

REPUBLIC OF AZERBAIJAN

On the rights of the manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**THE STUDY OF $\text{CuInSe}_2\text{-Ge(Sn,Pb)-Se}$ SYSTEMS AND THE
PROPERTIES OF THE OBTAINED PHASES**

Speciality: **2303.01** – Inorganic chemistry

Field of science: Chemistry

Applicant: **Allazova Nigar Mahmud**

Baku – 2021

The work was performed at the department of «General and Inorganic Chemistry» of Baku State University.

Scientific supervisor: Doctor of Chemistry, professor
Teymur Mammad Ilyasli

Official opponents: Doctor of Chemistry, professor
Ikhtiyar Bahram Bakhtiyarly

Doctor of Chemistry, professor
Yasin Nagi Babayev

Ph.D.Chem., associate professor
Yusif Hamid Yusifov

Dissertation Council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Catalysis and Inorganic Chemistry named after academician M.F.Nagiyev

Chairman of the Dissertation council:



D.Chem.Sci., academician
Dilgam Babir Tagiyev

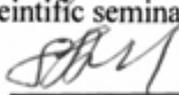
Scientific secretary of the dissertation council:



PhD on chemistry

Ulviyya Akhmed Mammadova

Chairman of the Scientific seminar:



D.Chem.Scie., prof.
Akif Shikhan Aliyev

GENERAL CHARACTERIZATION OF THE RESEARCH WORK

The actuality and usage rate of the topic. CuInSe₂-based solar photoelements with an efficiency factor of more than 21% have been already obtained. CuInSe₂ adsorbs 99% of solar rays, and the calculations show that the efficiency factor of photoelements prepared from this compound can be more than 40%. For that purpose, photosensitive perfect CuInSe₂ crystals must be grown.

There are two polymorphic forms of the CuInSe₂ compound and only low-temperature modification (chalcopyrite phase) has photosensitivity, while the high-temperature modification (sphalerite phase) is not photosensitive.

As is known, during the polymorphic transitions a lot of defects, dislocations and visual cracks are formed on the solid matters. The low-temperature α -CuInSe₂ crystals are formed very defectively due to high change of volume during the sphalerite \leftrightarrow chalcopyrite transition of CuInSe₂ at 810°C occurred in the solid phase and therefore, its photosensitivity falls down. Thus, the growing monocrystals of α -CuInSe₂ from stoichiometric composition is theoretically impossible. To reduce the number of defects in CuInSe₂, crystallization of the latter is required directly from the liquid phase. For this, the famous “melt-solvent” monocrystal growth method is used. There are some requirements for used solvents. At first, the phase equilibrium between compound and solvent must be simple eutectic and the solute must be dissolved in solid form as far as possible. Next, solute should not negatively effect on functional properties of main compound. Hence, the use of chalcogenides of germanium semigroup elements with the aim of growing the perfect α -CuInSe₂ crystals for the choice of adaptable solvent can be theoretically purposive and actual. So then, the investigation of phase equilibrium in CuInSe₂-Ge(Sn,Pb)-Se systems is required.

The aim and tasks of the study. The aim are determination of crystallization parameters directly from melt of chalcogenide phase of CuInSe_2 compound in $\text{CuInSe}_2\text{-Ge(Sn,Pb)-Se}$ ternary systems and the studying the effect of IVA group elements (and their chalcogenides) on electrophysical properties of chalcopyrite phase with more flawless structure. For this goal the following tasks were mooted and solved:

- Studying the physicochemical interaction occurring on $\text{CuInSe}_2\text{-GeSe}$, $\text{CuInSe}_2\text{-Ge}$, $\text{CuInGeSe}_4\text{-GeSe}$, $\text{CuInGeSe}_4\text{-Ge}$, $\text{CuInGeSe}_4\text{-Se}$, $\text{CuInSe}_2\text{-Se}$, $[\text{CuInSe}_2\cdot 4\text{Se-CuInSe}_2\cdot 4\text{Ge}]$, $\text{CuInSe}_2\text{-SnSe}_2$, $\text{CuInSe}_2\text{-SnSe}$, $\text{CuInSe}_2\text{-Sn}$, $[\text{CuInSe}_2\cdot 4\text{Se-CuInSe}_2\cdot 4\text{Sn}]$, $\text{CuInSe}_2\text{-PbSe}$, $\text{CuInSe}_2\text{-Pb}$, $[\text{CuInSe}_2\cdot 4\text{Se-CuInSe}_2\cdot 4\text{Pb}]$, $[\text{CuInSe}_2\cdot \text{Se-PbSe}]$ and $\text{CuInPbSe}_2\text{-PbSe}$ systems by the physicochemical methods of analysis and graphing their phase diagrams;
- Determination of parameters of mono- and invariant processes occurring in $\text{CuInSe}_2\text{-Ge-Se}$, $\text{CuInSe}_2\text{-Sn-Se}$, $\text{CuInSe}_2\text{-Pb-Se}$ quasi-ternary systems and graphing projection diagrams of liquidus surfaces;
- Studying the nature of sphalerite \leftrightarrow chalcopyrite transition in each three quasi-ternary systems, determination of initial crystallization limits and temperature interval of sphalerite and chalcopyrite phases;
- Determination of solution of IVA semigroup elements and their chalcogenides in chalcopyrite phase of CuInSe_2 compound;
- Investigation of current-voltage characteristics of electro-physical properties of samples with CuInSe_2 additives

The methods of the research. The studying high pure samples prepared for dissertation work has been carried out by some of the accustomed methods of physicochemical analysis - differential thermal analysis (DTA) automatically recorded in bicoordinated

H307/1 potentiometer, microstructural analysis and metering the microsolidity (MSA), X-Ray phase analysis (XRD). The temperature dependence of specific electrical conductivity of samples has been determined by compensation method. DTA was measured by chromel-alumel thermocouples in high sensitive self-recorder bicoordinated-H-307/1 potentiometer. The diffractograms of powder samples have been recorded in DRON-2.0 and D8 ADVANCE X-ray diffractometer of German Bruker Corporation. The microstructural analysis and measuring the microsolidity of the samples have been carried out by PMT-3 device.

The main provisions of the dissertation

- Studying the phase equilibria for all concentration and temperature intervals in $\text{CuInSe}_2\text{-Ge-Se}$, $\text{CuInSe}_2\text{-Sn-Se}$ and $\text{CuInSe}_2\text{-Pb-Se}$ quasi-ternary systems across the quasi- and nonquasibinary cross-sections by complex physicochemical analysis methods, graphing the state diagrams and projection diagrams of liquidus surfaces of quasi-systems;
- Determination of initial crystallization parameters of sphalerite \leftrightarrow chalcopyrite polymorphic transition and chalcopyrite phases of CuInSe_2 compound in $\text{CuInSe}_2\text{-Ge(Sn,Pb)-Se}$ systems;
- Investigation of existence of interphases and solid solution areas, their characteristic formation and properties in quasi-ternary systems;
- Studying the effect of chalcogenides of IVA group elements on electrophysical properties (electroconductivity and current-voltage characteristics) of chalcopyrite phase of CuInSe_2 compound;

Scientific innovation of the study. The following new results have been obtained according to the dissertation work:

- The character of the interaction occurring in the $\text{CuInSe}_2\text{-Ge}$, $\text{CuInSe}_2\text{-GeSe}$, $\text{CuInGeSe}_4\text{-GeSe}$, $\text{CuInGeSe}_4\text{-Ge}$, $\text{CuInGeSe}_4\text{-Se}$, $\text{CuInSe}_2\text{-Se}$, $\text{CuInSe}_2\text{-SnSe}$, $\text{CuInSe}_2\text{-Sn}$, $\text{CuInSe}_2\cdot 4\text{Se-CuInSe}_2\cdot 4\text{Sn}$, $\text{CuInSe}_2\text{-Pb}$, $\text{CuInSe}_2\cdot 4\text{Se-CuInSe}_2\cdot 4\text{Pb}$, $\text{CuInSe}_2\text{-Pb-PbSe}$, $\text{CuInSe}_2\text{-Se -PbSe}$ systems has been learned and their phase diagrams have been graphed for the first time. The equilibrium processes have been reviewed in $\text{CuInSe}_2\text{-GeSe}_2$, $\text{CuInSe}_2\text{-SnSe}_2$, $\text{CuInSe}_2\text{-PbSe}$ and $\text{CuInSe}_2\text{-Se}$ systems and improved their phase diagrams;
- The projection diagrams of liquidus surfaces of the $\text{CuInSe}_2\text{-Ge-Se}$, $\text{CuInSe}_2\text{-Sn-Se}$ and $\text{CuInSe}_2\text{-Pb-Se}$ quasi-ternary systems have been plotted, and the character and coordinates of the mono- and invariant processes occurred in the systems have been also determined;
- The limit of the initial crystallization areas of sphalerite and chalcopyrite phases belonging to CuInSe_2 in the $\text{CuInSe}_2\text{-Ge(Sn,Pb)-Se}$ systems has been found out;
- The existence of two new compounds with rational composition of CuInSnSe_2 and CuInPbSe_2 has been discovered by the peritectoid reaction;
- The temperature dependence of electroconductivity of 2mole% SnSe and 2mole% PbSe α -solid solutions based on CuInSe_2 chalcopyrite phase has been studied, the current-voltage characteristic has been measured at 300 K, as a result of which, it was clarified that the additives almost don't effect on electroconductivity of $\alpha\text{-CuInSe}_2$ and on the width of band gap.

