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ABSTRACT

of the dissertation for the degree of Doctor of Science

**PHYSICO-CHEMICAL BASES OF OBTAINING COPPER
AND SILVER CHALCOGENIDES WITH p²-ELEMENTS
AND MULTICOMPONENT FUNCTIONAL PHASES
BASED ON THEM**

Specialty: 2303.01 – inorganic chemistry

Field of science: chemistry

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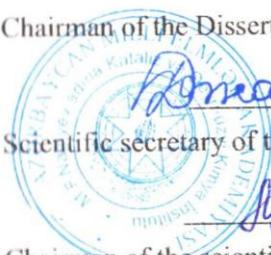
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GENERAL DESCRIPTION OF WORK

Relevance and degree of investigation of the topic. Modern scientific and technical progress is inconceivable without a continuous search, creation, and application of new functional materials with unique properties. Among such inorganic materials, an important place is occupied by metal chalcogenides, which have been in the field of view of researchers since the middle of the last century.

The development of nanomaterials science and the discovery of topological insulators at the beginning of our century gave a new powerful impetus to research in the field of chemistry and material science of chalcogenides. Recent studies have shown that binary compounds with a layered structure such as tetradimite and their ternary structural analogs are topological insulators - substances that, being an insulator or a classical semiconductor in bulk, exhibit high spin-polarized conductivity on the surface. Such an unusual surface state makes them extremely attractive for a variety of practical applications.

In the center of close attention of researchers are also complex chalcogenides based on copper and silver as environmentally safe functional materials that have thermoelectric, photoelectric, optical, and other properties and can be used in alternative energy devices and other areas of high technology. According to the literature data, many of these compounds have mixed ion-electron conductivity, which makes them very promising for use in the development of photoelectrode materials, electrochemical converters of solar energy, ion-selective sensors, photoelectrochemical visualizers, ionizers, etc.

Of particular note is the series of papers published in the last decade, which convincingly showed the effectiveness of the synthetic analogs of some natural chalcogenide minerals of copper and silver as environmentally friendly thermoelectric materials of the medium temperature range. Among the most intensively studied such materials, it is possible to note compounds of the argyrodite family with the

general formulas $A_3^I B^{IV} X_6$ and $Cu_2 B^{IV} X_3$ (A' -Cu, Ag; B^{IV} -Si, Ge, Sn; X-S, Se, Te) and phases based on them. According to the authors of several works, the presence of mixed electron-ion conductivity is one of the significant factors that positively affect their thermoelectric characteristics.

At the initial stage of development of new multicomponent materials, the use of the thermodynamic approach consists in studying phase equilibria in the corresponding systems and constructing phase diagrams that allow not only to establish the presence of novel compounds or phases of variable composition but also to establish their character of the formation, areas of primary crystallization and homogeneity, the presence of phase transformations, etc. The combination of these data underlies the development of methods for the synthesis, alloying, and growing of monocrystals with given composition, structure, and properties. An effective solution to the problems of optimizing the technological parameters of various processes requires a deeper thermodynamic analysis and the corresponding thermodynamic calculations. Carrying out these calculations with sufficient accuracy is possible only if reliable mutually agreed thermodynamic data complexes are available for the substances involved in the processes under consideration.

The above-mentioned determines the relevance of the formulation and conduct of systematic studies on the comprehensive study of phase equilibria and thermodynamic properties of the ternary and more complex chalcogenide systems based on copper and silver. Of particular interest are systems in which the formation of wide areas of solid solutions based on binary and ternary compounds with the corresponding functional properties can be expected, since varying the composition of solid solutions can purposefully change their properties.

