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ABSTRACT
of the dissertation for the degree of Doctor of Philosophy

PHASE EQUALIBRIA IN CERTAIN CONCENTRATION PLANES OF THE Cu-Sn-Sb-Se SYSTEM AND TERMODYNAMIC PROPERTIES OF SELENIDES WITH MIX CATIONS

Speciality: 2303.01 – Inorganic chemistry

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Applicant: Elnara Nadir Ismayilova

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The dissertation work was performed in the laboratory of "Functional materials based on transition metal compounds" and "Thermodynamics of inorganic compounds with functional properties" laboratories of PLE Institute of Chemistry of Ministry of Science and Education of the Republic of Azerbaijan.

Scientific supervisor: Doctor of Chemical Sciences, Professor
Ihtiyar Bahram Bakhtiyarly

Official opponents: Doctor of Chemical Sciences, Professor
Imir Ilyas Aliyev

Doctor of Chemical Sciences, Professor
Khudayar Ismayil Hasanov

Doctor of Philosophy in Chemistry, Associate Professor
Saba Huseynkhan Mammadova

Dissertation Council FD 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating in PLE Institute of Chemistry of Ministry of Science and Education of the Republic of Azerbaijan.

Chairman of the Dissertation Council: Corresponding member of ANAS, Professor.
Mahammad Baba Babanly

_____

Scientific Secretary of the Dissertation Council: Doctor of Philosophy in Chemistry, Associate Professor
_____ **Ulviyya Ahmed Mammadova**

Chairman of the Scientific Seminar: Doctor of Chemical Sciences, Professor
Akif Shikhan Aliyev

_____

GENERAL CHARACTERIZATION OF THE RESEARCH WORK

The actuality and usage rate of the topic.

The development of electronics, nanotechnology and computer technology requires the development of semiconductor materials with functional properties for the preparation of new thermoelectric converters (coolers, photoreceivers, thermogenerators). Such converters are distinguished by their environmental safety, small geometric dimensions, long service life, reliability, etc. The sharp change in properties when structural transition from a macrocrystalline structure to a nanostructure directly affects the thermoelectric properties of these materials and provides condition for their widespread application in alternative energy sources.

Chalcogenide phases, characterized by intrinsically low thermal conductivity among inorganic functional materials, can currently be a favorable basis for the development of high-performance thermoelectric materials. Solar cells fabricated based on such phases exhibit leading efficiency in terms of efficiency factor and posses significant potential for applications in advanced high-technology sectors. In particular, the properties of the above compounds, such as crystal structure, energy configuration and carrier dispersion, directly affect directly their thermoelectric properties and create the basis for their widespread use in alternative energy sources[1, 2, 3].

Binary and complex copper chalcogenides are geologically widespread in nature, their structure and chemical stability, and their richness in non-toxic components place these compounds in the category of environmentally friendly materials. In particular, synthetic

[1] Palchoudhury, S. Multinary copper-based chalcogenide nanocrystal systems from the perspective of device applications // Nanoscale Advances, - 2020, -vol.2, - p.3069-3082.

[2] Pejjai, B. Review on earth-abundant and environmentally benign Cu–Sn–X(X=S, Se) nanoparticles by chemical synthesis for sustainable solar energy conversion // Journal of Industrial and Engineering Chemistry, - 2018, -vol.60, -p.19–52.

[3] Mikuła, A. Copper chalcogenide-copper tetrahedrite composites– a new concept for stable thermoelectric materials dased on the chalcogenide system // Materials, – 2021. 14(10), – p.2635-2645.

analogues of natural minerals belonging to the Cu-Sb(As)-X (X=S, Se) systems, as well as solid solutions based on these compounds, show the high efficiency in the intermediate temperature range (450÷800 K), there by significantly expanding their application scope.

In this regard, in a series of works published in recent years have reflected interesting results on the properties of complex chalcogenide phases formed in four-component systems of the Cu-A^{IV}-B^{V}-Se (A^{IV}– Ge, Sn, Pb; B^{V} -Sb, Bi, As; X-S, Se) type and composite materials prepared based on these phases. In particular, Cu, Sn and Sb selenides have thermoelectric and optical properties, ionic and electronic conductivity in a wide energy range, and are promising systems in terms of synthesizing new functional materials and increasing the efficiency of energy conversion processes. However, the optimal compositions of these chalcogenide materials are often determined empirically - through numerous experiments. This approch presents significant challenges in defining the initial synthesis parameters technology, including thermal treatment conditions and the selection of optimal operating ranges for the target materials.

Taking into account the above, the study of phase equilibrium at certain concentration planes of the Cu-Sn-Sb-Se system, the study of composition-property dependencies of intermediate phases, and the discovery of thermodynamic functions are relevant and has scientific and practical importance for the development of materials with advanced functional properties.

Research object and research subject. The research object of the dissertation is the study of new thermoelectric materials with functional properties in Cu_2Se-$SnSe$-Sb_2Se_3, Cu_2SnSe_3-Sb_2Se_3-Se, Cu_2Se-Cu_3SbSe_4-Cu_2SnSe_3, Cu_2SnSe_3-Cu_3SbSe_4-Se concentration planes of the quaternary Cu-Sn-Sb-Se system. The subject of the research is the study of phase equilibria in these systems and the determination of the physicochemical and thermodynamic properties of the obtained new phases.

The aim and tasks of the study. The aim of the dissertation is to elucidate the comprehensive undenstanding of the phase equilibrium of the Cu-Sn-Sb-Se system at certain concentration planes, and to study the physicochemical, thermodynamic properties

of the phases that are separated individually from the system.

For this purpose, the following specific problems are planned to be solved in the dissertation:

- Experimental disign and planning of complex study of phase equilibrium using complex methods of physicochemical analysis (DTA, XRD, SEM, EMF);
- Study of the phase equilibria in the Cu_2Se-$SnSe$-Sb_2Se_3, Cu_2SnSe_3-Sb_2Se_3-Se, Cu_2Se-Cu_3SbSe_4-Cu_2SnSe_3, Cu_2SnSe_3-Cu_3SbSe_4-Se concentration planes;
- Development of phase diagrams (T-x) and liquidus surface projections (T-x-y) for the quasibinary and non-quasibinary polythermal sections;
- Determination of non- and monovariant equilibria occurring in systems, coordinates of isotherms and boundaries of crystallization areas of existing phases;
- Synthesis of samples with different compositions of non-stoichiometric phases found in the studied systems, and calculation of their crystallographic parameters;
- Using the EMF method, determination of the thermodynamic functions of the combination and variable composition phases formed in the studied systems.

Methods of the research

Differential thermal analysis (DTA), X-ray phase (XRD), electromotive force (EMF), and scanning electron microscopy (SEM) methods of analysis were used in the experimental part of the dissertation work. DTA measurements were performed using a multichannel setup based on a “TC-08 Thermocouple Data Logger” electronic data acquisition system, as well as on a NETZSCH-404 F1 Pegasus device. Powder diffraction patterns were recorded using a Bruker D2 Phaser diffractometer (Germany) and analyzed with the instrument’s dedicated computer software. SEM analysis of some polished samples was performed using a TESCAN Vega 3 SBH scanning electron microscope and a Thermo Scientific Ultra Dry Compact EDS detector. EMF measurements were carried out using a Keithley 2100 6½ high-resistance multimeter.

The main provisions of the dissertation.

1. New results obtained on phase equilibria in the Cu_2Se-$SnSe$-Sb_2Se_3, Cu_2SnSe_3-Sb_2Se_3-Se, Cu_2Se-Cu_3SbSe_4-Cu_2SnSe_3 and Cu_2SnSe_3-Cu_3SbSe_4-Se concentration planes of the Cu-Sn-Sb-Se system, phase diagrams of various polythermal and isothermal sections, projections of the liquidus surface and the mono- and nonvariant equilibria identidied therein;

2. Synthesis of variable composition phases obtained in the studied systems, their physicochemical properties;

3. New results on the fundamental thermodynamic functions of intermediate phases in the Sn-Se and Sn-Sb-Se systems

Scientific innovation of the study. The following scientific results were achieved in the dissertation work:

- The nature of the physicochemical interaction on the Cu_2Se-$SnSe$-Sb_2Se_3, Cu_2SnSe_3-Sb_2Se_3-Se, Cu_2Se-Cu_3SbSe_4-Cu_2SnSe_3 and Cu_2SnSe_3-Cu_3SbSe_4-Se concentration planes of the Cu-Sn-Sb-Se system was determined, as well as, it was shown that they are quasi-triplet intersections of the corresponding quaternary system, and formed extensive solid solution areas based on binary and ternary compounds in the systems;

- Projections of the liquidus surfaces of the indicated systems, phase diagrams of a number of their polythermal sections were plotted, the initial crystallization areas of individual phases, types and coordinates of non- and monovariant equilibria were determined;

- Based on EMF measurements carried out in concentration cells relative to a tin electrode at temperatures close to standard conditions, the partial molar functions of tin in the Sn–Se system alloys, as well as the integral thermodynamic functions of the SnSe and $SnSe_2$ compounds, were determined;

- The solid-state equilibria in the $SnSe$-Sb_2Se_3-Se system was determined using RFA and EMF methods, and the standard integral thermodynamic functions of intermediate ternary compounds and solid solutions were calculated.

The theoretical and practical significance of the research. The results on phase equilibrium, including T-x phase diagrams, T-x-y liquidus surface projections, and crystallographic and

thermodynamic properties of intermediate phases, are essential for solving relevant technological problems in Cu-Sn-Sb-Se systems.

The comprehensive and mutually consistent results obtained on the phase equilibrium, as well as data on crystallographic and thermodynamic properties, synthesis of multicomponent phases, constitute an important contribution to the chemistry of complex chalcogenides.

Phase diagrams of the studied systems, liquidus surface projections, as well as data obtained from crystallographic, physicochemical and physical studies of intermediate phases can be included in international scientific databases and reference handbooks as fundamental parameters.