The theoretical and practical significance of the research

The metallic Ge, Sn, Pb and their selenides can be used as a solvent

compound with the aim of initial crystallization of more perfect crystals of chalcopyrite directly from the liquid phase due to their eutectic interaction with CuInSe_2 in the $\text{CuInSe}_2\text{-Ge(Sn,Pb)-Se}$ systems. Melts subsequent to the border of certain sphalerite \leftrightarrow chalcopyrite metatectic transition of CuInSe_2 in the quasi-ternary systems enable to determine the technical parameters for getting low-temperature- α - CuInSe_2 monocrystals of the chalcopyrite phase directly from the liquid phase.

16 state diagrams, projection diagrams of the liquidus surfaces of three quasi-ternary systems plotted with CuInSe_2 can be included to proper electron-information bank and reference books as fundamental parameters. The obtaining phase equilibrium diagrams can be used in educational fields of "Physicochemical analysis" and "Inorganic materials science" courses.

Published articles and approbation of the work. 24 scientific works, in addition 10 essays (two of them in foreign scientific journals indexed in international bases, 14 theses in conference publication) have been published according to the dissertation topic.

Published works and approbation of the work. The results of the dissertation were presented and discussed at the following scientific conferences: "Physicochemical analysis and inorganic materials science" VII Republican scientific conferences (Baku, 2002); Baku State University "Young chemist" Materials of the II Republican scientific conference (Baku, 2006), "Synthesis and transformation of chemical compounds " Young researcher. III Respub. scientific conference (Baku, 2007); International scientific conference dedicated to the 90th anniversary of Baku State University (Baku, 2009); IX International Kurnakov Discussion on Physical and Chemical Analysis (Perm, 2010); "General and applied chemistry" XIX Mendeleev Congress on (Volgograd, 2011); Doctoral students, masters and young researchers dedicated to the 89th (94.95) anniversary of national leader Heydar Aliyev "Actual problems of chemistry" VI (XI) Republican Scientific Conference (Baku, 2012, 2017, 2018); "Physicochemical processes in condensed systems and interfacial boundaries" VI All-

Russian Conference entitled-FEBRUARY 2012 (Voronezh, 2012); VI International scientific conference of young researchers proceedings. (Baku, 2016); 2nd International Scientific and Technical Conference on "Problems of Metallurgy and Materials Science" (Baku, 2017); Materials of the scientific conference "Nagiyev readings" dedicated to the 110th anniversary of academician M. Nagiyev (Baku-2018).

24 scientific works on the topic of the dissertation, including 10 articles (2 articles in scientific journals indexed in international databases, 14 theses - in conference proceedings) were published.

The name of the research organization in which the dissertation work has been accomplished. The dissertation work has been performed in the department of "General and Inorganic Chemistry" of the Baku State University.

Volume and structure of the dissertation. The text of the dissertation consists of 132 computer pages (167471, excluding bibliography), 53 figures and 20 tables, a list of 220 references. The dissertation consists of an introduction (8845), six chapters (the first chapter 48953, the second chapter 25433, the third chapter 26273, the fourth chapter 45251, the fifth chapter 21452, the sixth chapter 13730) and the main results.

THE MAIN CONTENT OF THE WORK

The introduction formulates the actuality of the chosen topic, its aim, scientific innovation and practical value of the obtained results.

In the first chapter the character of CuInSe_2 formation, crystal and zone structure, semiconductive properties, the nature of physicochemical interaction of CuInSe_2 with various metallic selenides and semigroup elements of germanium with selenium and equilibrium diagrams, also reference information about obtaining monocrystals from low-temperature liquid melts have been given. These data are used for planning experimental investigations and processing their results.

Second chapter is dedicated to short statement about ways of synthesis of binary and ternary compounds, investigating melts and about common physicochemical methods of analysis. Initial compound

and alloys have been synthesized from high pure elements: indium In-000, monocrystalline germanium (impurities $10^{-8}\%$), tin OVC 0000, lead- C0000 and 17-3 Se. The surfaces of lead and copper are deoxidized before the usage.

The compounds have been synthesized under the vacuum condition ($\sim 0,1$ Pa) by the way of co-melting elements taken in stoichiometric amount. The melts were equilibrated thermally under the solidus temperature 30-50K for 100-200 hours after synthesis processes.

The investigations were carried out with common physicochemical ways of analysis: differential-thermal analysis (DTA), X-ray phase analysis (XRD), microstructure analysis (MSA) and measuring the microsolidity. The thermograms for DTA have been recorded in high-sensitive H1/307 bicoordinate potentiometer using chromel-almunel thermocouples. XRD - the diffractograms of powder compounds were obtained in X-ray diffractometer DRON 2.0 and Bruker D8 ADVANCE using $\text{CuK}\alpha$ monochromatic rays. The microstructure analysis of specially prepared solid melts and microsolidity of the phases has been carried out by PMT-3 device.

The dissertation work also describes methods for determining the temperature dependence of the electrical conductivity of homogeneous samples with additives of tin and lead and current-voltage characteristics.

11-13 samples were synthesized and subjected to infusion at intervals of 5-10 mole% for each test system. The temperature and continuation of the infusion were determined by taking into account the thermal effects on the thermograms of the samples for each system. The occurrence of equilibrium state in alloys as a result of infusion was monitored by microstructure analysis and measurement of some physical parameters (mainly the coefficient of thermoelectric driving force).

The methods of Differential Thermal Analysis (DTA), Microstructure Analysis (MSA), X-ray phase (XDA), as well as

measurement of thermoelectric driving force, electric conductivity and thermal conductivity have been used in investigations.

In the third chapter the results of phase equilibrium on polythermic cross-sections with respect to CuInSe₂-Ge-Se quasi-ternary system: the phase diagrams of CuInSe₂-GeSe, CuInSe₂-Ge, CuInGeSe₄-GeSe, CuInGeSe₄-Ge, CuInGeSe₄-Se, CuInSe₂-Se and [CuInSe₂-4Se-CuInSe₂-4Ge] and projection diagram of liquidus surface are given.

The obtained results can be annotated as following:

CuInSe₂-GeSe cross-section is nonquasibinary. There is no dissolution on the base of initial components. The metatectic point of polymorphic transition on the liquidus curve of CuInSe₂ was determined at 810⁰C and in 45mole%GeSe. The initial crystallization of α-CuInSe₂ with chalcopyrite structure from liquid melt occurs in interval of 45-78mole % GeSe (figure 1).

It can be noted that the presence of germanium phase doesn't prevent the initial crystallization of α-CuInSe₂ from liquid melt at temperatures below the 625⁰C isotherm. The 575⁰C isotherm indicates the crystallization of GeSe phase according to four-phase peritectic reaction.

CuInSe₂-Ge cross-section is quasibinary. The phase diagram is eutectic with monotectic nature. The monotectic process are realized in 87%Ge-alloy starting from the side of germanium, at 855⁰C and layering in the liquid phase is in the concentration range of 68-87mole% Ge (figure 2). The polymorphic transition temperature is almost stable and the composition of metatectic point corresponds to ~42 mole% Ge. The eutectic of the system is crystallized in 50mole % and at 790⁰C. The non-formation of intermediates has been demonstrated by XDA and MSA. The cross-section is quasi-stable cross-section of CuInSe₂-Ge-Se ternary system.