To solve a specific problem - to obtain new complex phases of variable composition based on copper (silver) chalcogenides with germanium (tin), reliable data on the phase equilibria and thermodynamic properties of the corresponding quaternary systems are needed,

especially on their stable concentration planes $2A_2^I X + BX_2^I \leftrightarrow 2A_2 X' - BX_2$, $Cu_2 X - Ag_2 X - B^{IV} X_2$ and $A_2^I X - GeX_2 - SnX_2$. An analysis of the literature data shows that by the beginning of the present study (2010), phase equilibria in these systems were practically not studied. In addition, the available data on phase equilibria in some boundary quasibinary components of the indicated systems are contradictory and require clarification.

The purpose and objectives of the study. Taking into account the foregoing, the main goal of the thesis was to create the physico-chemical foundations of the production of new phases based on chalcogermanates and chalcostannates of copper and silver based on complexes of mutually agreed data on phase equilibria and thermodynamic properties of the corresponding systems.

To achieve this goal, the following **specific tasks** were set and solved:

- planning and organization of experiments on a comprehensive study of phase equilibria and thermodynamic properties of ternary and quaternary copper (silver) and germanium (tin) containing chalcogenide systems by combining traditional methods of physicochemical analysis (DTA, XRD, microstructural analysis) with the EMF method with Cu^+ (Ag^+) conductive solid electrolyte;

- implementation of such a comprehensive study of ternary (Ag-Ge-Se, Ag-Sn-Se, $Cu_2 S - GeS_2$, $Cu_2 Se - GeSe_2$, $Ag_2 S - GeS_2$), ternary mutual $2A_2^I X + B^{IV} X_2^I \leftrightarrow 2A_2 X' + B^{IV} X_2$ and quasi-ternary $Cu_2 X - Ag_2 X - GeX_2$ (A' -Cu, Ag; B^{IV} -Si, Ge, Sn; X-S, Se, Te) systems, obtaining the corresponding data complexes;

- obtaining individually and identification of obtained new phases, determining their areas of homogeneity, types, and parameters of the crystal lattice;

- calculation of the partial molar functions of copper (silver) in the studied systems from the EMF measurements, their using to clarify the boundaries of phase regions, to determine the thermodynamic functions of the formation and phase transformations of compounds and solid solutions of the studied systems;

- a comparative analysis and generalization of the obtained complexes of experimental data, determination of the laws of phase formation and phase properties.

Research Methods. The studies were carried out by the methods of DTA, XRD, SEM, microstructural analysis, as well as by measuring the microhardness and EMF of cells relative to the two types of electrodes.

DTA was carried on Linseis STA PT 1600, "Termoscan-2" instruments, as well as on a multichannel DTA unit assembled based on the electronic TC-08 Thermocouple Data Logger. The phase transformation temperatures were measured using combined chromel-alumel and platinum-platinum-rhodium thermocouples. Powder X-ray diffraction patterns of the alloys were recorded on Bruker D2 Phaser and D8 ADVANCE diffractometers using $\text{CuK}\alpha$ - radiation. SEM images were taken with Field Emission Scanning Electron Microscope JEOLJSM-7600F and Tescan Vega 3 scanning electron microscopes. Alloy microstructures were studied with a C-4EQMM 500T metallographic microscope in reflected light. Microhardness measurements were carried out on a PMT-3 microhardness measure.

Scientific novelty and defense propositions. The following **new results** are obtained in the work, which constitute the scientific basis for the directed synthesis of new multi-component phases based on chalcogermanates (stannates) of copper and silver, which are **submitted for protection**:

- complete schemes of the phase equilibria in quasi-ternary $\text{Cu}_2\text{X} - \text{Ag}_2\text{X} - \text{GeX}_2$ and reciprocal systems $2\text{A}_2^{\text{I}}\text{X} + \text{B}^{\text{IV}}\text{X}'_2 \leftrightarrow 2\text{A}_2^{\text{I}}\text{X}' + \text{B}^{\text{IV}}\text{X}_2$, $6\text{Ag}_2\text{S} + \text{Ag}_8\text{SnSe}_6 \leftrightarrow 6\text{Ag}_2\text{Se} + \text{Ag}_8\text{SnS}_6$, were obtained, including various poly- and isothermal sections of diagrams and projections of liquidus surfaces, the fields of primary crystallization of phases, as well as types and coordinates of non- and monovariant equilibria were determined;