Approbation and application of the work. 19 scientific works were published on the topic of the dissertation. 7 of them were published in journals indexed in the international databases Web of Science and Scopus, and 3 articles were published in journals included in the list of the HAC. 9 scientific works were published as conference materials and report abstracts at international conferences. The main results of the dissertation work were reported and discussed at the following scientific conferences:

1. 3th International Turkic World Conference on Chemical Sciences and Technologie, Bakı, Azərbaycan (10-13 oktyabr 2017);
2. Ümummilli lider Heydər Əliyevin anadan olmasının 95, 97, 99, 100-cü ildönümlərinə həsr olunmuş "Müasir Təbiət və İqtisad Elmlərinin Aktual problemləri" Beynəlxalq elmi konfransları, Gəncə, Azərbaycan (04-05 may 2018; 12 noyabr 2020; 02 may 2022, 05-06 may 2023);
3. "XVI Всероссийская конференция и IX Школа молодых ученых, посвященные 100-летию академика Г.Г.Девятых" Нижний Новгород, Россия (28-31 may 2018);
4. 5th International Turkic World Conference on Chemical Sciences and Technologie, Sakarya, Turkey (25-29 oktyabr 2019);
5. "Electronic Processes in Organic and Inorganic Materials" Kamianets-Podilskyi, Ukraine, (1-5 iyun 2020);
6. 9th Rostocker İnternatıonal Conference: "Thermophysical Properties for Technical Thermodynamics", Rostock, Germany (15

oktyabr 2020)

The name of the research organization which the dissertation work was accomplished. The dissertation work was carried out in the laboratories of "Functional materials based on transition metal compounds" and "Thermodynamics of inorganic substances with functional properties" of the Institute of Chemistry of the Ministry of Science and Education of the Republic of Azerbaijan.

The author's personal contribution. The planning of scientific research conducted within the framework of the dissertation, including the experimental investigations, data analysis, and interpretation of the results were carried out directly by the author. The author's contribution to the co-authored publications is decisive.

The total symbolic volume and structure of the dissertation. The dissertation consists of an introduction (13396), 4 chapters (chapter I 54811, chapter II 30018, chapter III 44811, chapter IV 25334), main conclusion (4288) and includes 212 cited references and a list of the author′s publications on the dissertation topic, and comprises 170 pages. İn total including 76 figures and 25 tables were added to the dissertation.

Thanks. The author expresses sincere gratitude to Prof. Mahammad Babanly for his support throughout all stages of the dissertation research and for his valuable advice in thermodynamic studies, as well as to Assoc. Prof. Vagif Gasymov for his assistance in X-ray diffraction investigations.

THE MAIN CONTENT OF THE WORK

The introduction substantiates the actuality of the topic, provides information about the object, subject, aims and tasks of the research, research methods, the main provisions submitted for defense, the scientific innovation of the obtained results, their theoretical and practical significance, the approbation and application of the work, and the personal contribution of the applicant to the research.

The first chapter provides a literature review. Here, the

phase equilibria of binary, ternary and more complex selenides of copper, tin and antimony, some physical and chemical properties and their application prospects are analyzed. The selection of research objects is justified based on the above-mentioned literature data.

The second chapter describes the synthesis and physicochemical research methods used in the dissertation work. To conduct the research, binary compounds forming ternary systems - Cu_2Se, SnSe, Sb_2Se_3 were first prepared in stoichiometric amounts from high-purity elementary components, and the synthesis was carried out in quartz ampoules under vacuum conditions.

The alloys of the Cu_2Se-SnSe-Sb_2Se_3, Cu_2Se-Cu_2SnSe_3-Cu_3SbSe_4, Cu_2SnSe_3-Cu_3SbSe_4-Se, Cu_2SnSe_3-Sb_2Se_3-Se systems were prepared using previously synthesized initial binary compounds and synthesized according to the synthesis conditions given in the dissertation. The samples were thermally treated at selected temperatures appropriate for each system.

The homogenized samples were analyzed using DTA, XRD (X-ray diffraction), and SEM methods.

The third chapter presents the results of the physicochemical study of the Cu_2Se-SnSe-Sb_2Se_3, Cu_2Se-Cu_2SnSe_3-Cu_3SbSe_4, Cu_2SnSe_3-Cu_3SbSe_4-Se, Cu_2SnSe_3-Sb_2Se_3-Se systems [1-8, 10, 12, 13, 15-19].

A refined version phase diagram of the SnSe–Sb_2Se_3 boundary system in the Cu_2Se–SnSe–Sb_2Se_3 quasi-ternary system. There are two versions of the phase diagram of this system given in the literature by different authors. The presented T-x diagrams differ in the composition and number of intermediate ternary phases formed. For this reason, we present a new refined version of the T - x diagram of the SnSe - Sb_2Se_3 quasi-binary system. Results of XRD of annealed samples containing 33.3; 50 and 60 mol. % Sb_2Se_3 had diffraction patterns that differed from original components. On the other hand, samples containing 50 and 60 mol.% Sb_2Se_3 had the same qualitatively diffraction patterns (Figure 1). This confirms the existence of individual phases with compositions $Sn_2Sb_2Se_5$ $SnSb_2Se_4$ and $Sn_2Sb_6Se_{11}$ and shows that the latter two are isostructural to be within the homogeneity region of some

intermediate phase of variable composition. The powder diffraction pattern of a sample with a composition of 60 mol% Sb_2Se_3 ($Sn_2Sb_6Se_{11}$) was also completely indexed based on the crystallographic data of $SnSb_2Se_4$.

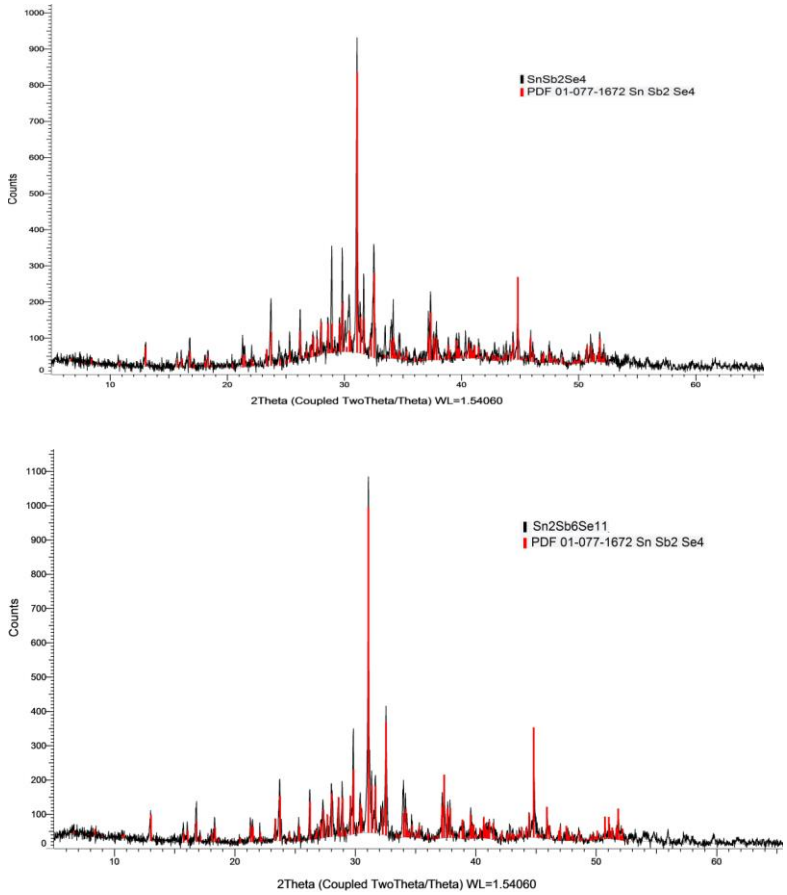


Figure 1. Powder XRD patterns for the alloy with composition 60 mol% Sb_2Se_3 ($Sn_2Sb_6Se_{11}$) and $SnSb_2Se_4$ compound [8].

The phase diagram constructed based on the DTA and RFA results differs significantly from the literature data (Figure 2). However, we found that the $SnSb_2Se_4$ and $Sn_2Sb_6Se_{11}$ phases are

isostructural and the incongruent melting ε-phase is located within the homogeneity region. The existence of a distectic point (given in the literature) corresponding to a composition of 60 mol% Sb_2Se_3 ($Sn_2Sb_6Se_{11}$) was not confirmed by us. The system is quasibinary and has two intermediate phases that decompose according to the peritectic reaction. The compound $Sn_2Sb_2Se_5$ crystallizes at 871 K according to the $L+\beta' \leftrightarrow Sn_2Sb_2Se_5$ reaction. (β' is a solid solution based on a high-temperature modification of SnSe). The second intermediate phase (ε) had a wide (48-60 mol.% Sb_2Se_3) region of homogeneity and crystallized at 833 K by $L+Sn_2Sb_2Se_5 \leftrightarrow \varepsilon$. An eutectic with coordinates 72 mol.% Sb_2Se_3 and 818 K was found in the system.

In addition, the temperature of the peritectic reaction of the formation of the $Sn_2Sb_2Se_5$ compound is 871 K, which is higher than that indicated in literature data (840 K). There are also discrepancies in the composition of the peritectic (p_1) and eutectic (e) points.

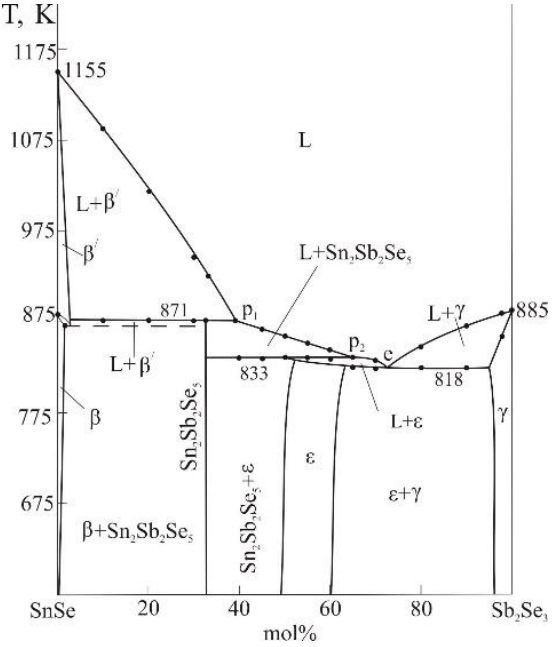


Figure 2. Phase diagram of the SnSe-Sb_2Se_3 system [8].

Thermal effects reflecting the phase transition in SnSe-based solid solutions were not found on the DTA curves. Apparently, these effects overlap with more intense peaks of the peritectic reaction (871 K).

Quasi-binary section SnSe–$CuSbSe_2$ of Cu_2Se-SnSe-Sb_2Se_3 system. Limited solubility based on the starting compounds is observed in the system (Figure 3). The liquidus of the system consists of 3 curves characterizing the solid solution based on SnSe (β-phase) and $CuSbSe_2$ (δ-phase) and the compound formed by the peritectic reaction. A eutectic equilibrium is established at ~63 mol. % $CuSbSe_2$ and 700 K in the system. The solubility based on SnSe (β-phase) and $CuSbSe_2$ (δ-phase) is maximum at the eutectic temperature and is ~25 and 5 mol.