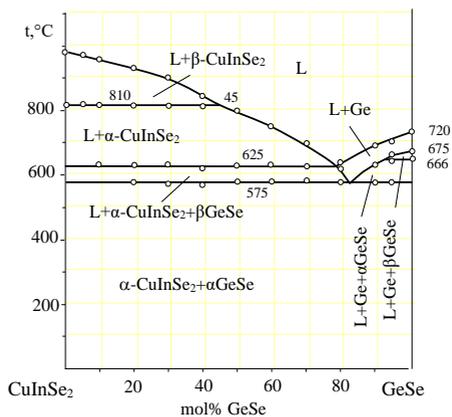


Figure 1. The state diagram of $\text{CuInSe}_2\text{-GeSe}$ system

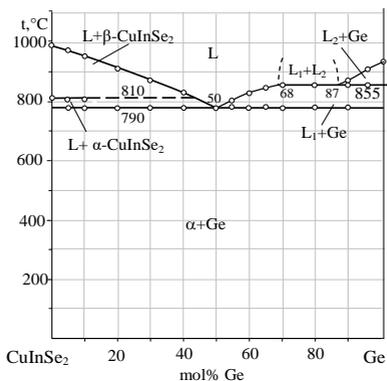


Figure 2. The state diagram of the $\text{CuInSe}_2\text{-Ge}$ system

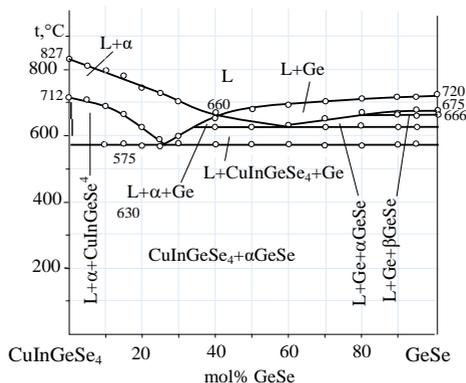


Figure 3. The state diagram of the $\text{CuInGeSe}_4\text{-GeSe}$ system

The $\text{CuInGeSe}_4\text{-GeSe}$ system is quasi-stable. The phase diagram is completed by crystallization together of initial components. The system liquid consists of the initial crystallization curves of the solid solution phase α and germanium based on CuInSe_2 , which intersect at 41 mol.% GeSe and $\sim 660^\circ\text{C}$ (Figure 3). The temperature generated by the peritectic reaction of the quaternary compound at 712°C continues to decrease to 575°C under the action of GeSe. Two CuInGeSe_4 and GeSe phases crystallize at 575°C in subsolidus as a result of four-phase peritectic reaction $\text{L} + \alpha \leftrightarrow \text{CuInGeSe}_4 + \text{GeSe}$.

$\text{CuInGeSe}_4\text{-Ge}$ system is nonquasibinary. The liquidus of the $\text{CuInGeSe}_4\text{-Ge}$ system consists of initial crystallization curves of germanium and α -solid solution based on chalcopyrite phase. These curves intersect in the composition of 50mole % Ge (40at.% Ge) and at 640°C , and α and Ge phases crystallize together in the presence of liquid phase

The $\text{CuInGeSe}_4\text{-Se}$ system is nonquasibinary. The liquidus of the system consists mainly of initial crystallization curve of CuInSe_2 chalcopyrite phase. The second polythermic curve continues from 712°C to 200°C and indicates the formation of CuInGeSe_4 according to the peritectic reaction in the presence of selenium.

The CuInGeSe₂-Se system is quasibinary. The phase diagram is eutectic with monotectic nature. The eutectic crystallizes at 210⁰C very close to composition of pure selenium and most probably degenerated in terms of the composition (figure 4).

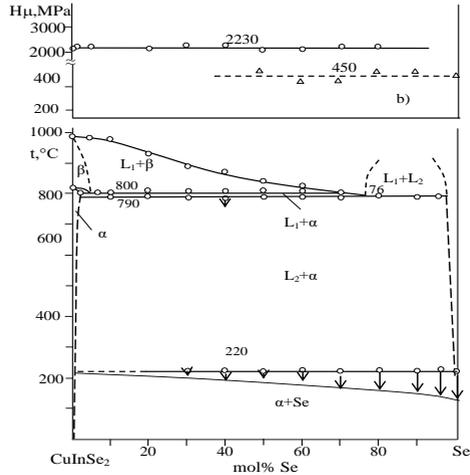


Figure 4. The phase diagram of the CuInSe₂-Se system (a) and the composition dependence of microsolidity (b)

The liquidus of the system consists of initial crystallization curve of β -solid solution formed on base of β -CuInSe₂. Sphalerite \leftrightarrow chalcopyrite phase transition is observed by 800⁰C isothermal line in the samples.

The projection diagram of the liquidus surface of the CuInSe₂-Ge-Se quasi-ternary system. The reference information about binary systems has been arranged on the base of experimental results of above-mentioned cross-sections (figure 5).

Due to the formation of only one compound (GeSe₂) from one dystectic reaction in a quasi-ternary system, it triangulates into triangle with two dependents. There are 5 ternary invariant equilibrium

processes in the system, two of them are eutectic (E_1 , E_2), three of them are peritectic (P_1 - P_3) processes (table 1).

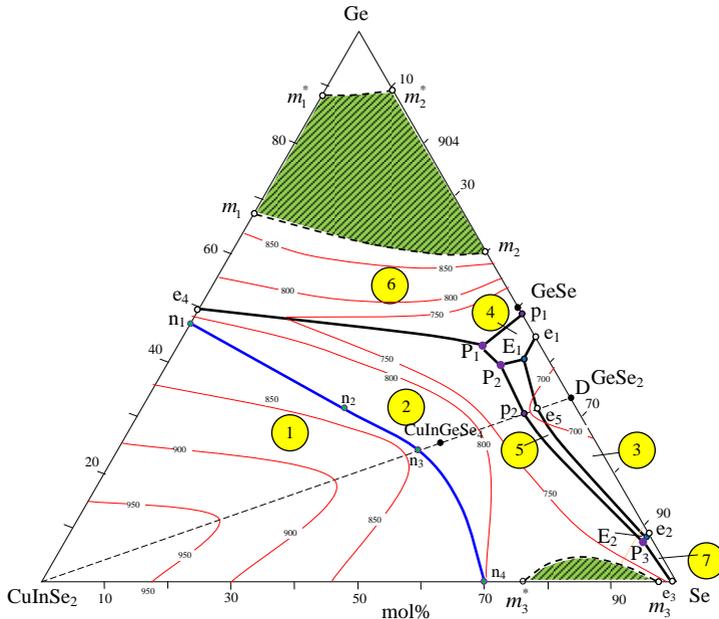


Figure 5. The projection of liquidus surface of the CuInSe_2 -Ge-Se quasi-ternary system. The initial crystallization areas: 1- β - CuInSe_2 , 2- α - CuInSe_2 , 3- GeSe_2 , 4- GeSe , 5- CuInGeSe_4 , 6-Ge, 7-Se

The CuInSe_2 -Ge-Se quasi-ternary system consists of 7 initial crystallization areas limited by monovariant curves. The biggest area belongs to CuInSe_2 (α and β polymorphic forms together). The second biggest initial crystallization area is suitable for the germanium phase. The common area of these two phases is $\sim 95\%$. The sum of the initial crystallization areas of rest GeSe_2 , GeSe , CuInGeSe_4 and Se phases is $\sim 5\%$ of initial crystallization of the quasi-ternary system.

The $n_1n_2n_3n_4$ invariant curve determined in the quasi-ternary system limits the initial crystallization areas of the β -CuInSe₂ and α -CuInSe₂ phases.

Table 1

The mono- and invariant equilibria in the CuInSe₂-Ge-Se system

№	Non and mono variant processes	Reactions	composition			Temperature t°C
			CuInSe ₂	Ge	Se	
1	e ₁	L ↔ GeSe + GeSe ₂	–	44	56	586
2	e ₂	L ↔ GeSe ₂ + Se	–	8	92	212
3	e ₃	L ↔ CuInSe ₂ + Se	0	–	100	220
4	e ₄	L ↔ CuInSe ₂ + Ge	50	50	–	675
5	e ₅	L ↔ CuInGeSe ₄ + GeSe ₂	65.38	11.54	23.08	790
6	p ₁	L + Ge ↔ GeSe	–	49	51	675
7	p ₂	L + α ↔ CuInGeSe ₄	17.57	27.48	54.95	712
8	D	L ↔ GeSe ₂	–	33.33	66.67	742
9	E ₁	L ↔ GeSe ₂ + GeSe + CuInGeSe ₄	3.5	40.5	56	560
10	E ₂	L ↔ GeSe ₂ + CuInGeSe ₄ + Se	0.3	8.2	91.5	210
11	P ₁	L + Ge ↔ GeSe + α	9	43	48	650
12	P ₂	L + α ↔ CuInGeSe ₄ + GeSe	8.5	39.5	52	575
13	P ₃	L + α ↔ CuInGeSe ₄ + Se	1	7.5	91.5	215
14	e ₁ E ₁	L ↔ GeSe ₂ + GeSe				586-560
15	E ₁ e ₃ E ₂	L ↔ CuInGeSe ₄ + GeSe ₂				560-790-210
16	e ₂ E ₂	L ↔ GeSe ₂ + Se				212-210
17	e ₃ P ₃	L ↔ α + Se				220-215
18	P ₂ E ₁	L + GeSe ₂ ↔ CuInGeSe ₄ + GeSe				675-500
19	P ₃ E ₂	L ↔ CuInGeSe ₄ + Se				215-210
20	P ₂ p ₂ P ₃	L + α ↔ CuInGeSe ₄				575-712-215

21	p_1P_1	$L+Ge \leftrightarrow GeSe$				675-650
22	P_1P_2	$L \leftrightarrow \alpha + GeSe$				630-575
23	e_4P_1	$L \leftrightarrow \alpha + Ge$				675-650
24	$n_1 \div n_4$	$L + \beta \leftrightarrow \alpha$				810-840-800

There are 13 invariant equilibrium points, 10 monovariant curves on the projection diagram of the quasi-ternary system.