- within the framework of the study of the above planes of quaternary systems, the phase equilibria in ternary Ag-Ge (Sn) -Se and quasi-binary $\text{Cu}_2\text{S} - \text{GeS}_2$, $\text{Cu}_2\text{Se} - \text{GeSe}_2$, $\text{Ag}_2\text{S} - \text{GeS}_2$ systems were re-

studied, new variants of their phase diagrams differing from known ones were constructed;

- the thermodynamic analysis and 3D visualization of the liquidus surfaces and immiscibility in the Ag-Ge(Sn)-Se systems were carried out; the results obtained are in good agreement with the experiment;

- it was found that in the studied quasiternary and reciprocal systems, sections connecting ternary compounds of the $A_8B^{IV}X_6$ type, are either quasibinary or stable below the solidus and are characterized by unlimited mutual solubility of high-temperature modifications and the formation of wide (or continuous) solid solutions based on low-temperature modifications of the starting compounds. Quasibinary or partially quasi-binary are also sections between the $A_2B^{IV}X_3$ compounds, which also show continuous or wide areas of solid solutions;

- the partial thermodynamic functions ($\Delta\bar{G}$, $\Delta\bar{H}$, $\Delta\bar{S}$) of the copper (silver) in alloys and the standard thermodynamic functions of the formation of several ternary chalcogenides of copper (silver), as well as the cation and anion-substituted solid solutions based on them, were calculated from the data of measurements of the EMF of concentration cells with $Cu^+(Ag^+)$ conducting solid electrolytes. The heats and entropies of polymorphic transformations of the Cu_8GeS_6 , Cu_8GeSe_6 , Ag_8GeSe_6 , and Ag_8SnSe_6 , compounds, were also determined for the first time.

- a number of the "composition-property" diagrams (dependences of the parameters of the crystal lattice, microhardness, emf of concentration cells, partial molar functions on the composition) were constructed, the analysis of which made it possible to establish the boundaries of the phase regions on the solid-phase equilibria diagrams and, in particular, areas of homogeneity of the obtained new phases;

- based on the obtained experimental data complexes, the solid solutions with a given composition were isolated in pure form, the types and parameters of their crystal lattices were determined;

- some regularities of the phase equilibria and phase formation in the quasiternary $\text{Cu}_2\text{X}-\text{Ag}_2\text{X}-\text{GeX}_2$, $\text{A}^1_2\text{X}-\text{GeX}_2-\text{SnX}_2$, and reciprocal systems $2\text{A}^1_2\text{X} + \text{BX}'_2 \leftrightarrow 2\text{A}_2\text{X}' + \text{BX}_2$ and thermodynamic properties of the compounds and solid solutions formed in them were revealed.

Provisions for Defense.

1. The obtained set of experimental data, constituting the physico-chemical basis for the synthesis of new complex phases based on copper and silver chalcogermanates and chalcostanates:

- the constructed pictures of the phase equilibria of the studied ternary, quasi-ternary and reciprocal systems, including the projections of the liquidus surfaces as well as various polythermal and isothermal sections;

- results of analytical 3D modeling and thermodynamic analysis of phase diagrams of Ag-Ge (Sn) -Se systems;

- partial molar and standard integral thermodynamic functions of the studied ternary compounds and solid solutions based on them, thermodynamic functions of polymorphic transitions of some ternary compounds;

- crystallographic data of the revealed new phases.

2. Revealed regularities of phase formation and phase equilibria in the studied quasi-ternary and reciprocal systems, as well as the thermodynamic properties of intermediate phases formed in them.

Scientific direction. The complex of the new scientific results obtained in the thesis can be characterized as the development of an important scientific direction - the creation of physicochemical foundations for obtaining complex phases including copper and silver chalcogenides based on mutually agreed data sets on phase equilibria and thermodynamic properties of the corresponding systems.

