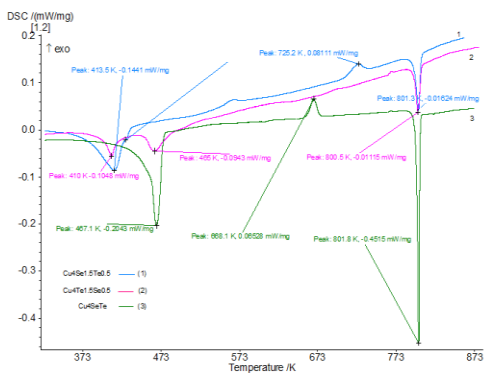
**Figure 7**



**Figure 8**



**Figure 9**



**Figure 10**

## MAIN RESULTS

1. To fully cover the issues risen for the topic and purpose of the dissertation, Compounds and solid solutions of  $\text{Cu}_4\text{SSe}$ ,  $\text{Cu}_4\text{SeTe}$ ,  $\text{Cu}_4\text{Te}_{2.3}$ ,  $\text{Cu}_4(\text{SeTe})_{1.33}$ ,  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ ,  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  were synthesized, the lattice constant and structure of them was determined.

2. Crystal structures of the  $\text{Cu}_4\text{SSe}$  and  $\text{Cu}_4\text{Te}_{2.3}$  compounds were designated using the method for determining crystal structures based on roentgen diffractometric data from Ritvald polycrystalline samples. It was determined that the basic of the designated crystalline structures make up  $1/\text{Cu}_2\text{X}_{2/\infty}$  which is stable structure fragment composed of covalently bound Cu-Cu atoms and its structure indicates.

3. Temperature-dependent structural transitions in  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ ,  $\text{Cu}_4\text{SeTe}$ ,  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$ ,  $\text{Cu}_4(\text{SeTe})_{1.33}$  using high-temperature X-ray diffraction method under vacuum conditions and Differential Scanning Calorimetry device under argon environment was studied. The analysis of the results showed that, depending on the research method used, structural changes in crystals have mechanisms with different characteristics.

4. It was found that in experiments using high-temperature X-ray diffraction method, the room temperature trigonal phase  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  with cell parameters of  $a_h = 4.162 \text{ \AA}$ ,  $c_h = 20.66 \text{ \AA}$  at temperature 573 K changes into a cubic phase with  $a = 5.899 \text{ \AA}$ , the transition is donor and s.gr. = Fm-3m.

5. It was found that in the same method, vacuum-based experimental studies show the similar mechanisms in intermediate phase transitions in crystals  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  and  $\text{Cu}_4\text{SeTe}$ , although their changed phase composition is different. Thus, in the first crystal, production of the transition at 770 K, is the hexagonal  $\text{Cu}_2(\text{SeTe})_{0.5}$  ( $a = 4.231 \text{ \AA}$ ,  $c = 7.223 \text{ \AA}$ ) and the cubic  $\text{Cu}_2\text{Te}$  ( $a = 6.061 \text{ \AA}$ ), while in the second at 673 K is a super cubic ( $a = 11.82 \text{ \AA}$ ) and a sub-cubic ( $a = 6.05 \text{ \AA}$ ) phase with  $\gamma\text{-Cu}_2\text{Te}$  type structure. In the next temperature rise, at 850 K in the second at 773 K, both phases are

transformed into a single cubic structure whose parameter is  $a = 6.055 \text{ \AA}$ .

6. Using RFA and DSC methods, Structural phase transformations in  $\text{Cu}_4(\text{SeTe})_{1.33}$  crystals were determined, and it was clear that the investigated compound with cell parameters:  $M = 397.198$ ,  $a = 7.3062 \text{ \AA}$ ,  $V = 389.961 \text{ \AA}^3$ , s.gr.P-43m,  $Z = 4$ ,  $\rho = 6.599 \text{ g/cm}^3$  (room temperature) by the first method at 693K, and by the second method at 629K is changed to a cubic phase with cell parameters:  $a = 5.8439 \text{ \AA}$ ,  $V = 199.631 \text{ \AA}^3$ , s.gr. F-43n.