The investigating quasi-ternary system consists of two dependent ternary systems: $CuInSe_2 - GeSe_2 - Se$ and $CuInSe_2 - GeSe_2 - Ge$.

There are 6 invariant equilibrium processes in the first dependent ternary system and two of them are four-phase peritectic and eutectic processes:



The first reaction expresses the ternary peritectic process occurred in P_3 composition and at about $215^\circ C$. The second equation indicates the equilibrium process occurred on the point of ternary eutectic.

The initial crystallization areas of α and also β polymorphic forms of $CuInSe_2$ in this system are limited by the n_3n_4 line (figure 5). The initial crystallization area of high-temperature sphalerite phase is approximately 66% larger than initial crystallization area of chalcopyrite phase.

The layering formed in the concentration range 76-97mole % Se of the system expands toward inside of dependent ternary system and is about 1.2%. Namely, some of the initial crystallization of α - $CuInSe_2$ occurs beneath the layering.

There are 8 invariant processes in the second dependent ternary system. Two of them are four-phase peritectic, one is four-phase eutectic process:



$L + \alpha \leftrightarrow \text{CuInGeSe}_4 + \text{GeSe}$ in the composition of P_2

$L \leftrightarrow \text{GeSe}_2 + \text{GeSe} + \text{CuInGeSe}_4$ in the eutectic point E_1

α indicates the solid solution phase based on chalcopyrite phase ($\alpha\text{-CuInSe}_2$). The crystallization process finishes with co-crystallization of GeSe_2 , GeSe and CuInGeSe_4 phases in E_1 ternary eutectic at 560°C .

The projection diagram of liquidus surface of quasi-ternary system has been plotted for the first time. Here, non- and monovariant equilibrium curves were plotted and the border of $\alpha \leftrightarrow \beta$ transition was determined. It can be said that the initial crystallization area of the chalcopyrite phase expands in the direction of $\alpha \leftrightarrow \beta$ transition border $\text{Ge} \rightarrow \text{GeSe} \rightarrow \text{GeSe}_2 \rightarrow \text{Se}$ in CuInSe_2 -solvent systems. The largest concentration interval (up to 30% mole Se) belongs to the CuInSe_2 -Se system. However, the layering by Se, partial crystallization of α -phase under the layering causes technological difficulties in formation of perfect $\alpha\text{-CuInSe}_2$. And this shows that the use of germanium selenide or germanium diselenide compounds and their alloys as an auxiliary product is suitable for initial crystallization of $\alpha\text{-CuInSe}_2$ monocrystals from alloy.

In the fourth chapter the phase diagrams and projection diagram of liquidus surface has been given as the result of phase equilibrium in the CuInSe_2 - Sn -Se quasi-ternary system investigated on the $\text{CuInSe}_2\text{-SnSe}_2$; $\text{CuInSe}_2\text{-SnSe}$; $\text{CuInSe}_2\text{-Sn}$; $|\text{CuInSe}_2 \cdot 4\text{Se}| - |\text{CuInSe}_2 \cdot 4\text{Sn}|$ cross-sections.

$\text{CuInSe}_2\text{-SnSe}_2$ system is eutectic with polymorphic transition (figure 6). Liquidus of the system consists of three parts: β -solid solution, α -solid solution, the initial crystallization curve of SnSe_2 . The initial crystallization of α -solid solution from liquid alloy formed on base of $\alpha\text{-CuInSe}_2$ is in 57-87mole % SnSe_2 concentration interval. The eutectic of the system crystallizes in 87mole % SnSe_2 composition and at 610°C (figure 6).

The sphalerite \leftrightarrow chalcopyrite transition of CuInSe_2 in $\text{CuInSe}_2\text{-SnSe}$ system is eutectoid and isothermic appears at 800°C . The metatectic point here, was determined in composition of ~ 52 mole% SnSe. The second isothermic line passes from 730°C and is related to monotectic process. The layering in the liquid phase has been determined in the concentration interval of 63-81 mole% SnSe.

The third isothermic process is related to crystallization eutectic. Eutectic crystallizes in 82 mole% SnSe composition and at 715°C (figure 7.I).

$\text{CuInSe}_2\text{-Sn}$ system is quasibinary, 4 isothermic processes are observed in the phase diagram. It is classified as a eutectic phase diagram with monotectic and lateral limited solution.

The first isothermic process occurs at 810°C and is related to polymorphic transition proper to CuInSe_2 . As can be seen, elemental tin has virtually no effect on the polymorphic transition of CuInSe_2 . It can be concluded that there is no solution based on $\beta\text{-CuInSe}_2$. However, a solution based on $\alpha\text{-CuInSe}_2$ was found. The microstructural analysis of a sample with 1 mol% Sn shows this. On the other hand, the diffraction lines observed in the samples slide at a greater angle than the corresponding diffraction lines of $\alpha\text{-CuInSe}_2$. This can be seen in the diffractograms of several examples.

The second isothermic process is related to monotectic process at 650°C . Here, the non-mixing of the two liquid phases was recorded in the concentration range of 55-95 mol% Sn. Interestingly, the binodal curve of stratification in this region was recorded using DTA.

The third isothermic process is related to the formation of compound that rational composition is CuInSnSe_2 . CuInSnSe_2 is not determined at room temperature in samples cooled at normal rates. It decomposes again at $\sim 300^\circ\text{C}$.

The eutectic of the system invariably crystallizes at 200°C and 95 mole% Sn. (figure 7.II). The eutectic composition is easily determined

by the Tamman triangle, because the thermal effects observed at 200°C are large and vary sharply depending on the composition.

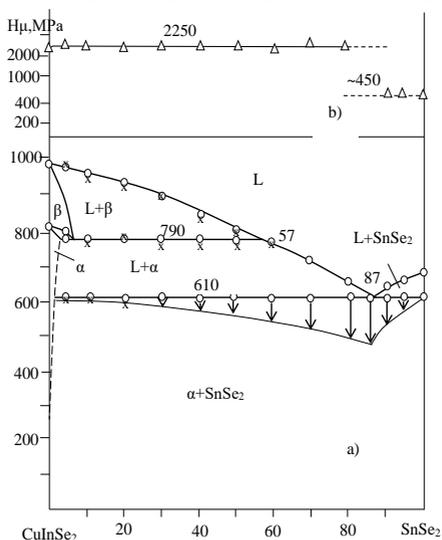


Figure 6. The phase diagram of CuInSe_2 - SnSe_2 system (a) and the composition dependence of the microsolidity (b)

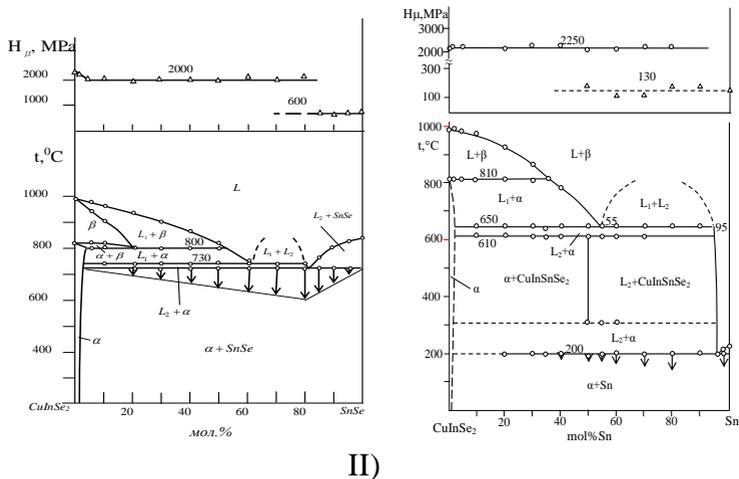


Figure 7. The phase diagrams of the CuInSe_2 - SnSe (I) and CuInSe_2 - Sn (II) systems (a) and the composition dependence of the microsolidity (b)

The projection diagram of the liquidus surface of $\text{CuInSe}_2\text{-Sn-Se}$ quasi-ternary system was plotted (figure 8).