The theoretical and practical significance of the work. The obtained new complexes of the mutually agreed data on phase equilibria, thermodynamic and crystal-chemical characteristics of the studied systems make a significant contribution to the chemistry, thermodynamics, and materials science of complex copper and silver

chalcogenides. The practical significance of these results lies in the fact that they form the scientific basis for the development of methods and optimization of the synthesis and growth of monocrystals of new phases with a given composition and properties formed in the corresponding systems. These data are also fundamental characteristics of substances and can be included in relevant handbooks and information databanks. Some of the results obtained in the work are included in the data banks of the international scientific information agencies as Springer, Elsevier and Tomson Reuters. According to Google Scholar Citations, over 131 references have been made to 14 author's articles.

An analysis of the literature data for the initial binary and ternary compounds of the studied systems shows that the obtained new multicomponent phases of variable composition based on them are potential multifunctional materials with mixed ion-electron conductivity, thermoelectric, photovoltaic, and optical and other properties and after studying their respective physical properties, they can find practical applications. Of particular note is the expansion of the lower boundary of the thermal stability of solid solutions based on high-temperature cubic modifications of compounds with high ionic conductivity to temperatures below room temperature, which makes them very attractive as photoelectrode materials, electrochemical converters of solar energy, ion-selective sensors, photoelectrochemical visualizers, ionistors, etc.

The results of the thesis can also be used in the magistracy of the National Academy of Sciences and higher educational institutions of the republic when teaching special courses "Physicochemical Analysis", "Inorganic Materials Science", "Thermodynamics of Solutions", "Thermodynamics of Phase Equilibria", etc.

Testing and application. The results of the work were reported and discussed at the following scientific conferences:

Republican scientific conferences dedicated to the 85th and 90th anniversary of acad. T.N. Shakhtakhtinsky (Baku, 2011, 2015); 11th Meeting "Fundamental problems of solid-state ionics" (Chernogolovka, 2012); All-Russian Conference "Solid State Chemistry

and Functional Materials - 2012" (Ekaterinburg, 2012); XIV International Scientific and Technical Conference "High-tech Chemical Technologies-2012" (Tula - Yasnaya Polyana - Kulikovo Pole, 2012); All-Russian Conference "Modern Problems of Chemical Science and Education" (Cheboksary, 2012); IV, VII International scientific conference "Modern methods in theoretical and experimental electrochemistry" (Ples, 2012, 2015); XII International conference on crystal chemistry of intermetallic compounds (Lviv, 2013); XIX and XX International Conference on Chemical Thermodynamics in Russia (Moscow, 2013; Nizhny Novgorod, 2015); XVI Russian Conference on Physical Chemistry and Electrochemistry of Molten and Solid Electrolytes (Yekaterinburg, 2013); X, XI International Kurnakov Conference on physico-chemical analysis (Samara, 2013, Voronej, 2016); XV Scientific-technical conference "High-tech chemical technologies-2014" (Moscow, 2014); International Scientific Conference "Kinetics and Mechanism of Crystallization. Crystallization as a Form of Self-Organization of Matter" (Ivanovo, 2014); Scientific conference "Modern problems of chemistry and biology" (Ganja, 2014, 2016, 2017); International Conference Applied Mineralogy and Advanced materials, AMAM- 2015 (Castellaneta Marina, 2015); 1st, 2nd, and 3th International Turkic World Conference on Chemical Sciences and Technologies, (Sarayevo, 2015; Skopje, 2016; Baku, 2017); XV International Conference on Physics and Technology of Thin Films and Nanosystems, ICPTTFN-XV (Ivano-Frankovsk, 2015); XV All-Russian Conference "High-Purity substances and materials. Obtaining, analysis, application" (Nizhny Novgorod, 2015); International scientific conference "Polyfunctional Chemical Materials and Technologies" (Tomsk, 2015); 13th International Conference "Fundamental Problems of Solid State Ionics" (Chernogolovka, 2016); VIII All-Russian Conference "Physico-chemical processes in condensed matters and at interphase boundaries- FAGRAN 2018" (Voronezh, 2018); All-Russian conference "Solid State Chemistry and Functional Materials" and the XII All-Russian Symposium with international participation "Thermodynamics and materials science" (St. Petersburg, 2018); 10th International conference on theory and