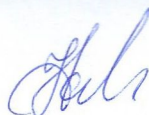
## Scientific work printed on thesis subject

1. Gasimova, N.A. Structure and Phase Transitions of  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  / N.A. Gasimova, I.R. Amiraslanov, Y.I. Aliyev [ et al.] // American Journal of Physics, AJP Conf. Proc., - 2011. Vol. 1400, №1,- p.476-479.
2. Gasimova, N.A., Amiraslanov, I.R., Aliyev, Y.I., Guseinov G.G. Structure and phase transitions of  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$  // “Advances in applied physics & materials science congress”, - Antalya- 12-15 May, - 2011, Vol.II, - p.209.
3. Aliyeva, N.A., Guseinov, G.G., Jafarov, G.M. Phase- transitions in the crystal of  $\text{Cu}_4\text{SeTe}$  // VII Republic conference “Modern problems of Physics”-Baku-2013, -p.131-132.
4. Aliyeva, N.A., Aliyev, Yu.I., Guseinov, G.G., Mageramov, A.B. Structural phase transformations and electrophysical properties of solid solution  $\text{Cu}_2\text{Te}_{0.75}\text{Se}_{0.25}$  crystal // Proceedings of the international conference "Fundamental and Applied Problems of Physics", -Tashkent -14-15 November, -2013, -p.75-76.
5. Aliyeva, N.A. Structural phase transitions in  $\text{Cu}_4\text{SeTe}$  polycrystals // N.A. Aliyeva, G.G. Guseinov, V. A.Gasimov [et al.] // Inorganic materials, -2017. Vol. 51, №7,-p.1-4.
6. Aliyeva, N.A. Crystal structure of the room temperature phase of  $\text{Cu}_2\text{Te}$  ( $x=0.25$ ) Compound // VII Republic conference “Modern problems of Physics”-Baku-2015, -p.173-175.7. Aliyeva, N.A. Investigation of phase transition in  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  solid solution by high-temperature roentgenography method / N.A. Aliyeva, G.G. Guseinov, G.M. Agamirzoyeva // AJP Fizika, - 2016. Vol. XXII, №1, - p.19-22.
8. Amiraslanov, I.R. Crystalline Structure of  $\text{Cu}_4\text{SSe}$  / I.R. Amiraslanov, N.A. Alieva, G.G Guseinov // Crystallography Reports, - 2016. Vol. 61, №1, - p. 1–4.
9. Amiraslanov, I.R. Crystal Structure of  $\text{Cu}_{2-m}\text{Te}$  ( $m=0.25$ ) / I.R. Amiraslanov, N.A. Alieva, G.G. Guseinov [et al.] // Crystallography Reports, - 2017. Vol. 62, №. 2, - p. 210–214.
10. Aliyeva, N.A. Acquisition and investigation structure –phase transformation of  $\text{Cu}_3\text{SeTe}$  compounds / N.A. Aliyeva,

G.F.Ganizadeh, G.G.Guseyinov [et al.] // AJP Physics,-2017. Vol. XXIII, №3, - p. 24-27.

11. Aliyeva, N.A. Investigation structure-phase transitions in  $\text{Cu}_4\text{SeTe}$  by the calorimetric method of high-temperature // Baku: AJP Physics,-2019. Vol. XXV, №3,- p.13-16.

12. Aliyeva, N.A. Determination of structural phase transitions in the crystals of  $\text{Cu}_4\text{Se}_{1.5}\text{Te}_{0.5}$ ,  $\text{Cu}_4\text{Te}_{1.5}\text{Se}_{0.5}$  solid solutions by the differential scan calorimetric method of high temperature // -Baku, Scientific works, fundamental sciences, AZTU-2019, №3, - p.71-73.







The defence will be held on 07 April 2021 at 11<sup>00</sup> at the meeting of the Dissertation council ED 1.14 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Physics of Azerbaijan National Academy of Sciences.

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

The dissertation is accessible at the Institute of Physics Azerbaijan National Academy of Sciences Library

Electronic versions of the dissertation and it's abstract are available on the official website of the Institute of Physics of Azerbaijan National Academy of Sciences.

Abstract was sent to the required addresses on 02 March 2021

Signed for print: 26.02.2021

Paper format: A5

Volume: 368883

Number of hard copies: 20