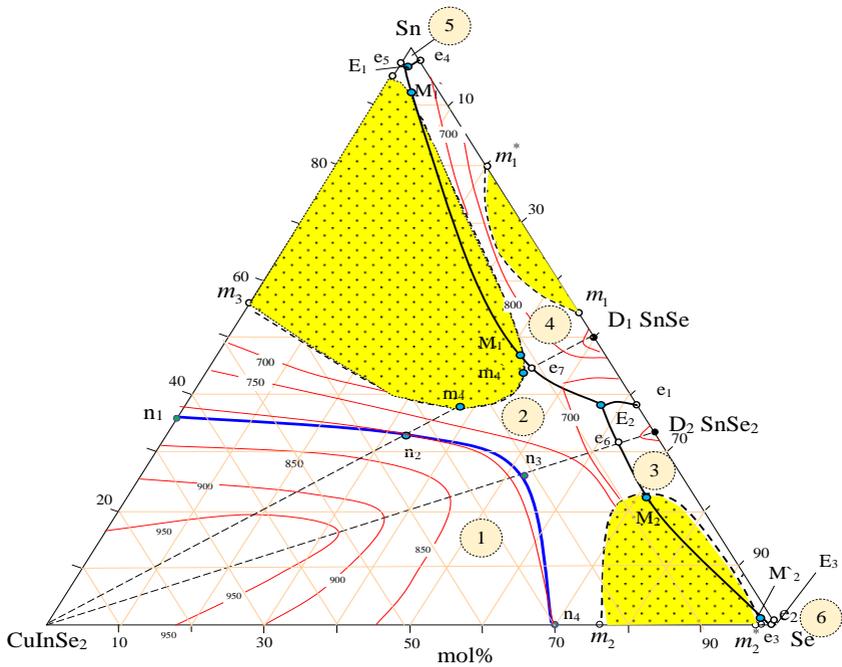


Figure 8. The projection of liquidus surface of the $\text{CuInSe}_2\text{-Sn-Se}$ quasi-ternary system. Initial crystallization areas: 1- $\beta\text{-CuInSe}_2$, 2- $\alpha\text{-CuInSe}_2$, 3- SnSe_2 , 4- SnSe , 5-Sn, 6-Se

There are 6 initial crystallization areas in the projection diagram of liquidus surface. The initial crystallization areas of tin and selenium practically degenerated.

The initial crystallization areas of $\alpha\text{-CuInSe}_2$, as well as of $\beta\text{-CuInSe}_2$ are separated along the $n_1n_2n_3n_4$ line. The temperature of this line falls down gradually from 810°C to 790°C in direction of $n_4 \rightarrow n_1$.

5 invariant equilibrium processes, 6 monovariant curves appeared in the projection diagram of the quasi-ternary system. The invariant equilibria existing in the $\text{CuInSe}_2\text{-Sn-Se}$ system are shown in the table 2.

Table 2

The invariant equilibria in the CuInSe₂-Sn-Se system

№	Invariant points	Reactions	composition, mole%			t°C
			CuInSe ₂	Sn	Se	
1	e ₁	L↔SnSe+SnSe ₂	-	38	62	625
2	e ₂	L↔SnSe+Se	-	-	~100	220
3	e ₃	L↔CuInSe ₂ +Se	1	-	99	210
4	e ₄	L↔SnSe+Sn	-	100	-	232
5	e ₅	L↔CuInSe ₂ +Sn	2	98	-	220
6	e ₆	L↔α-CuInSe ₂ +SnSe ₂	6	32	62	615
7	e ₇	L↔α-CuInSe ₂ +SnSe	11	45	44	715
8	D ₁	L↔SnSe	-	50	50	880
9	D ₂	L↔SnSe ₂	-	33,3	66,7	675
10	E ₁	L↔α-CuInSe ₂ +SnSe ₂ +Se	1	-	99	210
11	E ₂	L↔α-CuInSe ₂ +SnSe ₂ +SnSe	5	38	57	570
12	E ₃	L↔α-CuInSe ₂ +SnSe+Sn	-	~100	-	220
13	m ₁ (m ₁ [*])	L ₆ ↔L ₅ +SnSe	-	53(70)	47(30)	882
14	m ₂ (m ₂ [*])	L ₄ ↔L ₃ +α-CuInSe ₂	24(2)	-	76(98)	790
15	m ₃ (m ₃ [*])	L ₂ ↔L ₁ +α-CuInSe ₂	45(5)	55(95)	-	650
16	m ₄ (m ₄ [*])	L ₂ ↔L ₁ +α-CuInSe ₂	23(12)	38(46)	39(42)	730
17	M ₁ (M ₁ [*])	L ₂ +SnSe↔L ₁ +α-CuInSe ₂	8(1)	22(98)	70(1)	650
18	M ₂ (M ₂ [*])	L ₄ +SnSe ₂ ↔L ₃ +α-CuInSe ₂	11(4)	47(92)	42(4)	550
19	n ₁	L+β-CuInSe ₂ ↔α-CuInSe ₂	64	36	-	810
20	n ₂	L+β-CuInSe ₂ ↔α-CuInSe ₂	35	33	32	800
21	n ₃	L+β-CuInSe ₂ ↔α-CuInSe ₂	21	27	52	790
22	n ₄	L+β-CuInSe ₂ ↔α-CuInSe ₂	30	-	70	800

As mentioned, the quasi-triangular system CuInSe₂-SnSe and CuInSe₂-SnSe₂ are divided into three sub-triangles by means of diagonal sections: CuInSe₂-Se-SnSe₂, CuInSe₂-SnSe₂-SnSe, CuInSe₂-Sn.

I. The CuInSe₂-Se-SnSe₂ system is characterized by a twisted triple eutectic, a triple monotectic process, and a triple polymorphic

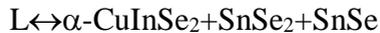
transition point. The main part of this triangle is occupied by the initial crystallization of β -CuInSe₂. Part of β -CuInSe₂ occurs under stratification and this process lasts up to 96 mol% Se. Here, the initial crystallization of α -CuInSe₂ takes up little space, and the tendency of the liquidity curve to change sharply with temperature due to stratification. The following process takes place at the point of triple eutectic:



The monovariant curve from e_6 to E_1 intersects the stratification region, and the following equilibrium occurs at the nonvariant points $M_2(M_2')$:



II. The CuInSe₂-SnSe₂-SnSe system is distinguished by the presence of a triple eutectic. At point E_2 , the following process takes place:



Stratification occupies a very small part of this subordinate triple system. Here, the sphalerite-chalcopyrite transition characteristic of CuInSe₂ is bounded by the line n_2n_3 .

III. The CuInSe₂-SnSe-Sn system occupies a large area of the primary crystallization area of α -CuInSe₂. Triple eutectic E_3 coincides with e_5 , which is the eutectic of the CuInSe₂-Sn quasibinary section. In this triple system, no initial crystallization area was formed for the CuInSnSe₂ compound. This may be due to the large number of m_3M_1/e_5 due to the peritectic reaction of CuInSnSe₂. In this system, the sphalerite \leftrightarrow chalcopyrite transition is arranged along the n_3n_4 line.

Thus, projection diagram of the liquidus surface of CuInSe₂-Sn-Se quasi-ternary system has been plotted for the first time. Here, the border of $\alpha \leftrightarrow \beta$ transition for in- and monovariant equilibrium curves were confirmed. According to the diagram of the projection surface, it is possible to say that the initial crystallization interval of chalcopyrite phase expands by changing the solvents in direction of $\alpha \leftrightarrow \beta$ transition

border $\text{Se} \rightarrow \text{SnSe}_2 \rightarrow \text{SnSe} \rightarrow \text{Sn}$. And this allows offering tin or tin and SnSe alloys as auxiliary substances in crystallization of $\alpha\text{-CuInSe}_2$ monocystals from melts.

In the fifth chapter, the characteristic of physicochemical interaction occurring in the $\text{CuInSe}_2\text{-Pb-Se}$ system with respect to $\text{CuInSe}_2\text{-PbSe}$, $\text{CuInSe}_2\text{-Pb}$, $\text{CuInSe}_2\cdot 4\text{Se-CuInSe}_2\cdot 4\text{Pb}$, $\text{CuInSe}_2\cdot \text{Se-PbSe}$, $\text{CuInPbSe}_2\text{-PbSe}$ cross-sections are presented as state diagrams. At the same time, the projection diagram of the liquidus surface is given as a result of generalization of these investigations.

$\text{CuInSe}_2\text{-PbSe}$ system is eutectic with polymorphic transition in one side and limited dissolution. The polymorphic transition in melts occurs at 800°C . Eutectic crystallizes at 735°C and in 72mole% PbSe composition.

The second isothermal line observed in the $\text{CuInSe}_2\text{-Pb}$ system exceeds 675°C and shows a monotectic equilibrium process. Here, the non-mixing of the two liquid phases was recorded in the concentration range of 49-98 mole% Pb. The isothermal crystallization process related to the eutectic of the system passes through 315°C . The eutectic of the system is practically wrapped around the lead. However, due to the low eutectic temperature of pure lead relative to the melting point, the content of the eutectic nonvariant point in the case diagram is shown as 99 mole% Pb. Note that the thermal effects observed at 315°C are large. The Tamman triangle, based on them, also shows that eutectic is crystallized around lead.

Finally, the isothermal phase transitions observed at 650°C indicate the formation of a new compound by the peritectic reaction. Although the thermal effects observed here are weak, they correspond to a composition with the most intense 50mole% Pb. The rational chemical formula of the compound corresponding to this composition is CuInPbSe_2 . In gradually cooled samples, it is not possible to determine this compound with the help of either MSA or XRD. This is because the compound only exists in a certain temperature range. The isothermal process observed at 325°C in the case diagram probably indicates the low resistance temperature of this compound. Thus, the chemical

compound with the formula CuInPbSe_2 , first discovered by us, is stable in the range of $325\text{--}650^\circ\text{C}$. Another isothermal process was recorded in this interval. This process, observed at 575°C , may be related to the polymorphic transition of the new compound, given the rules of physicochemical analysis of phase diagrams (Figure 9a).