application of soft computing, computing with words and perceptions - ICSCCW 2019 (Prague, Czech Republic, 2019).

56 scientific works were published, including 36 articles in journals included in the High Attestation Commission list based on the materials of the dissertation. Of these, 19 articles in international journals indexed in the Science Citation Index.

The name of the organization in which the work was carried out. The work was performed at the Department of Chemistry of Ganja State University and in the laboratory of physico-chemical analysis of the Institute of Ecology and Natural Resources of the Ganja Branch of Azerbaijan National Academy of Sciences.

Volume and structure of work. The dissertation consists of an introduction (18.422 symbols), six chapters (Chapter I - 18.422 symbols, II-46.821, III-31.271, IV-53.320, V-62.912, VI-87.096), the main results and conclusions, the list of used literature and published works of the author on the topic of the dissertation (499 items). The thesis is presented in 350 pages, contains 131 figures and 56 tables.

The contribution of the author. The author belongs to the formulation of the goals and objectives of the dissertation, the development of methodological methods for their solution, processing and generalization of the results, as well as a significant part of the results of experimental studies.

Acknowledgments. The author expresses deep gratitude to prof. Imamaddin Amiraslanov (Institute of Physics, ANAS) and Vagif Gasimov (ICIC, ANAS) for providing comprehensive assistance in conducting X-Ray studies and interpretation of their data, dosent Ziya Aliyev (Azerbaijan State University of Oil and Industry) for his help in research using the SEM method.

MAIN CONTENT OF WORK

In the introduction, the relevance of the dissertation topic is substantiated, the goal, tasks, scientific novelty, the theoretical and practical significance of the results obtained in the dissertation are formulated.

The first chapter briefly describes and critically analyzes the literature data on the T-x diagrams of the binary systems $A^I(B^{IV})-X$ (A^I -Cu, Ag; B^{IV} -Ge, Sn; X-S, Se) and the physicochemical properties of chalcogenides of copper and silver; phase equilibria in the $A^I-B^{IV}-X$ ternary systems, especially in quasi-ternary systems of the $A^I_2X-B^{IV}X_2$ type, as well as the physicochemical and thermodynamic properties of their ternary phases.

At the end of the chapter, data on the state of knowledge of complex systems, including chalcogenides of copper (silver) and p² elements, are presented; the choice of objects of study is substantiated. Subsection 1.5 is devoted to the latest work on the study of various functional properties of copper and silver chalcogenides with p²-elements and materials based on them.

The second chapter is devoted to the methodological aspects of planning and organizing of interconnected study of phase equilibria and thermodynamic properties of systems, methods for the synthesis of compounds and alloys (subsection 2.3), as well as experimental research methods and related instruments and devices (subsection 2.4).

For the syntheses, the elemental components of a high degree of purity purchased from the German company Alfa Aesar were used.

Alloys of the studied systems were prepared from previously synthesized and identified binary and ternary compounds in vacuumed up to $\sim 10^{-2}$ Pa and sealed quartz ampoules. The synthesis modes are given in the corresponding sections of the dissertation.

The experimental research methods used in the work and the corresponding instruments and installations are described above (p. 6).

The third chapter presents the results of an experimental study and 3D-modeling of phase diagrams of the Ag-Ge-Se and Ag-Sn-Se systems.