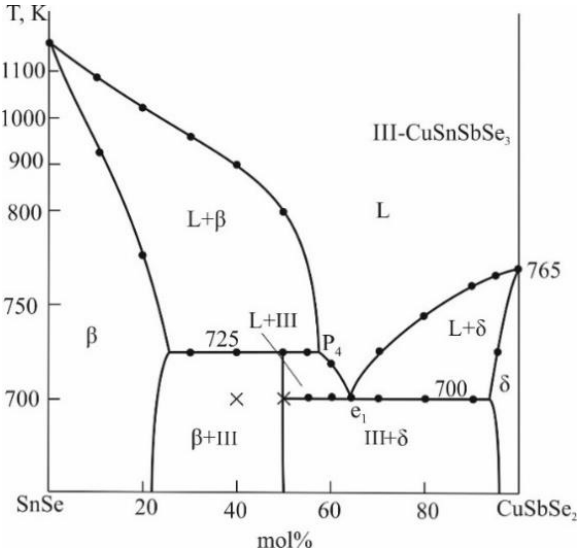


Figure 3. Phase diagram of the SnSe–$CuSbSe_2$ system [15].

Solid-phase equilibria in the Cu_2Se–SnSe–Sb_2Se_3 system at the 300 K. The results of studying the synthesized and thermally treated samples using the methods described in chapter 2 of the dissertation, together with the processing of literature data on boundary quasi-binary systems, made it possible to obtain a refined picture of phase equilibria in this system. Figure 4 shows a diagram

of solid-phase equilibria in the Cu_2Se–$SnSe$–Sb_2Se_3 system at room temperature. Solid solutions based on the compound $CuSbSe_2$ (δ-phase) and Sb_2Se_3 (γ-phase), which are in a connode bond with each other and the ε-phase are observed in the system.

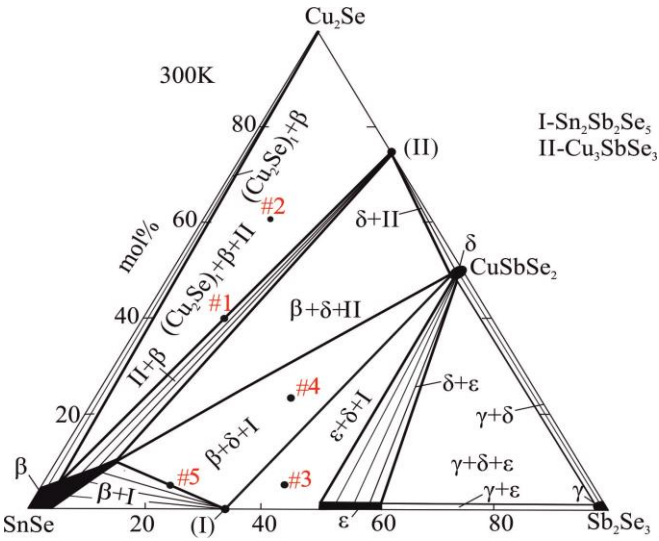


Figure 4. Diagram of solid-phase equilibria in the Cu_2Se–$SnSe$–Sb_2Se_3 system at the 300 K [15].

The β-phase also forms connode bonding with the Cu_3SbSe_3 and $Sn_2Sb_2Se_5$ compounds, as well as with the low-temperature modification of Cu_2Se. The phase compositions of the alloys present in the system were confirmed by XRD and SEM analysis. As an example, the powder X-ray diffraction patterns and SEM images of selected alloys (3–4) are presented in Figure 5. As can be seen, samples #3 and #4 are three-phase (ε+δ+I, β+δ+I), and their phase compositions are in good agreement with the solid-phase diagram. The powder XRD results of some alloys shown in the diagram are presented in the dissertation and discussed in detail.

As a result, the concentration triangle is divided into 7 two-phase (II+β, II+δ, δ+ε, γ+δ, γ+ε, β+I, $(Cu_2Se)_I$+β) and 5 three-phase ($(Cu_2Se)_I$+β+II, β+δ+II, β+δ+I, ε+δ+I, γ+δ+ε) regions.

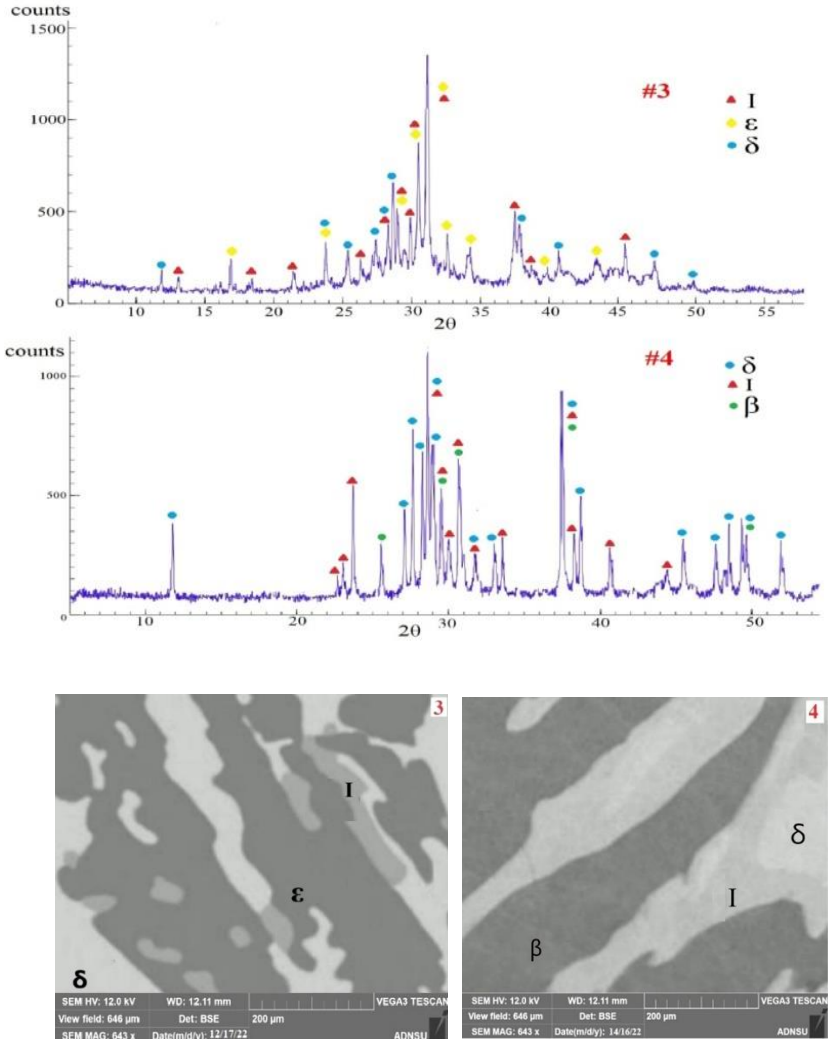


Figure 5. Powder X-ray diffraction patterns and SEM images of samples #3 and #4 (see Figure 4)

Liquidus surface. Through the combined analysis of the DTA, XRD, and SEM results of the studied samples, as well as literature

data on phase equilibria in boundary quasi-binary systems and the properties of intermediate phases, the projection of the liquidus surface of the Cu_2Se–SnSe–Sb_2Se_3 system was constructed (Figure 6). The fields of primary crystallization of α- and β'-phases based on high-temperature modifi-cations of binary Cu_2Se and SnSe compounds, as well as γ-phase based on Sb_2Se_3 (Figure 6, fields 1–3) have the greatest extent. Fields 4–7 refer to ternary compounds formed on boundary quasi-binary systems or solid solutions based on them. The crystallization surface of the quater-nary compound $CuSnSbSe_3$ (region 8) has a small area and is bordered by the fields of pri-mary crystallization of five adjacent phases.

There are 17 invariant equilibria in the system, including the boundary quasi-binary. The types and coordinates of these equilibria are given in Table 1, and the types and temperature ranges of monovariant equilibria are shown in Table 2.

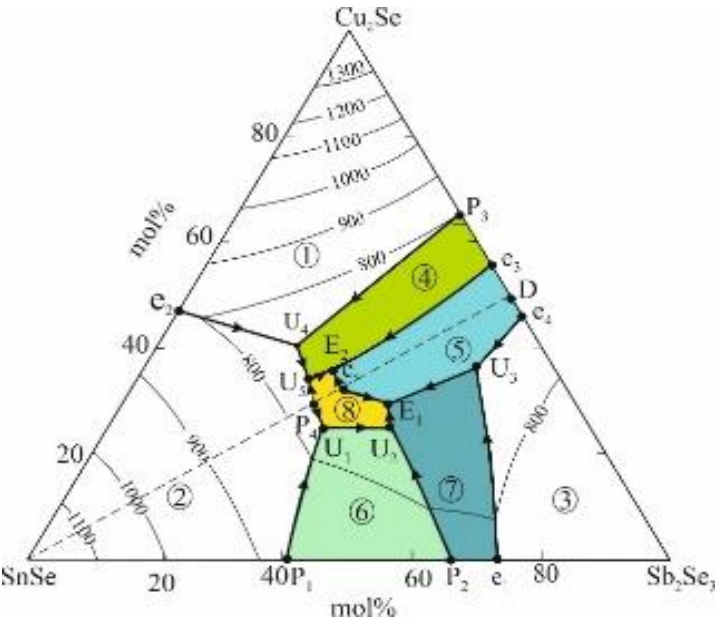


Figure 6. Projection of the liquidus surface of the Cu_2Se–SnSe–Sb_2Se_3 system [15].