The liquidity of the system consists of almost a curve. This is the initial crystallization curve of the CuInSe_2 compound. Crystallization of CuInSe_2 up to 49 mole% Pb occurs from L_1 liquid, and in subsequent concentrations from L_2 liquid. The sphalerite modification of CuInSe_2 crystallizes to ~ 35 mole% Pb, followed by chalcopyrite modification to eutectic. Part of the initial crystallization of $\alpha\text{-CuInSe}_2$ occurs under stratification in the 49–99 mole% Pb concentration range.

$\text{CuInSe}_2\cdot 4\text{Se}\text{-CuInSe}_2\cdot 4\text{Pb}$ system is non-quasibinary. Its liquidus consists of only initial crystallization of CuInSe_2 compound. $\beta\text{-CuInSe}_2$ crystallizes from the side of $\text{CuInSe}_2\cdot 4\text{Se}$, $\alpha\text{-CuInSe}_2$ crystallizes from the side of $\text{CuInSe}_2\cdot 4\text{Pb}$.

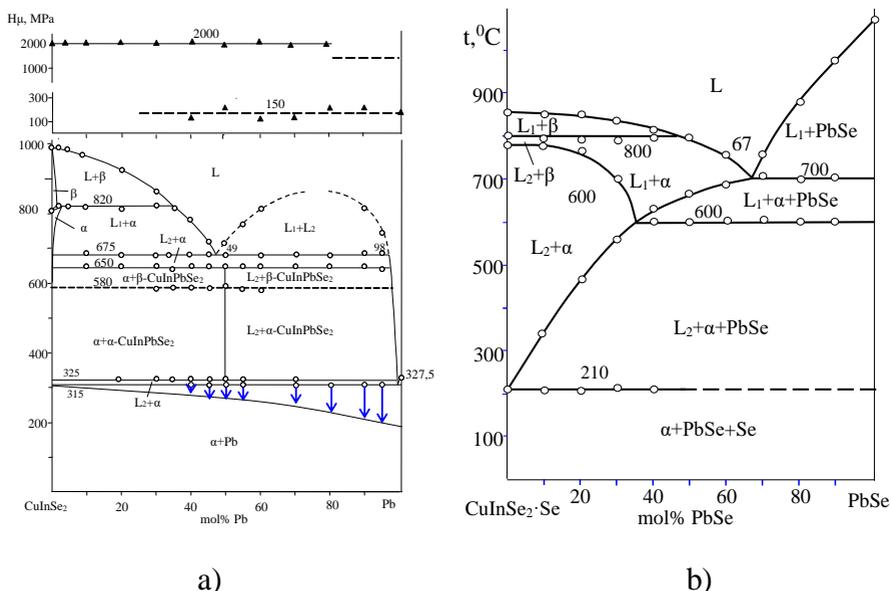


Figure 9. The phase diagrams of the $\text{CuInSe}_2\text{-Pb}$ (a) and $\text{CuInSe}_2\cdot\text{Se}\text{-PbSe}$ (b) systems

CuInSe₂-Se-PbSe system is non-quasibinary. Its liquidus consists of curves of initial crystallization of CuInSe₂ and PbSe. These curves intersect in composition of 67mole% PbSe. The second crystallization of CuInSe₂ in the concentration range 67-100mole% PbSe occurs isothermally at 700⁰C. The second isothermal process in the system observed at 600⁰C is related to the monotectic process recorded in the CuInSe₂-Se system. This process begins with secondary monotectic process observed in the CuInSe₂-Se system at 800⁰C and the temperature decreases gradually up to 600⁰C with an increase in the amount of PbSe in the system (figure 9b).

The projection diagram of the liquidus surface of CuInSe₂-Pb-Se system has been plotted according to the information extracted from the Pb-Se, CuInSe₂-PbSe, CuInSe₂-Pb, CuInSe₂-Se, CuInSe₂-4Se - CuInSe₂-4Pb, |CuInSe₂-Se|-PbSe and |CuInPbSe₂|-PbSe systems (figure 10).

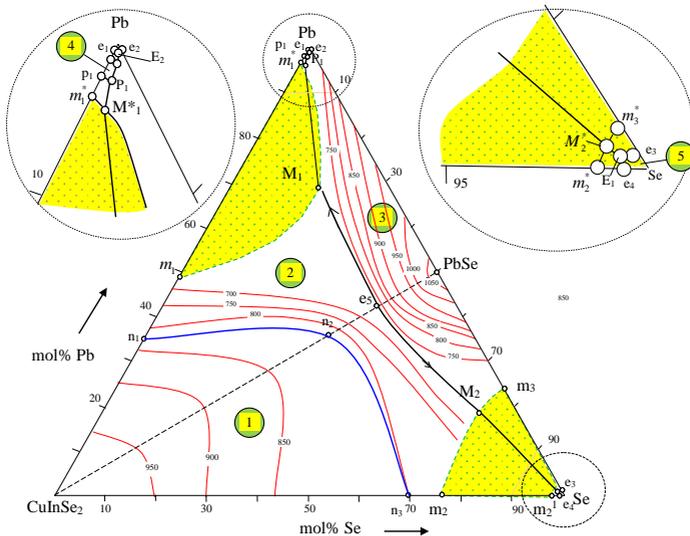


Figure 10. The projection of the liquidus surface of CuInSe₂-Pb-Se system. The initial crystallization areas: 1- α -CuInSe₂; 2- β - CuInSe₂; 3- PbSe; 4-CuInPbSe₂

The first three of these are quasi-binary, and the others are non-quasi-binary. CuInSe₂-PbSe-quasi-binary system CuInSe₂-Pb-Se quasi-triangular system divides into two subordinate triangles: CuInSe₂-PbSe-Se and CuInSe₂-PbSe-Pb triangles. These sub-triangles are equal in terms of the areas of concentration they occupy, but the physicochemical processes that take place in them are different. For example, in both subordinate triple systems, stratification areas were found in the liquid phase, and the monovariant curve representing the binary crystallization (α -CuInSe₂ + PbSe) intersects these stratification areas. Intersections are nonvariant and represent 4-phase monotectic processes. The compositions and equilibrium temperatures of these nonvariant points were determined using the non-quasibinary sections mentioned above.

Although the crystallization in both systems was eutectic, the complete triple system had to have two triple non-variant eutectic equations. However, in the Pb-Se, CuInSe₂-Se, and CuInSe₂-Pb systems, the binary eutectics are practically twisted, so the two triple eutectics are also twisted.

Table 3.

The invariant equilibriums in the CuInSe₂-Pb-Se system

№	Invariant points	Reactions	composition, mol.%			t, °C
			CuInSe ₂	Pb	Se	
1	e ₁	L ↔ CuInSe ₂ + Pb	1	99	-	315
2	e ₂	L ↔ PbSe + Pb	-	100	-	327
3	e ₃	L ↔ PbSe + Se	-	-	100	220
4	e ₄	L ↔ CuInSe ₂ + Se	-	-	~99	210
5	e ₅	L ↔ CuInSe ₂ + PbSe	16,28	41,86	41,86	735
6	p ₁	L ₂ + α ↔ αCuInPbSe ₂	2	98	-	650
7	D ₁	L ↔ PbSe	-	50	50	1080,7
8	E ₁	L ↔ α-CuInSe ₂ + PbSe + Se	-	-	~100	220
9	E ₂	L ↔ α-CuInSe ₂ + PbSe + Pb	-	~100	-	315
10	P ₁	L ₂ + α ↔ αCuInPbSe ₂ + PbSe	1	98	1	625
11	m ₁ (m ₁ *)	L ₁ ↔ L ₂ + α-CuInSe ₂	51	49	98	675
12	m ₂ (m ₂ *)	L ₂ ↔ L ₃ + α-CuInSe ₂	29(~0)	-	71(~100)	800

13	$m_3(m_3^*)$	$L_2 \leftrightarrow L_4 + \text{PbSe}$	-	26(~0)	74(~100)	678,3
14	$M_1(M_1^*)$	$L_2 + \text{CuInSe}_2 \leftrightarrow L_1 + \alpha\text{-PbSe}$	13(2)	69(97)	18(1)	650
15	$M_2(M_2^*)$	$L_2 + \text{CuInSe}_2 \leftrightarrow L_3 + \text{PbSe}$	8(1)	19(1)	73(98)	600
16	n_1	$L + \beta\text{-CuInSe}_2 \leftrightarrow \alpha\text{-CuInSe}_2$	65	35	0	820
17	n_2	$L + \beta\text{-CuInSe}_2 \leftrightarrow \alpha\text{-CuInSe}_2$	29	35	36	800
18	n_3	$L + \beta\text{-CuInSe}_2 \leftrightarrow \alpha\text{-CuInSe}_2$	12	16	72	800

5 binary eutectics (e_1, e_2, e_3, e_4, e_5), 2 ternary eutectics (E_1, E_2), one binary peritectic (p_1), one ternary peritectic (P_1), one dystectic and some monotectic equilibrium points have been observed in the system (tab.3). The ternary eutectics have been degenerated around selenium and lead.