The analysis of literature data carried out in the dissertation showed that ternary systems of the $A^I-B^{IV}-X$ (A^I -Cu, Ag; B^{IV} -Ge, Sn; X-S, Se) type have been studied in a number works, but there are no systems among them whose phase diagram is sufficiently reliable.

Since quasi-binary sections of the $A_2^I X-B^{IV} X_2$ -type of these systems are boundary for the quasi-binary ($Cu_2 X-Ag_2 X-GeX_2$) and reciprocal ($2A_2^I X+B^{IV} X'_2 \leftrightarrow 2A_2^I X'+B^{IV} X_2$) systems studied by us, the reliable data needed for the correct interpretation of the experimental data on them. Therefore, we performed thorough experiments to refine the T-x diagrams of some sections of the $A_2^I X-B^{IV} X_2$ -type, while two ternary systems Ag-Ge-Se and Ag-Sn-Se were re-studied in the entire concentration area.

Ag-Ge-Se system. It was shown that only one ternary compound $Ag_8 GeSe_6$ is formed in the system with congruent melting at 1175 K and polymorphic transformation at 321 K. The ternary compounds $Ag_2 GeSe_3$ and $Ag_8 GeSe_5$ previously mentioned in the literature have not been confirmed.

The liquidus surface of the Ag-Ge-Se system (Fig. 1) consists of seven fields corresponding to the primary crystallization of the α -phase based on Ag, the α' -phase based on the high-temperature modification of $Ag_2 Se$, $Ag_8 GeSe_6$, $GeSe$ and $GeSe_2$ compounds, as well as elementary Ge and Se. The latter is degenerate at the selenium corner of the phase diagram. The types and coordination of all nonvariant equilibria, including boundary binary systems, are presented in Table. 1.

Based on phase diagrams of boundary binary systems using a limited number of DTA data, the analytical equations for the liquidus surfaces and the immiscibility of the ternary Ag-Ge-Se system were obtained and their 3D- modeling and visualization were performed (Fig. 2).

Ag-Sn-Se system. A projection of the liquidus surface, a number of polythermal sections, and an isothermal section at room temperature of the phase diagram are constructed. It was shown that the system is characterized by the formation of two ternary compounds - $Ag_8 SnSe_6$ and $Ag_x Sn_{2-x} Se_2$. The former melts congruently at 1015 K and undergoes a polymorphic transformation at 355 K, the second forms with decomposition according to the peritectic reaction at 860 K. The compound $Ag_2 SnSe_3$, previously mentioned in the literature, has not been confirmed.