Table. 1. Invariant equilibria in the Cu_2Se–SnSe–Sb_2Se_3 system [15]

Point in Figure 6	Equilibrium	Composition, mol%		T, K
		Cu_2Se	Sb_2Se_3	
D	$L \leftrightarrow CuSbSe_2(\delta)$	50	50	765
P_1	$L+\beta \leftrightarrow Sn_2Sb_2Se_5$	–	41	871
P_2	$L+Sn_2Sb_2Se_5 \leftrightarrow \varepsilon$	–	66	833
P_3	$L+\alpha \leftrightarrow Cu_3SbSe_3$	65	35	808
P_4	$L+\beta \leftrightarrow CuSnSbSe_3$	30	30	725
U_1	$L+\beta \leftrightarrow Sn_2Sb_2Se_5+CuSnSbSe_3$	25	34	715
U_2	$L+Sn_2Sb_2Se_5 \leftrightarrow \varepsilon+CuSnSbSe_3$	26	42	687
U_3	$L+\gamma \leftrightarrow \delta+\varepsilon$	36	48	735
U_4	$L+\alpha \leftrightarrow \beta+Cu_3SbSe_3$	40	22	727
U_5	$L+\beta \leftrightarrow Cu_3SbSe_3+CuSnSbSe_3$	34	27	705
e_1	$L \leftrightarrow \gamma+\varepsilon$	–	72	818
e_2	$L \leftrightarrow \alpha+\beta$	47	–	815
e_3	$L \leftrightarrow Cu_3SbSe_3+\delta$	55	45	748
e_4	$L \leftrightarrow \gamma+\delta$	46	54	750
e_5	$L \leftrightarrow \delta+CuSnSbSe_3$	32	32	700
E_1	$L \leftrightarrow CuSnSbSe_3+\delta+\varepsilon$	30	40	675
E_2	$L \leftrightarrow Cu_3SbSe_3+CuSnSbSe_3+\delta$	35	30	680

Table 2. Monovariant equilibria in the Cu_2Se–SnSe–Sb_2Se_3 system [15]

Curve in Figure 6	Equilibrium	T,K
P_1U_1	$L+\beta \leftrightarrow Sn_2Sb_2Se_5$	871–715
P_4U_1	$L+\beta \leftrightarrow CuSnSbSe_3$	723–715
U_1U_2	$L \leftrightarrow Sn_2Sb_2Se_5+CuSnSbSe_3$	715–687
P_2U_2	$L+Sn_2Sb_2Se_5 \leftrightarrow \varepsilon$	833–687
U_2E_1	$L \leftrightarrow CuSnSbSe_3+\varepsilon$	687–675
e_1U_3	$L \leftrightarrow \gamma+\varepsilon$	818–735
e_4U_3	$L \leftrightarrow \gamma+\delta$	750–735
U_3E_1	$L \leftrightarrow \delta+\varepsilon$	735–675
e_5E_1	$L \leftrightarrow CuSnSbSe_3+\delta$	700–675
e_2U_4	$L \leftrightarrow \alpha+\beta$	815–727
P_3U_4	$L+\alpha \leftrightarrow Cu_3SbSe_3$	808–727
U_4U_5	$L \leftrightarrow \beta+Cu_3SbSe_3$	727–705
P_4U_5	$L+\beta \leftrightarrow CuSnSbSe_3$	723–705
U_5E_2	$L \leftrightarrow Cu_3SbSe_3+CuSnSbSe_3$	705–680
e_3E_2	$L \leftrightarrow Cu_3SbSe_3+\delta$	748–680

e_5E_2	$L \leftrightarrow CuSnSbSe_3+\delta$	700–680

In the dissertation, T–x diagrams of some polythermal sections of the $Cu_2Se–SnSe–Sb_2Se_3$ system phase diagram are also presented and discussed in detail. Among these, particular attention should be paid to the non-quasibinary $Cu_2Se–SnSb_2Se_4$ section, which passes through most of the primary crystallization fields of the liquidus surface.

The $Cu_2Se–SnSb_2Se_4$ polythermal section (Figure 7). The liquidus curve consists of five branches corresponding to the α, Cu_3SbSe_3, δ, $CuSnSbSe_3$ and $Sn_2Sb_2Se_5$ phases (see Figure 6). Below the liquidus, crystallization continues according (from left to right) to monovariant peritectic (P_3U_4), and eutectic U_4U_5, e_3E_2, e_5E_2, e_5E_1, U_2E_1 and U_1U_2 reactions. Despite the complexity of the picture of phase equilibria, especially in the composition range of 40–80 mol% $SnSb_2Se_4$, the correct in-terpretation of the DTA data is beyond doubt, since the sequence of crystallization processes in the arrangement of heterogeneous regions in Figure 7 is in full agreement with the general T–x–y diagram of the $Cu_2Se–SnSe–Sb_2Se_3$ system (Figure 6). Crystallization is completed by the invariant reactions U_4 (727K), U_5 (705K), E_2(680K), and E_1 (675K) with the formation of three-phase mixtures $\alpha+\beta+Cu_3SbSe_3$, $\beta+Cu_3SbSe_3+CuSnSbSe_3$, $\delta+Cu_3SbSe_3+CuSnSbSe_3$ and $\delta+\varepsilon+ CuSnSbSe_3$.

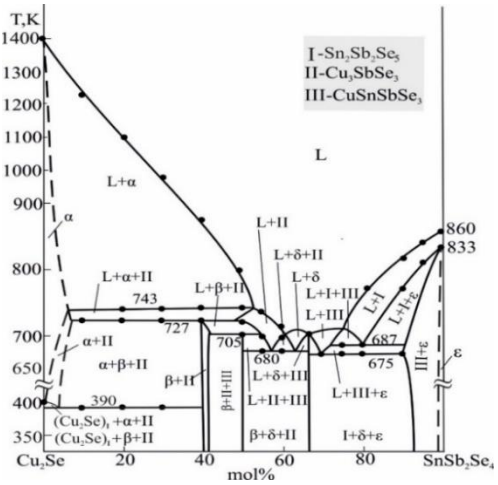


Figure 7. Phase diagram of the Cu_2Se–$SnSe_2Se_4$ system [15].

Isothermal section at 900 K (Figure 8a). This isothermal section reflects the equilibria of the α- and β/ - phases with the liquid based on the high-temperature modifications of the Cu_2Se and SnSe compounds, leading to the formation of wide two-phase regions: L+α və L+β/. The liquid phase extends over a very wide composition range.

Isothermal section at 800 K (Figure 8b). As can be seen from the figure, a 100 K decrease in temperature significantly changes and complicates the phase equilibrium relations of the system. The primary crystallization from the liquid occurs on this isothermal section, α- and β/-phases, γ-phase based on Sb_2Se_3, as well as intermadiate ternary compounds ($Sn_2Sb_2Se_5$-I, Cu_3SbSe_3-II) and solid solutions based on them (ε-phase). There are 6 (six) liquidus isotherms and corresponding two-phase fields (L+α, L+β/, L+γ, L+I, L+II, L+ε) in the system that reflect these two-phase equilibria. In addition to these, two-phase regions are also formed in the subsolidus: L+α+β/, L+α+II, L+β/+I, L+ε+I və L+γ+ε.

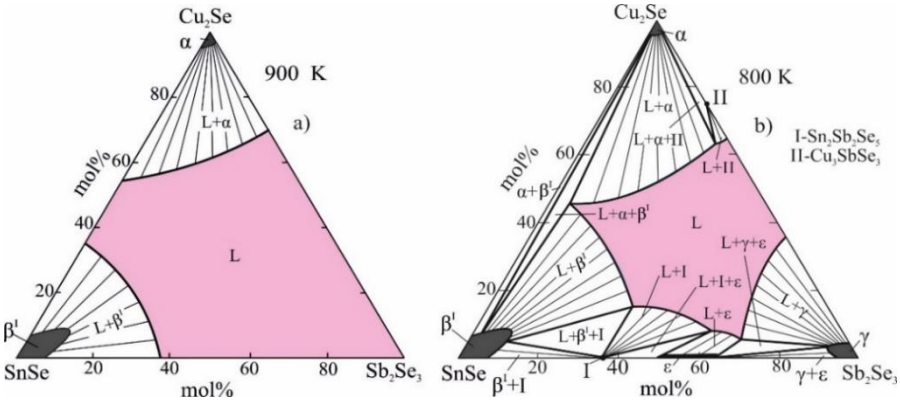


Figure 8. Isothermal sections of the phase diagram at 900 K (a) and 800 K (b).

Cu_2SnSe_3–Sb_2Se_3–Se system. The projection of the liquidus surface of the Cu_2SnSe_3–Sb_2Se_3–Se system is shown in Figure 9. It can be seen that the liquidus surface of the Cu_2SnSe_3-Sb_2Se_3-Se system consists of two main and one degenerate sections. Region 1 corresponds to primary crystallisation of α_1 and α_2 phases based on two crystalline modifications of Cu_2SnSe_3, while region 2 corresponds to primary crystallization of β-solid solutions based on Sb_2Se_3. The third region corresponds to elemental selenium and was degenerate in the corresponding angle of the concentration triangle. A typical feature of the system is that the immiscibility region existing on the side quasi-binary section of Cu_2SnSe_3–Se (contour mm^1 at 910 K) suddenly penetrates inside the triangle forming a wide region ($mMKM^1m^1$) of immiscibility of two liquid phases (L_1+L_2).

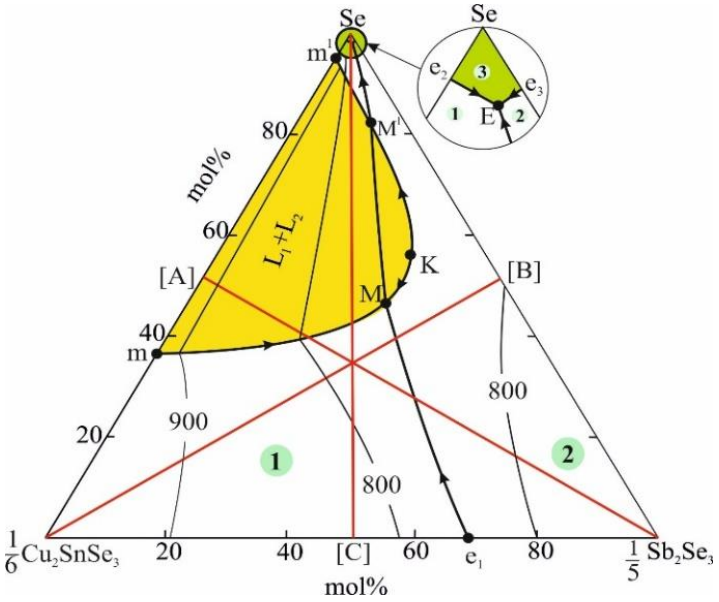


Figure 9. Liquidus surface of the Cu_2SnSe_3–Sb_2Se_3–Se system. Red lines are the studied polythermal sections [17]

This region crosses the curve coming out from the eutectic point (e_1) of the Cu_2SnSe_3–Sb_2Se_3 system and takes a part of the liquidus surface of β-phase (MKM^1). In the MM^1 interval the eutectic curve crosses the immiscibility region, and the eutectic equilibrium L ↔ α+β turns into a non-variant monotectic equilibrium L ↔ L_2+α+β. All non-variant and monovariant phase equilibria observed in the system, including side systems, are presented in Table 3. The conjugated curves mM and mM^1 limiting the immiscibility region reflect the process of crystallisation of α-phase while the conjugated curves MK and KM^1 reflect the monovariant crystallisation of β-phase upon monotectic reactions. The process of crystallisation in the system completes with the formation of a triple eutectic mixture α_2+β+Se (E; 490 K). Eutectic points e_2 and e_3 on boundary quasi-binary systems as well as point E and eutectic curves e_2E и e_3E are degenerate. This part of the phase diagram is presented in Figure 9 as an enlarged view (representative scale).