Here, the initial crystallization areas $n_1 n_2 n_3$ of $\alpha\text{-CuInSe}_2$, as well as $\beta\text{-CuInSe}_2$ have been determined.

VI chapter devoted to investigation of an influence of IVA group elements on electrophysical properties of $\alpha\text{-CuInSe}_2$. It is known that CuInSe_2 has defect structure. These defects are not located in the place common to the crystalline knots in excess of vacancy ($V_{\text{Cu}}, V_{\text{In}}, V_{\text{Se}}$) and stoichiometry of copper and indium atoms in chalcopyrite lattice knots, but can be located in the place of another. These defects are electrochemically active and solvent plays important role in the formation of electrophysical properties of the compound. In the other hand, the results of some studies show that some impurity additives practically do not affect the electrophysical properties of CuInSe_2 compound.

The results of interaction of CuInSe_2 compound with germanium semigroup elements and their selenide substances taken as auxiliary solvent compound (flux) are discussed in dissertation work. One part of this interaction is simple eutectic. Only in $\text{CuInSe}_2\text{-SnSe}$ and $\text{CuInSe}_2\text{-PbSe}$ systems, at room temperature on the bases of chalcopyrite phase, 2 mole% solid solution areas appeared.

It is known that the second requirement when choosing solvents in the growing monocrystals at low temperature or obtaining a phase with a more perfect structure is that they should not affect to functional properties of the main compound. To study this requirement, the temperature dependence of the electrical conductivity of the samples taken from the regions of the solid solution based on α -CuInSe₂ from CuInSe₂-SnSe and CuInSe₂-PbSe systems was plotted in the temperature range of 300-800K. (fig. 11, fig. 12).

As is seen, the transition temperature to the area of the special conductivity is practically stable. The activation energy of the additives and the band gap width change insignificantly.

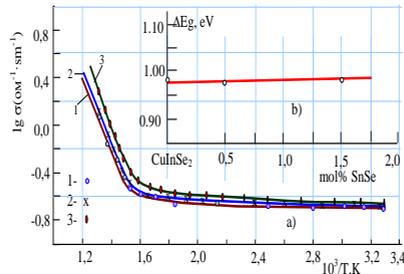


Figure 11. The temperature (a) dependence of the special electroconductivity of the alloys with $\text{CuInSe}_2)_{1-x}(\text{SnSe})_x$ composition and composition (b) dependence of band gaps. Composition: 1-CuInSe₂; 2- $x = 0,005$; 3- $x = 0,015$ (a)

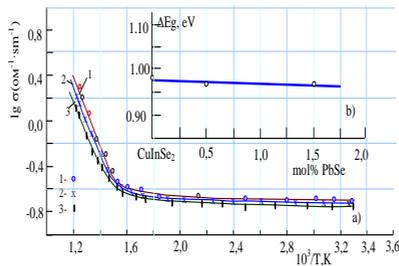


Figure 12. The temperature dependence of the special electroconductivity of $\text{CuInSe}_2)_{1-x}(\text{PbSe})_x$ solid solution (a); and composition dependence of band gaps of $\text{CuInSe}_2)_{1-x}(\text{PbSe})_x$ solid solution (b)

Width of prohibited zones calculated by curves from picture in solid solution area decrease merely from 0.97eV to 0.96eV. The value of the electroconductivity remains practically unchanged.

To measure the current-voltage characteristics, pure CuInSe_2 , as well as CuInSe_2 -based solid solution were synthesized and processed thermally under same condition. The electrical resistivity of the samples is 4-50m \cdot sm at room temperature and they have electron transition. The cylindrical panels with ~3 mm thickness have been prepared for measurement. The magnitude of the current obtained by increasing the voltage drop in direction of thickness was measured. The obtained results were arranged graphically (fig 13, fig 14)

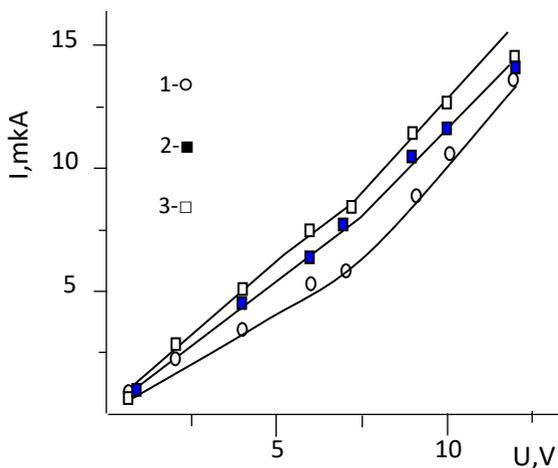


Figure 13. The current-voltage characteristics of alloys with $(\text{CuInSe}_2)_{1-x}(\text{SnSe})_x$ composition: composition, mole%SnSe; 1- CuInSe_2 ; 2- $x=0.01$; 3- $x=0.015$

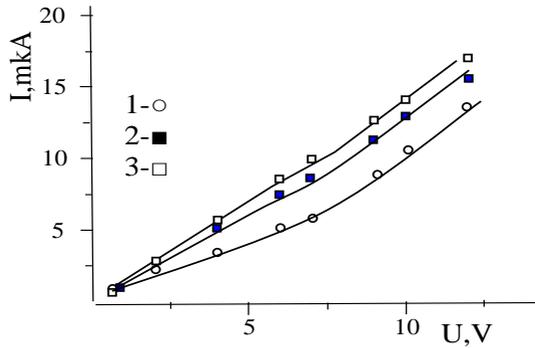


Figure 14. The current-voltage characteristics of alloys with $(\text{CuInSe}_2)_{1-x}(\text{PbSe})_x$ composition. Composition, mole% PbSe: 1- CuInSe_2 ; 2- $x=0.01$; 3- $x=0.015$

The current-voltage characteristics of $(\text{CuInSe}_2)_{1-x}(\text{SnSe})_x$ alloys changes nonlinearly up to 10-12V in the order of the measurement error, then the current rise changes linearly depending on voltage. In the solid solution area (2 and 3 samples), the coefficient of nonlinearity in current-voltage characteristics (up to 10-12V) decreases with an increase in the dissolved amount of SnSe and PbSe.

From the experimentally plotted graphics, it can be concluded that SnSe and PbSe don't seriously effect on electroconductivity of the chalcopyrite phase, although they form a solid solution with CuInSe_2 and therefore, they can play the role of a flux solvent for crystallization of $\alpha\text{-CuInSe}_2$ directly from the liquid melt.

MAIN CONCLUSIONS

1. The nature of physicochemical interaction in $\text{CuInSe}_2\text{-Me-Se}$ (Me-Ge,Sn,Pb) quasi-ternary systems have been determined by DTA, XRD methods, microstructure analysis and measurement of microsolidity; and T-x diagram of 16 cross-sections,

projection diagram of the liquidus surfaces in the quasi-ternary systems have been plotted.

2. The liquidus surface of $\text{CuInSe}_2\text{-Me-Se}$ (Me-Ge, Sn, Pb) quasi-ternary system consists of initial crystallization area of component ($\sim\alpha\text{-CuInSe}_2$, $\beta\text{-CuInSe}_2$, Me, MeSe, MeSe_2 , CuIn_3Se_5 , CuIn_5Se_8 and Se) which exists in binary systems. (In all states, the initial crystallization of selenium degenerates). The monovariant equilibrium curve and invariant equilibrium point, which the initial crystallization areas form with each other, were recorded. The coordinates of the mono- and invariant processes were determined.
3. The maximum dissolving area 2mole % SnSe (PbSe) was found out at room temperature in studying systems on based of CuInSe_2 . There is no dissolution in $\text{CuInSe}_2\text{-GeSe}$ systems.
4. Quaternary compounds of rational composition CuSn(Pb)InSe_2 also appear in $\text{CuInSe}_2\text{-Sn(Pb)-Se}$ systems: CuSnInSe_2 compound is formed as a result of peritectic reaction and exists in a certain temperature range.
5. According to the temperature dependence of special electroconductivity of $(\text{CuInSe}_2)_{1-x}(\text{MeSe})_x$ solid solution, it was found that the special electrical conductivity and band gap width of solid solution with chalcogenide-additives of germanium semigroup elements practically does not change.
6. The current-voltage characteristic of samples in solid solution areas is nonlinear.
7. Semigroup elements of selenium and germanium and their selenides can be used as auxiliary compounds for the growing $\alpha\text{-CuInSe}_2$ crystals directly from liquid phase in $\text{CuInSe}_2\text{-Me-Se}$ (Me-Ge,Sn,Pb) systems.