Table 1
Nonvariant equilibria in the Ag-Ge-Se system

Point on Fig.1	Equilibrium	Composition, mol%		T,K
		Ge	Se	
D ₁	$L \leftrightarrow (Ag_2Se)_{II}$	-	33.33	1170
D ₂	$L \leftrightarrow GeSe_2$	33.33	66.67	1013
D ₃	$L \leftrightarrow (Ag_8GeSe_6)_{II}$	6.67	33.33	1178
p	$L+Ge \leftrightarrow (GeSe)_{II}$	49	51	948
e ₁	$L \leftrightarrow \alpha + Ge$	24.5	-	924
e ₂	$L \leftrightarrow Ag + (Ag_2Se)_{II}$	2	32.5	1113
e ₃	$L \leftrightarrow GeSe_2 + Se$	2	98	488
e ₄	$L \leftrightarrow GeSe + (GeSe)_I$	44	56	860
e ₅	$L \leftrightarrow Ge + (Ag_8GeSe_6)_{II}$	12	38	938
e ₆	$L \leftrightarrow \alpha + (Ag_8GeSe_6)_{II}$	6.5	35.5	995
e ₇	$L \leftrightarrow \beta + (Ag_8GeSe_6)_{II}$	19	52	813
e ₈	$L \leftrightarrow \alpha' + (Ag_8GeSe_6)_{II}$	5	38	1083
e ₉	$L \leftrightarrow \alpha' + Se$	-	>99	490
e ₁₀	$L \leftrightarrow (Ag_8GeSe_6)_{II} + Se$		>99	492
U	$L + Ge \leftrightarrow (Ag_8GeSe_6)_{II} + (GeSe)_I$	23.5	47.5	745
E ₁	$L \leftrightarrow \alpha' + (Ag_8GeSe_6)_{II} + \alpha$	5	35.5	973
E ₂	$L \leftrightarrow \alpha + ((Ag_8GeSe_6)_{II} + Ge)$	10.5	35.5	885
E ₃	$L \leftrightarrow (Ag_8GeSe_6)_{II} + \beta + (GeSe)_I$	22.5	50	685
E ₄	$L \leftrightarrow \alpha' + (Ag_8GeSe_6)_{II} + Se$		>99	490
E ₅	$L \leftrightarrow (Ag_8GeSe_6)_{II} + GeSe_2 + Se$		~98	485
m ₁ (m ₁ ')	$L_1 \leftrightarrow L_2 + Ag$	-	12(32)	1163
m ₂ (m ₂ ')	$L_2 \leftrightarrow L_3 + \alpha'$	-	44.5(95)	890
m ₃ (m ₃ ')	$L_1 \leftrightarrow L_2 + Ge$	86(60)	14(40)	1178
m ₄ (m ₄ ')	$L_2 \leftrightarrow L_3 + (Ag_8GeSe_6)_{II}$	6	49.5	970
M ₁ (M ₁ ')	$L_1 \leftrightarrow L_2 + \alpha + Ge$	21(10.5)	9(33.5)	905
M ₂ (M ₂ ')	$L_2 \leftrightarrow L_3 + \alpha' + (Ag_8GeSe_6)_{II}$	1.5(0.5)	45(95.5)	853
M ₃ (M ₃ ')	$L_2 \leftrightarrow L_3 + \beta + (Ag_8GeSe_6)_{II}$	15.5(10)	60(85)	750

Note: α , α' , β -solid solutions based on Ag, a high-temperature modification of Ag_2Se and $GeSe_2$. The indices indicate a low temperature (I) or high-temperature modification (II) of the compound.

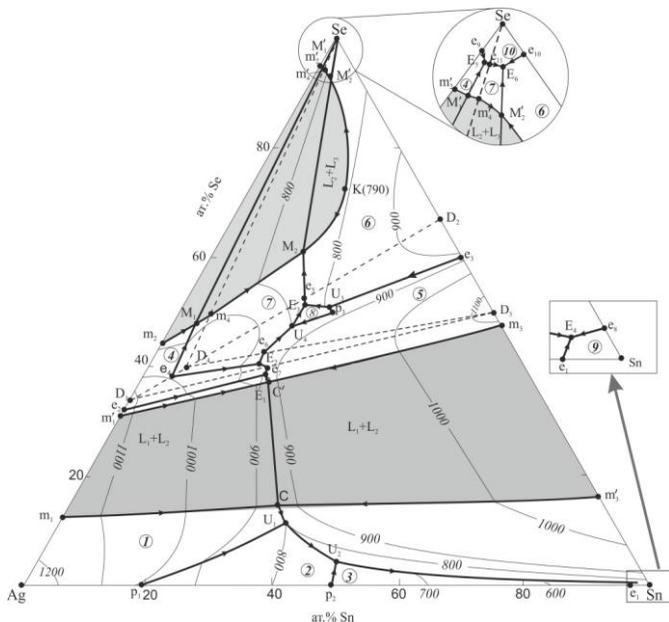


Fig. 4. The projection of the liquidus surface of the Ag-Sn-Se system. Fields of primary crystallization: 1- α ; 2- ξ ; 3- ϵ ; 4- α' ; 5-(SnSe)_{II}; 6- SnSe₂; 7-(Ag₈SnSe₆)_{II}; 8- γ ; 9-Sn; 10-Se. Dotted lines are quasi-binary sections.