Table 3.
Non-variant and monovariant phase equilibria in the Cu_2SnSe_3–Sb_2Se_3–Se system [17]

Point and curve in Fig.9	Equilibrium	Composition, mol%		T,K
		$0{,}2Sb_2Se_3$	Se	
m(m′)	$L_1 \leftrightarrow L_2+\alpha$	-	36(95)	910
e_1	$L \leftrightarrow \alpha+\beta$	68	-	769
e_2	$L \leftrightarrow \alpha+Se$	-	>99	493
e_3	$L \leftrightarrow \beta+Se$	<1	>99	491
M(M′)	$L_1 \leftrightarrow L_2+\alpha+\beta$	35(13)	45(82)	730
E	$L \leftrightarrow \alpha+\beta+Se$	<1	>98	490
e_1M	$L_1 \leftrightarrow \alpha+\beta$			769-730
M′E	$L_2 \leftrightarrow \alpha+\beta$			730-490
e_2E	$L \leftrightarrow \alpha+Se$			493-490
e_3E	$L \leftrightarrow \beta+Se$			491-490
mM(m′M′)	$L_1 \leftrightarrow L_2+\alpha$			910-730
KM(KM′)	$L_1 \leftrightarrow L_2+\beta$			750-730

Cu_2Se-Cu_3SbSe_4-Cu_2SnSe_3 system. X-ray phase analysis of the alloys annealed at 700 K along the Cu_3SbSe_4–Cu_2SnSe_3 boundary section of system (Figure 10) showed the formation of solid solution regions based on the initial components with compositions of 25 mol% Cu_2SnSe_3 (α) and 30 mol% Cu_3SbSe_4 (β), respectively. In the 30–75 mol% Cu_3SbSe_4 concentration range, α+β solid solutions crystallize together. The X-ray diffraction patterns of samples containing 75–100 mol% Cu_3SbSe_4 are qualitatively identical to the Cu_3SbSe_4 compound. Based on DTA and XRD data, a phase diagram of the Cu_2SnSe_3-Cu_3SbSe_4 system was constructed (Figure 11a). It was established that this system is quasi-binary, forms a eutectic-type T-x diagram, and is characterized by the formation of wide solid solutions (α- and β-phases) based on both initial components.

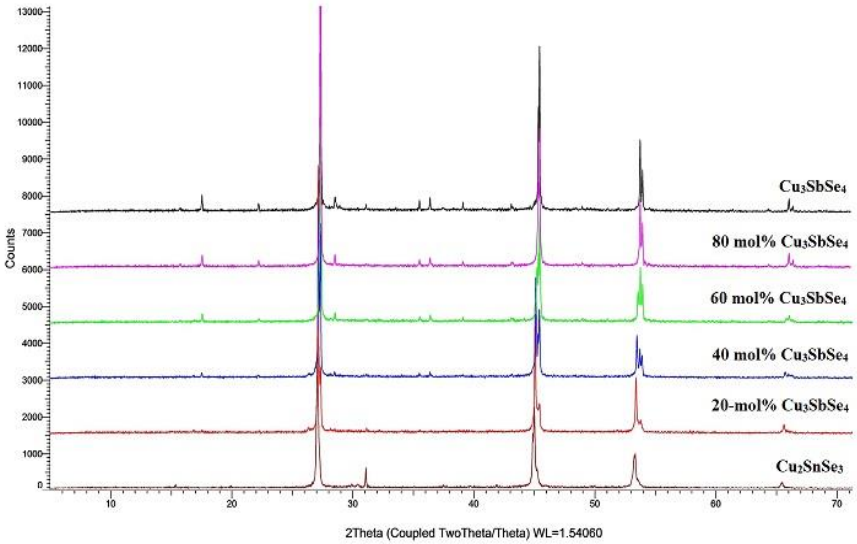


Figure 10. Powder XRD patterns of alloys of the Cu_2SnSe_3-Cu_3SbSe_4 system

The compositional dependence of the unit cell parameters of the α- and β-solid solutions formed based on the initial components within the solubility ranges exhibits a linear character and follows Vegard's law (Figure 11b). The dependence of the crystal lattice parameters is in good agreement with the phase diagram.

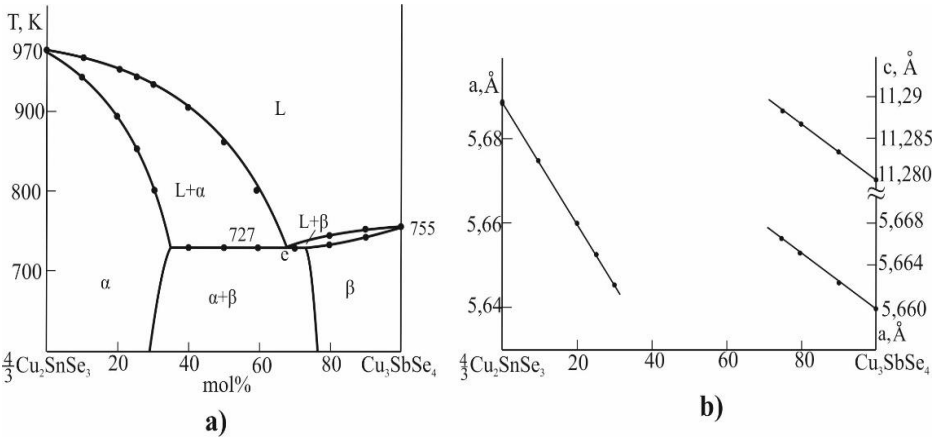


Figure 11. Phase diagram of the Cu_2SnSe_3–Cu_3SbSe_4 system (a), and composition dependence of the lattice parameters of the solid solutions (b).

Figure 12 shows a diagram of the solid phase equilibria established on the basis of the results of XRD and SEM of annealed at 600 K samples of the Cu_2Se-Cu_2SnSe_3-Cu_3SbSe_4 system. The system is characterized by the formation of wide region of solid solution based on the initial components. Area of solid solutions based on HT-Cu_2Se are 5-6 mol%.

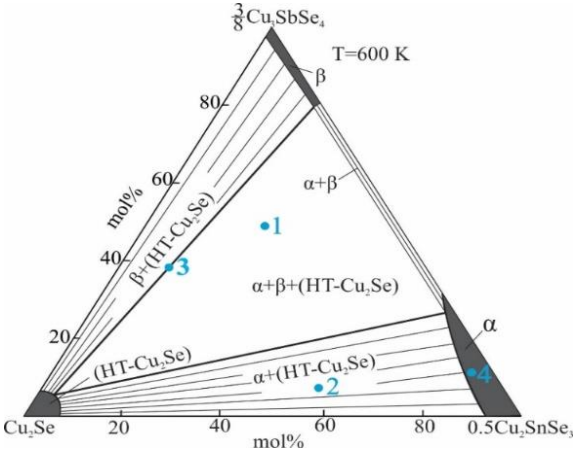
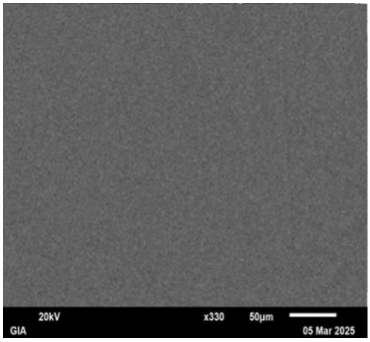


Figure 12. Diagram of solid-phase equilibria in the Cu_2Se-Cu_3SbSe_4 -Cu_2SnSe_3 at the 600 K [19].

Homogeneity areas of α- and β- solid solutions formed along

the Cu_2SnSe_3-Cu_3SbSe_4 section penetrate into the 3-8 mol % of concentration triangle and the corresponding single-phase bands are formed. (HT-Cu_2Se), α- and β- phases with each other produce three two-phase: (HT-Cu_2Se)+α, (HT-Cu_2Se)+β, α+β areas and one three-phase (HT-Cu_2Se)+α+β area. The phase areas were confirmed by XRD and SEM technique. For example, Figure 13 shows the SEM image of the α-phase with the composition 10 mol% Cu_3SbSe_4 (alloy 4 in Figure 12). The element composition of the alloy is shown using results of the EDS analysis and corresponds to the formula $Cu_{2.1}Sb_{0.1}Sn_{0.9}Se_{3.1}$.



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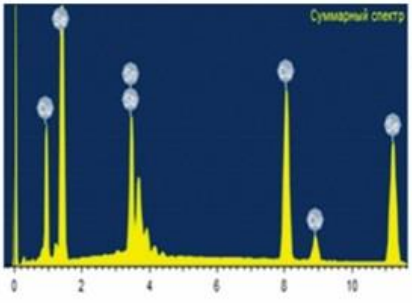

2

Element	Çəki%	Atom %
Cu *K*	25,2	33,87
Sb *K*	3,1	1,62
Sn *L*	22,0	14,51
Se *L*	49,7	50
Ümumi	**100,0**	**100,0**

3

Figure 13. SEM image (1), EDS spectrum (2), and elemental analysis results (3) of the α-phase with composition $Cu_{2.1}Sb_{0.1}Sn_{0.9}Se_{3.1}$ [19].

Liquidus surfase. The liquidus surface of the Cu_2Se-Cu_2SnSe_3-Cu_3SbSe_4 system consists of three fields of primary crystallization of (HT-Cu_2Se), α- and β- phases. The curves from the eutectic points of boundary quasibinary systems (e_1E, e_2E, e_3E) intersect in the triple eutectic point.