The main results of the dissertation work have been published in the following publications:

1. Аббасова Р.Ф., Мусаева Ш.З., Аллазова Н.М., Кулиева У.А., Бабанлы М.Б. Фазовые диаграммы систем $\text{CuInSe}_2\text{-SnSe}$ и $\text{CuInSe}_2\text{-SnSe}_2$ //VIII Республиканская научная конференция «Физико-химический анализ и неорганическое материаловедение». Сборник статей. Баку: 2002, с.22-27
2. Аллазова Н.М. Фазовая диаграмма системы $\text{CuInSe}_2\text{-PbSe}$. // Вестник Бакинского Университета, сер.ест.наук, 2006, №2, с.23-27
3. Allazov N.M. $\text{CuInSe}_2\text{-Sn-Se}$ sistemində $\alpha\text{-CuInSe}_2 \leftrightarrow \beta\text{-CuInSe}_2$ polimorf keçidinin sərhəddinin təyini. /Bakı Dövlət Universiteti "Gənc kimyaçı" II Respublika elmi konfransının materialları (17-18 may 2006-cı il) Bakı-2006, səh 118-119
4. Mirzəyeva R.C., Allazova N.M., Allazov M.R. CuInSe_2 birləşməsinin Mn, Fe, Co, Ni, Pb monoselenidləri ilə qarşılıqlı təsiri. /"Kimyəvi birləşmələrin sintezi və çevrilmələri" Gənc tədqiqatçı. III Respub.elmi konf.mat, Bakı 2007.17-28 may, s.128-129.
5. Allazova N.M., Allazov N.M., Allahverdiyev C.Ə., İlyaslı T.M. Ge və Si xalkogenidlərinin CuInSe_2 -nin fiziki-kimyəvi xassələrinə təsiri. "Kimyəvi birləşmələrin sintezi və çevrilmələri" / Gənc tədqiqatçı.III Respub.elmi konf.mat. Bakı, 2007, 17-28 may, s.130-131
6. Allazova N.M., İlyaslı T.M. Allazov N.M. $\text{CuInSe}_2\text{-GeSe}$ sisteminin tədqiqi//AzTU.Elmi əsərlər.Fundamental elmlər. 2007, №3, cild VI(23), s. 45-47
7. Allazova N.M., İlyaslı T.M. $\text{CuInSe}_2\text{-Pb}$ sisteminin faza tarazlığı. // Bakı Dövlət Universitetinin xəbərləri , təbiət elmləri seriyası, 2008, №4, c.37-41
8. Allazova N.M., İlyaslı T.M., Abbasova R.F. $\text{CuInPbSe}_2\text{-PbSe}$ sisteminin tədqiqi// Bakı Dövlət Universitetinin 90 illik yubileyinə həsr olunmuş beynəlxalq elmi konfransın materialları. Bakı- 2009, s.340-341
9. Аллазова Н.М., Аббасова Р.Ф., Ильяслы Т.М. Характер кристаллизации фаз в системах $\text{CuInSe}_2\text{-SiSe}$ и $\text{CuInSe}_2\text{-GeSe}$ / Тез. докл. IX Междунар. Курнаковская совещ. по физ.-хим. анализу. 5-9 июля, 2010, Пермь, с.126

10. Аллазова Н.М., Аббасова Р.Ф., Ильяслы Т.М. Влияние селенидов Si, Ge и Pb на кристаллизацию халькопиритной фазы CuInSe₂// XIX Менделеевский съезд по общей и прикладной химии. Волгоград, 25-30 сентября 2011г, т.3., с.19
11. Аллазова Н.М., Аббасова Р.Ф., Ильяслы Т.М. Область первичной кристаллизации в системе CuInSe₂ – Sn-Se. // Ж.Неорган.химии, 2011, Т.56, №10, с.1714-1719
12. Allazova N.M., Həsənlı Ş.M. İlyaslı T. M.CuInSe₂)_{1-x}(PbSe)_x (x≤0.02) bərk məhlullarının elektirik keçiriciliyi və volt amper xarakteristikası/Ümummillı lideri Heydər Əliyevin anadan olmasının 89-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların “Kimyanın aktual problemləri” VI Respublika Elmi Konfransının materialları, Bakı, 15-16 may 2012, s.147-148
13. Аллазов Н.М.,Аббасова Р.Ф.,Ильяслы Т.М.Тройная системы CuInSe₂–Pb–Se// VI Всероссийская конференция «Физико-химические процессы в конденсированных средах и на межфазных границах» FAQRAN 2012, Воронеж,15-19 октября 2012, с.286-287
14. Аллазова Н.М., Ильяслы Т.М.Область первичной кристаллизации халькопиритной фазы в системе CuInSe₂-Pb-Se//Azərbaycan.kimya jurnalı, 2015, № 1, s.60-66
15. Həsənlı Ş.M., Allazova N.M., İlyaslıT.M., Mirzəyeva R.C., Qurbanova T.R.CuInSe₂-nin elektrofiziki xassələrinin cərəyan tezliyindən asılılığı/VI International scientific conference of young researchers proceedings. Qafqaz University 2016, 29-30 April, Baku, Azerbaijan, s.209-210
16. Allazova N.M., İlyaslı T.M., Qurbanova T.R.CuInSe₂ birləşməsinin faza keçidinə germanium selenidlərinin təsiri//Bakı Universiteti xəbərləri №4, 2016, s.11-15
17. Allazova N.M., Mustafayeva K.Z., İlyaslı T.M. CuInGeSe₄-GeSe sistemində qarşılıqlı təsirin tədqiqi//Bakı Dövlət Universiteti, Ümummillı lider Heydər Əliyevin anadan olmasının 94-cü ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların «Kimyanın aktual problemləri» XI Respublika Elmi Konfransının materialları. Bakı-2017, s.171-172

18. İlyaslı T.M., Həsənli Ş.M., Allazova N.M., Hüseynova A.Q. Germanium və qurğuşun monoselenidləri ilə aşqarlarının CuInSe₂-nin xalkopirit fazasının elektrofiziki xassələrinə tezliyin təsiri /“Metallurgiya və materialşünaslığın problemləri” mövzusunda 2-ci Beynəlxalq Elmi-texniki konfransı (Bakı, 2017), səh108-109
19. Allazova N.M, İlyaslı T.M., Qurbanova T.R., Hüseynova A.Q., Həsənli Ş.M. (CuInSe₂)_{1-x}(SnSe)_x Bərk məhlullarının elektrik keçiriciliyi// Akademik M.Nağıyevin 110 illiyinə həsr olunmuş “Nağıyev Qiraətləri” elmi konfransının materialları, Bakı -2018, səh 256
20. Allazova N.M., İlyaslı T.M., Abbasova R.F., Allazov M.R. Effect of lead selenide on the CuInSe₂ phase change// Bakı Dövlət Universiteti, Ümummilli lider Heydər Əliyevin anadan olmasının 94-cü ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların «Kimyanın aktual problemləri» XII Respublika Elmi Konfransının materialları. Bakı- 2018, 03-04 may, s.17
21. Allazova N.M., İlyaslı T.M., Aliyev I.I., Allazov M.R. CuInSe₂·4Se- CuInSe₂·4Pb sistemində fiziki-kimyəvi qarşılıqlı təsirin xarakteri//BDU-nun Xəbərləri, №4.2018,səh 5-9, ISSN 1609-0586 www.bsu.edu.az
22. Allazova N.M. Phase equilibrium of CuInSe₂ with Silicon, Germany, Tin and Lead monoselenides//Chemistry Research Journal, 2019, 4(6), p:22-26, www.chemrj.org
23. Allazova N.M., Abbasova R.F., İlyaslı T.M., Aliyev I.I., Allazov M.R. Phase equilibria in the CuInSe₂-Ge-Se quasiternary system// Chemical Problems, 2020, 2(18), p.244-249, ISSN 2221-8688 <http://chemprob.org>
24. Аллазова Н.М., Электропроводимость халькопритной фазы CuInSe₂, кристаллизованных непосредственно из жидкого расплава //BDU-nun Xəbərləri, №2, 2021, səh 5-9, ISSN 1609-0586 www.bsu.edu.az



The defence will be held on October «14», 2021 at «13⁰⁰» the meeting of the Dissertation Council ED 1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev

Adress: H.Cavid, 113, AZ-1143, Baku, Azerbaijan

Dissertation is accessible at the Institute of Catalysis and Inorganic Chemistry named after M.Nagiyev of ANAS Library

Electronic versions of dissertation and its abstract are available on the official website of the Institute of Catalysis and Inorganic Chemistry named after M.Nagiyev of ANAS

Abstract was sent to the required addresses on «13» September 2021

Signed for print: 11.09.21

Paper format: 64x84^{1/16}

Volume: 36700

Number of hard copies: 25