These curves are characterized by the following monovariant eutectic equilibria:

$L \leftrightarrow$ (HT-Cu_2Se) + α (e_1E;, 940-725 K) (1)

$L \leftrightarrow$ (HT-Cu_2Se) + β (e_2E; 750-725 K) (2)

$L \leftrightarrow$ α+ β (e_3E; 733-725 K) (3)

The following nonvariant equilibrium is formed at the triple eutectic point E (725 K): $L \leftrightarrow$ (HT-Cu_2Se) + α+ β

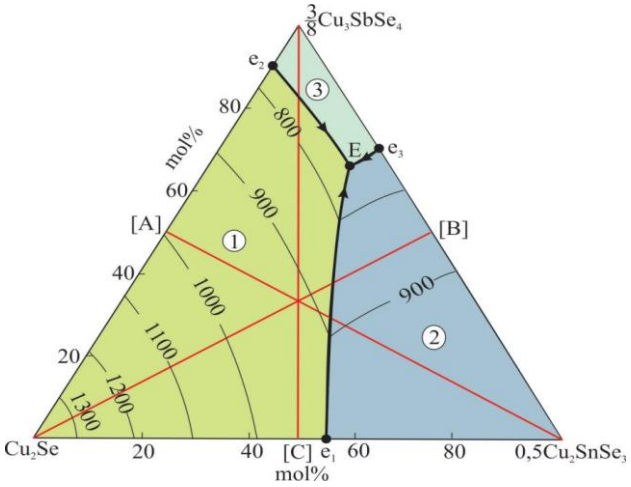

Figure 14. Liquidus surfase of the Cu_2Se- Cu_3SbSe_4-Cu_2SnSe_3 system. Primary crystallization fields: 1-HT-Cu_2Se; 2-α-phase; 3- β-phase [19]

As can be seen from the projection of the liquidus surface, the considered plane of the Cu–Sn–Sb–Se concentration triangle represents a quasi-ternary system, and its T–x–y phase diagram is of

the eutectic type.

In the dissertation, in order to visually observe the crystallization processes in the system is systematically analyzed through phase equilibrium along three polythermal sections extending from the vertices to opposite sides of the T–x–y diagram, which are presented and discussed in detail.

To confirm the nature of the chemical interaction occurring in the quaternary system, we additionally studied the Cu_3SbSe_4-$SnSe_2$ cross section passing through the Cu_3SbSe_4-Cu_2SnSe_3-Se and Cu_2SnSe_3-Sb_2Se_3-Se subsystems of the Cu_2Se-$SnSe_2$-Sb_2Se_3-Se solid tetrahedron.

According to the results of the X-ray phase analysis of the annealed samples, substitutional solid solutions with a tetragonal structure based on Cu_3SbSe_4 are formed in the system within the concentration range of 0–20 mol% $SnSe_2$ and the unit cell parameters of the $Cu_3Sb_{1-x}Sn_xSe_4$ solid solutions change only slightly (Figure 15).

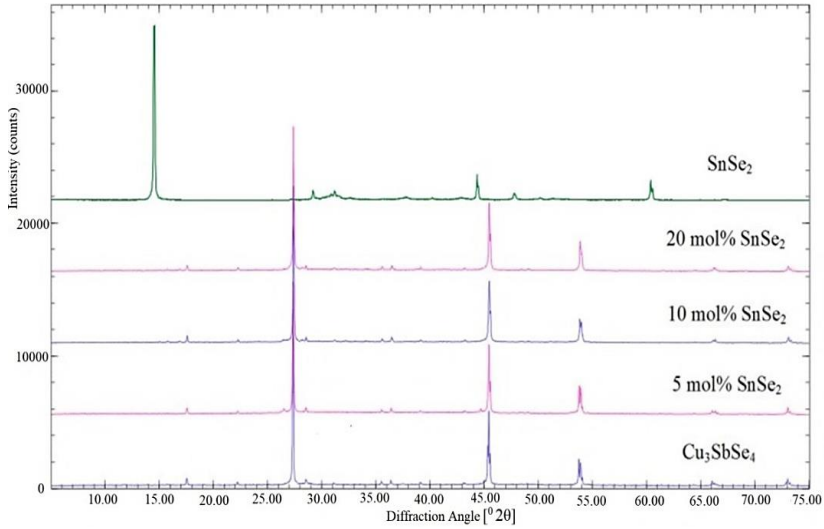

Figure 15. Powder X-ray diffraction patterns of some samples of the Cu_3SbSe_4–$SnSe_2$ system [13]

It was determined that in the 20–57 mol% $SnSe_2$ compositions range alloys consist of a four-phase mixture of α+ Cu_2SnSe_3+Sb_2Se_3+Se. The alloy containing 60 mol% $SnSe_2$ is a three-phase mixture of Cu_2SnSe_3 + Sb_2Se_3 + Se, whereas the samples containing more than 60 mol% $SnSe_2$ consist of a four-phase mixture of Cu_2SnSe_3 + Sb_2Se_3 + $SnSe_2$ + Se.

Based on the data obtained, it can be concluded that the Cu_3SbSe_4-$SnSe_2$ section is located in 4-phase regions Cu_2SnSe_3+Sb_2Se_3+$SnSe_2$+Se (area 1 in Figure 16) and Cu_3SbSe_4+Cu_2SnSe_3+Sb_2Se_3+Se (area 3 in Figure 16) of the concentration tetrahedron Cu_2Se-$SnSe_2$-Sb_2Se_3-Se. These regions are separated by the stable Cu_2SnSe_3–Sb_2Se_3–Se concentration triangle, and point A in Figure 16 corresponds to the composition of the alloy containing 60 mol% $SnSe_2$ on the Cu_3SbSe_4–$SnSe_2$ section.

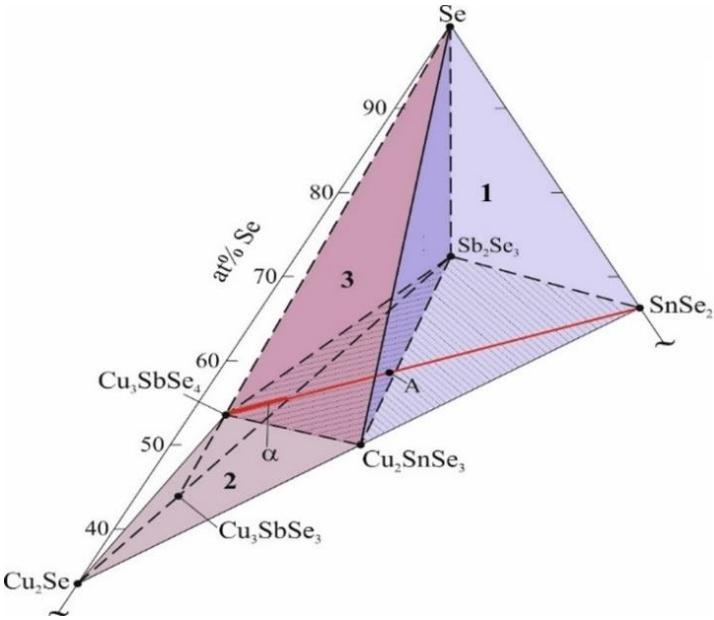

Figure 16. Concentration tetrahedron Cu_2Se-$SnSe_2$-Sb_2Se_3-Se [13]

Considering the above results, it can be concluded that the

nature of phase equilibrium in the Cu_3SbSe_4–$SnSe_2$ system is complex in the $SnSe_2$-rich area and the alloys consist of various heterogeneous mixtures. However, we found that the Cu_3SbSe_4-$SnSe_2$ system is generally non-quasi-binary and is characterized by a complex interaction.

It is important to note that the formation of solid solutions over a wide range in the Cu_3SbX_4–$MeSe_2$ (Me = Ge, Sn; X = S, Se) systems based on the initial ternary compounds is explained by the fact that the crystallographic radii of these ions do not differ significantly from each other. On the other hand, during the substitution of Sb^{+5} ions by Me^{+4} ions, charge balance is maintained through the conversion of Cu^{+1} ions to Cu^{+2} ions.

In the fourth chapter, the thermodynamic properties of binary and ternary phases formed within the $SnSe$-Sb_2Se_3-Se concentration range of the Sn-Sb-Se ternary systems were studied by the EMF method, and the obtained results were systematically analyzed [9, 11, 14].

For the thermodynamic investigation of tin selenides and tin–antimony selenides, the concentration cells of the (1) and (2) type were constructed.

(-) Sn (s.) | liquid electrolyte, Sn^{2+} | (Sn in alloy) (s.) (+) (1)
(-)SnSe (s.) | liquid electrolyte, Sn^{2+} | (Sn in alloy) (s.) (+) (2)

The concentration cell of type (1) was used for the thermodynamic investigation of binary compounds. However, its application to the study of the Sn–Sb–Se ternary system did not yield positive results. İnitial experiments showed that the EMF values were not reproducible during the measurements and instead exhibited a gradual decrease. Therefore, concentration cells of type (2) were constructed for the thermodynamic investigation of tin–antimony selenides.

For the concentration cell of type (1), the left electrode was elemental tin, whereas in type (2) cells tin selenide was selected as

the left electrode. The right electrodes consisted of thermally treated alloys taken from the two-phase and three-phase regions of the Sn-Sb-Se system.

In the research, the KCl glycerol solution with the addition of 0.5 wt% $SnCl_2$ served as the electrolyte. The emf was measured in a cell with an inert atmosphere with a Keithley 2100 6 ½ digit multimeter in the temperature range 300–450 K.

To plan our studies, the diagram of solid-phase equilibria in the SnSe–Sb_2Se_3–Se system (Figure 17) was constructed based on the literature data on phase equilibria in the systems Sn (Sb)–Se and SnSe ($SnSe_2$)–Sb_2Se_3. It was established that, in the system, both ternary compounds ($Sn_2Sb_2Se_5$ and $SnSb_2Se_4$) and the γ-phase based on $Sn_2Sb_6Se_{11}$ are in conodal equilibrium with $SnSe_2$.

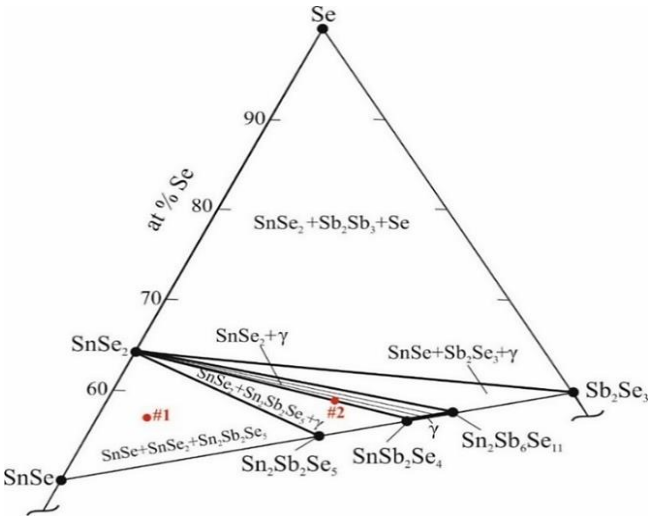

Figure 17. Diagram of solid-phase equilibria in the SnSe–Sb_2Se_3–Se system [14]

The EMF measurements obtained from the concentration cells of type (2) are in good agreement with the solid-phase equilibrium diagram of the SnSe–Sb_2Se_3–Se system. The measurements of the emf of the cells of type (1) gave reproducible results, which were in full agreement with the diagram of solid-phase equilibria in the

SnSe–Sb_2Se_3–Se system. Within each three-phase region at a given temperature, the emf values are equal (with an accuracy of ±0.5 mV), regardless of the total composition of the right-electrode alloys.

Figure 18 presents the E–x dependence along the section SnSe–Sb_2Se_3, which shows that, at the interface between the two-phase regions SnSe + $Sn_2Sb_2Se_5$ and $Sn_2Sb_2Se_5$ + γ, the emf varies stepwise; within the homogeneity region of the γ-phase, it is a function of the composition; and in the two-phase fields, it remains constant. For all the studied electrode alloys, the temperature dependences of the emf are linear (Figure 19).

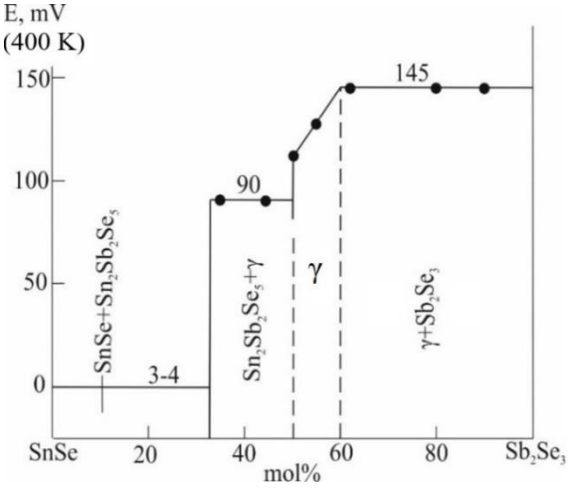

Figure 18. Composition dependence of the emf of cells of type (1) at 400 K in the SnSe–Sb_2Se_3 system [14]

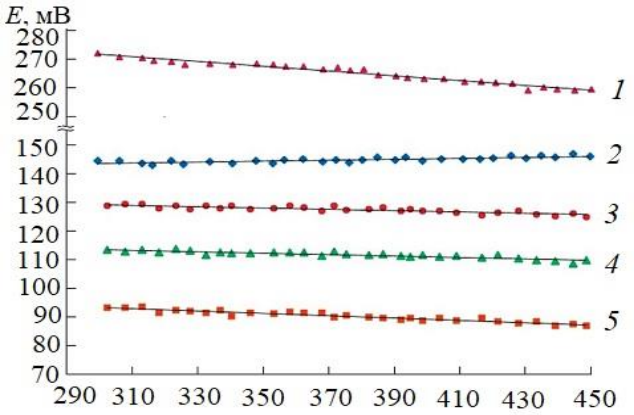

Figure 19. Temperature dependences of the emf of cells of type (2) in some phase regions of the Sn–Sb–Se system [14]

This is related to the fact that the compositions of phases in equilibrium remain constant and independent of temperature. Therefore, the obtained experimental data were processed using Microsoft Office Excel 2003 by the least-squares method under the assumption of the linear temperature dependence of the emf. Based on the linear equations accepted in modern literature the partial molar functions of the SnSe component in alloys at 298 K were calculated based on the following expressions and are given in Table 4.

$$\Delta\bar{G}_{SnSe}=-zFE \quad (3)$$

$$\Delta\bar{S}_{SnSe}=zF\left(\frac{\partial E}{\partial T}\right)_p = zFb \quad (4)$$

$$\Delta\bar{H}_{SnSe}= -z\,F[E - T\left(\frac{\partial E}{\partial T}\right)_p] = -zFa \quad (5)$$

Table 4.
Partial thermodynamic functions of SnSe in alloys in the Sn–Sb–Se system at 298.15 K [14]

Faza sahəsi	$-\Delta\bar{G}_{SnSe}$	$-\Delta\bar{H}_{SnSe}$	$-\Delta\bar{S}_{SnSe}$
	kC/mol		$CK^{-1}mol^{-1}$

$SnSe_2 + Sb_2Se_3 + Se$	52.45 ± 0.10	57.20 ± 0.43	-15.93 ± 1.12
$Y + SnSe_2 + Sb_2Se_3$	27.71 ± 0.08	26.76 ± 0.34	3.21 ± 0.89
$Y + SnSe_2$	24.99 ± 0.08	26.38 ± 0.34	-4.64 ± 0.90
$SnSb_2Se_4 + SnSe_2$	21.98 ± 0.08	23.43 ± 0.36	-4.85 ± 0.94
$Sb_2Se_5 + SnSb_2Se_4 + SnSe_2$	18.09 ± 0.08	20.40 ± 0.34	-7.75 ± 0.90

The partial molar functions of tin in the above phase regions were calculated by combining the data in Table 4 with the relative partial thermodynamic functions of Sn in SnSe (Table 5).

Table 5.
Partial thermodynamic functions of tin in alloys in the Sn–Sb–Se system at 298.15 K [14]

Faza sahəsi	$-\Delta\overline{G}_{Sn}$	$-\Delta\overline{H}_{Sn}$	$-\Delta\overline{S}_{Sn}$
	kC/mol		$CK^{-1}mol^{-1}$
$SnSe_2 + Sb_2Se_3 + Se$	119.96 ± 0.20	122.20 ± 0.87	-7.54 ± 2.28
$Y + SnSe_2 + Sb_2Se_3$	95.22 ± 0.18	91.76 ± 0.78	11.60 ± 2.05
$Y + SnSe_2$	92.20 ± 0.18	91.38 ± 0.78	3.76 ± 2.06
$SnSb_2Se_4 + SnSe_2$	89.49 ± 0.18	88.43 ± 0.80	3.56 ± 2.10
$Sn_2Sb_2Se_5 + SnSb_2Se_4 + SnSe_2$	85.60 ± 0.18	85.40 ± 0.78	0.67 ± 2.06

It is easy to show that the partial molar functions of tin in the three-phase regions $SnSe_2 + Sb_2Se_3 + Se$, $\gamma(Sn_2Sb_6Se_{11}) + SnSe_2 + Sb_2Se_3$, and $Sn_2Sb_2Se_5 + \gamma(SnSb_2Se_4) + SnSe_2$ are thermodynamic functions of the following potential-forming reactions (all the substances are crystalline):

$$Sn + 2Se = SnSe_2 \quad (6)$$
$$Sn + SnSe_2 = 2SnSe \quad (7)$$
$$Sn + SnSe_2 + 3Sb_2Se_3 = Sn_2Sb_6 \quad (8)$$
$$Sn + SnSe_2 + 2SnSb_2Se_4 = 2Sn_2Sb_2 \quad (9)$$

According to these reactions, the integral thermodynamic functions of the compounds $SnSe_2$, $Sn_2Sb_2Se_5$, and $Sn_2Sb_2Se_5$ were calculated are given in Table 6. The standard integral thermodynamic functions of the γ-phase of the stoichiometric composition $SnSb_2Se_4$ were calculated by integrating the Gibbs–Duhem equation along the ray that originates at the Sn vertex of the concentration triangle and passes through the $SnSb_2Se_4$ composition point.

The integral thermodynamic functions of the ternary phases were calculated using the literature data on the corresponding thermodynamic characteristics of Sb_2Se_3, and also the standard entropies of tin (51.55 ± 0.21 J/(K mol)) and selenium (42.13 ±0.21 J/(K mol).

The values of the standard heat of formation and entropy of the compounds shown in Table 6 also practically coincide with the calorimetric data. The Gibbs free energy was determined by us for the first time.

Table 6.
Standard integral thermodynamic functions of binary and ternary compounds in the subsystem $SnSe–Sb_2Se_3–Se$

Birləşmə	$-\Delta_fG^0(298K)$	$-\Delta_fH^0(298K)$	$S_f^0(298K)$	$S°(298K)$
	kC/mol		$CK^{-1}mol^{-1}$	
$SnSe_2$	120.9±0.3	122.2±0.9	−7.5 ± 2.3	128.3±3.0
SnSe	93.6±0.1	93.2±0.4	⍰	95.0±1.6
$Sn_2Sb_6Se_{11}$	592.9 ± 9.4	596.9 ± 5.2	–13.1±5.5	827.8 ± 15.2

$SnSb_2Se_4$	232.8 ± 3.2	234.9 ± 2.4	-6.7 ± 3.9	306.5 ± 6.0
$Sn_2Sb_2Se_5$	335.4 ± 3.4	338.6 ± 3.3	-3.5 ± 6.1	396.8 ± 8.6

Thus, as a result of studies conducted for various phase fields of the Sn-Sb-Se system using the EHQ method, the relative partial thermodynamic functions of tin in alloys, as well as the standard thermodynamic functions of formation of the $SnSe_2$, $Sn_2Sb_6Se_{11}$ $Sn_2Sb_2Se_5$ and $SnSb_2Se_4$ compounds, were calculated. Our results for $SnSe_2$ in the ternary system are very close to the corresponding functions of pure $SnSe_2$. This indicates that there is no appreciable solid solution domain formed based on $SnSe_2$ in the ternary system.

Finally, Conclusions summarizes the conducted research and the obtained results.

Conclusion

1. The Cu_2Se-$SnSe$-Sb_2Se_3, Cu_2SnSe_3-Sb_2Se_3-Se, Cu_2Se-Cu_3SbSe_4-Cu_2SnSe_3 and Cu_2SnSe_3-Cu_3SbSe_4-Se concentration planes of the Cu-Sn-Sb-Se quaternary system was studied comprehensively using DTA, XRD, SEM and EMF methods, and the nature of their physicochemical interaction was determined. The initial regions of phase crystallization from the alloy, the types and coordinates of non- and monovariant processes reflecting the phase equilibrium were determined in the given concentration planes. It was shown that these systems are quasi-ternary sections of the Cu-Sn-Sb-Se concentration tetrahedron and are characterized by the formation of extensive regions of solid solutions based on the initial compounds [6, 15, 17, 18].
2. A new refined version of the phase diagram of the $SnSe$-Sb_2Se_3 boundary system was constructed as part of the study of the Cu_2Se-$SnSe$-Sb_2Se_3 system. In the presented T-x diagram, $SnSb_2Se_4$, $Sn_2Sb_2Se_5$ and $Sn_2Sb_6Se_{11}$ compounds, mentioned in the literature, are reflected in the T-x diagram of the system, and it was found that the phases containing $SnSb_2Se_4$ and $Sn_2Sb_6Se_{11}$ are

isostructural and are located in the homogeneity region of incongruently melting γ-phase. In addition, it was found that the $Sn_2Sb_2Se_5$ compound melts at 871 K decomposing through a peritectic reaction [8].

3. The solid phase equilibrium diagram, the liquidus surface projection, and a number of polythermal and isothermal sections of the phase diagram of the quasi-ternary Cu_2Se-SnSe-Sb_2Se_3 system were plotted at 300 K. It was found that the liquidus surface of the system consists of eight regions, reflecting the initial crystallization of solid solutions based on the initial binary and ternary compounds. In this work, the phase diagram of the quasi-binary section SnSe-$CuSbSe_2$ was refined, and it was established that the quaternary compound containing $CuSnSbSe_3$ is formed as a result of a peritectic reaction at a temperature of 725 K. However, this phase exists in a very narrow temperature range and decomposes within a solid phase at temperatures below 650 K [15].
4. As part of a physicochemical study of the Cu_2SnSe_3-Cu_3SbSe_4-Se concentration, a T-x diagram of its Cu_2SnSe_3-Cu_3SbSe_4 boundary system was plotted. It was established that this system is quasi-binary, belongs to the eutectic type, and wide solid solution regions are formed on the basis of the initial compounds. The quasi-ternary Cu_2SnSe_3-Cu_3SbSe_4-Se system is characterized by eutectic and monotectic equilibria. The liquid stratification regions, existing on the sides of the solid triangle Cu_2SnSe_3-Se and Cu_3SbSe_4-Se, form a wide continuous stratification band within the quasi-ternary system. The eutectic curve passing through this region is transformed into a non-variant monotectic equilibrium [16, 18].
5. It was established that the Cu_2SnSe_3-Sb_2Se_3-Se system is a quasi-ternary plane of the corresponding concentration tetrahedron and has eutectic and monotectic equilibria. The liquidus consists of three surfaces reflecting the initial crystallization of solid solutions and elemental selenium based on the initial selenide compounds, the last one was degraded. A wide stratification region existing in the Cu_2SnSe_3-Se boundary system sharply

penetrates to the interior of the concentration triangle, intersecting the eutectic curve emanating from the Cu_2SnSe_3-Sb_2Se_3 boundary system, it leads to its transformation into a non-variant monotectic equilibrium [17].

6. The Cu_2Se-Cu_2SnSe_3-Cu_3SbSe_4 system is also quasi-ternary and belongs to the eutectic type. Extensive substitutional solid solutions based on all three principal compounds were identified in this system. Solid solutions based on ternary compounds offer new opportunities for optimizing their functional properties, particularly their thermoelectric characteristics [18,19].
7. The Sn-Se system was studied using a glycerol-based liquid electrolyte by the EMF method, in the temperature range close to room temperature of the solid-state cycles relative to the tin electrode. Based on the measurement results, partial thermodynamic functions of tin in the two-phase $SnSe_2$+Se and SnSe+SnSe2 regions, as well as the standard thermodynamic functions of formation and standard entropies of $SnSe_2$ and SnSe compounds, were calculated. The obtained results proved to be more reliable in comparison to conflicting literature data on the thermodynamic properties of tin selenides [9].
8. The Sn-Sb-Se system was investigated in the SnSe-Sb_2Se_3-Se concentration region by the EMF method using a glycerol electrolyte. The non-reversible nature of the cycles relative to the tin electrode was determined, and concentration cycles relative to the SnSe electrode were used in the studies. Based on the EMF measurements, partial thermodynamic functions of the SnSe quasi-component and tin in the alloys were calculated. Based on the equilibrium diagram of the solid phase of the studied system, reactions from the hypothetical potential-forming reactions corresponding to these partial molar functions were determined, and new sets of mutually consistent quantities related to the standard integral thermodynamic functions of the ternary compounds $Sn_2Sb_6Se_{11}$, $SnSb_2Se_4$, $Sn_2Sb_2Se_5$ [11, 14] were obtained.

The main results of the dissertation work are reflected in the following scientific works:

1. Ismayilova, E. N.,Mashadieva, L.F., Babanly, K.N., Shukurova, G.M. Isopleth sections SnSe-$CuSbSe_2$ and SnSe- Cu_3SbSe_3 of phase diagram of the Cu-Sb-Sn-Se system // 3RD International Turkic World Conference on Chemical Sciences and Technologies, -Bakı, -Azərbaycan, -2017, -p.216.
2. Исмаилова, Э. Н., Машадиева,Л.Ф., Бабанлы, К.Н., Юсибов, Ю.А. Фазовые равновесия в системе Cu_2Se-SnSe-$CuSbSe_2$ // "XVI Всероссийская конференция и IX Школа молодных ученых посвященные 100-летию академика Г.Г.Девятых" - Нижний Новгород, - Россия, -2018, с.152.
3. Ismayilova, E. N., Mashadieva, L.F. Phase equilibria in the Cu_2Se-SnSe-Sb_2Se_3 system along the SnSe-Cu_3SbSe_3 section // Condensed Matter and Interphases, -2018, 20(2), -p.218–221.
4. Исмаилова,Э.Н. Машадиева, Л.Ф., Бабанлы, К.Н., Юсибов, Ю.А. Поверхность ликвидуса системы Cu_2Se-SnSe-$CuSbSe_2$ // "Müasir Təbiət və İqtisad Elmlərinin aktual problemləri" Gəncə Dövlət Universiteti Beynəlxalq Elmi Konfrans, -Gəncə, - Azərbaycan, -2018, c.8-10.
5. Ismayilova, E. N., Mashadieva, L.F., Shukurova, G.M. Polythermal section SnSe-$CuSbSe_2$ of phase diagram of the Cu_2Se-SnSe-Sb_2Se_3 system // Azerbaıjan Chemıcal Journal, -2019, №.4, -p-29-32.
6. Ismailova, E. N. Phase equilibria in the Cu_2Se–SnSe–$CuSbSe_2$ system / E. N. Ismailova, L.F.Mashadieva, I. B.Bakhtiyarly [et al.] // Russian Journal of Inorganic Chemistry, -2019, 64(6), -p. 801–809.
7. Ismayilova,E.N., Mashadieva,L.F., Mirzəyeva,R.J., Babanly, D.M., Imamaliyeva, S.Z. Solid-phase relations in the Cu_2Se-SnSe-Sb_2Se_3 system // 5th International Turkic World Conference On Chemical Sciences And Technologies, -Sakarya, -Turkey, -2019, -p.207.
8. Ismayilova, E.N., Bakhtiyarly,I.B., Babanly, M.B. Refinement of the phase dıagram of the SnSe - Sb_2Se_3 system // Chemıcal

Problems, -2020, 2(18), -p.250-257.
9. Ismayilova, E.N. Thermodynamic functions of tin selenides / E.N. Ismayilova, D.M. Babanly, V.P. Zlomanov [et al.] // New Materials, Compounds and Applications, -2020, 4(2), pp.132-140.
10. Ismayilova, E. N., Mashadiyeva, L.F., Shevelkov, A.V., Bakhtiyarly,I.B., Babanly, M.B. New phases of variable composition based famatinite mineral-potential environmental friendly termoelectric materials // Electronic Processes in organic and inorganic materials, -Ukraine, -2020, -p.219.
11. Исмаилова, Э.Н., Машадиева, Л.Ф., Бахтиярлы, И.Б., Babanly, M.B. Термодинамические свойства соединений $SnSe_2$ и $Sn_2Sb_6Se_{11}$ // "Müasir Təbiət və İqtisad Elmlərinin actual problemləri" Gəncə Dövlət Universiteti Beynəlxalq Elmi Konfrans, -Gəncə, -Azərbaycan, -2020, s.11-15.
12. Ismayilova, E. N., Hasanova, Z.T, Babanly, K.N, Mashadiyeva, L.F. Solid solutions based on Cu_3SbSe_4 in the Cu_3SbSe_4-$SnSe_2$ ($GeSe_2$) systems // 9 th Rostocker International Conference "Techical Thermodynamics: Thermophysical Properties and Energy Systems", -Rostok, -Germany, -2020, -p.84.
13. Ismayilova, E.N. X-ray study of phase equilibria of the Cu_3SbSe_4-$SnSe_2$ system // News of Azerbaijan Higher Technical Educational Institutions, -2021, 23(5), -p.21-25.
14. Ismailova, E.N. Diagram of solid-phase equilibria in the SnSe–Sb_2Se_3–Se system and thermodynamic properties of tin antimony selenides / E.N Ismailova, L.F. Mashadiyeva, D.M.Babanly [et al.] // Russian Journal of Inorganic Chemistry, -2021, 66(1), -p. 96–103.
15. Ismayilova, E.N.Phase equılıbrıa in the Cu_2Se–SnSe–Sb_2Se_3 system / E. N. Ismailova, L.F. Mashadiyeva, I.B.Bakhtiyarly [et al.] //Azerbaijan Chemical Journal, -2022, -vol.1, -p. 73-82.
16. İsmayılova, E.N. Məşədiyeva L.F., Bəxtiyarlı, İ.B. Cu_2SnSe_3-Cu_3SbSe_4-Se sisteminin likvidus səthi // "Müasir Təbiət və İqtisad Elmlərinin aktual problemləri" Gəncə Dövlət Universiteti Beynəlxalq Elmi Konfrans, -Gəncə, -Azərbaycan -2022, -s.25.
17. Ismayilova, E. N. Phase equilibria in the Cu_2SnSe_3–Sb_2Se_3–Se system / E.N. Ismayilova, L. F. Mashadiyeva, I.B. Bakhtiyarly

[et al.] // Condensed Matter and Interphases, -2023, 25(1), -p.47–54.
18. Ismayilova, E. N. Mashadieva, L.F., Shukurova, G.M., Bakhtiyarly, I.B. Solid phase equilibria in the Cu_2Se-Cu_2SnSe_3-Cu_3SbSe_4 system // "Müasir Təbiət və İqtisad Elmlərinin actual problemləri" Gəncə Dövlət Universiteti Beynəlxalq Elmi Konfrans, Gəncə, -Azərbaycan, -2023, s.32.
19. Ismailova, E.N.Phase equilibria in the Cu_2Se-Cu_3SbSe_4-Cu_2SnSe_3 system / E.N. Ismayilova, L.F. Mashadieva, I.B. Bakhtiyarly [et al.] // Chemical Problems, -2025, 1(23), -p.36-46.

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