The fourth and fifth chapters give the results on phase equilibria in quasi-ternary $\text{Cu}_2\text{X}-\text{Ag}_2\text{X}-\text{GeX}_2$ and $2\text{A}^{\text{I}}_2\text{S}-\text{B}^{\text{IV}}\text{Se}_2 \leftrightarrow 2\text{A}^{\text{I}}_2\text{Se}-\text{B}^{\text{IV}}\text{S}_2$ reciprocal systems, respectively. These systems are interesting for the search for new chalcogenide phases of variable composition with $\text{Cu} \leftrightarrow \text{Ag}$ and $\text{S} \leftrightarrow \text{Se}$ substitutions. The results for the two reciprocal systems are given below.

The $2\text{Cu}_2\text{S}+\text{SnSe}_2 \leftrightarrow 2\text{Cu}_2\text{Se}+\text{SnS}_2$ system is reciprocal, i.e. does not have a stable diagonal. Only the $\text{Cu}_2\text{SnS}_3-\text{Cu}_2\text{SnSe}_3$ section is quasibinary of peritectic type (Fig. 5) and divides the concentration square into two independent subsystems.

Isothermal sections at 800 and 300 K (Fig. 6). As can be seen, at 800 K the interaction of the α , β , γ_1 - and γ_2 - phases, as well as the compounds Cu_4SnS_4 and $\text{Cu}_2\text{Sn}_3\text{S}_7$ lead to the formation of several two- and three-phase regions.

Table 2
Nonvariant equilibria in the Ag-Sn-Se system

Point on the fig.4	Equilibria	Composition, mol %		T, K
		Sn	Se	
D ₁	$L \leftrightarrow (Ag_2Se)_{II}$	-	33.3	1170
D ₂	$L \leftrightarrow SnSe_2$	33.3	66.7	948
D ₃	$L \leftrightarrow (SnSe)_{II}$	50	50	1153
D ₄	$L \leftrightarrow (Ag_8SnSe_6)_{II}$	6.67	40	1015
e ₁	$L \leftrightarrow \varepsilon + Sn$	96.2	-	494
e ₂	$L \leftrightarrow Ag + (Ag_2Se)_{II}$	-	32.5	1113
e ₃	$L \leftrightarrow (SnSe)_{II} + SnSe_2$	39	61	901
e ₄	$L \leftrightarrow (Ag_8SnSe_6)_{II} + \alpha'$	5	38.5	995
e ₅	$L \leftrightarrow (Ag_8SnSe)_{II} + SnSe_2$	19	52.5	768
e ₆	$L \leftrightarrow (Ag_8SnSe_6) + (SnSe)_{II}$	18	42	873
e ₇	$L \leftrightarrow \alpha' + (SnSe)_{II}$	19.5	40	832
e ₈	$L \leftrightarrow (SnSe)_I + Sn$	>99	<1	505
e ₉	$L \leftrightarrow \alpha' + Se$	-	>99	490
e ₁₀	$L \leftrightarrow SnSe_2 + Se$	<1	>99	493
e ₁₁	$L \leftrightarrow (Ag_8SnSe)_{II} + Se$	<1	>99	493
p ₁	$L + \alpha \leftrightarrow \xi$	19.5	-	997
p ₂	$L + \xi \leftrightarrow \varepsilon$	49.6	-	753
p ₃	$L + (SnSe)_{II} \leftrightarrow \gamma$	25	50	860
U ₁	$L + \alpha \leftrightarrow (SnSe)_{II} + \xi$	36	12	808
U ₂	$L + \xi \leftrightarrow (SnSe)_I + \varepsilon$	47	5	733
U ₃	$L + (SnSe)_{II} \leftrightarrow \gamma + SnSe_2$	23.5	51	833
U ₄	$L + (SnSe)_{II} \leftrightarrow \gamma + (Ag_8SnSe_6)_{II}$	20	47	815
E ₁	$L \leftrightarrow \alpha + \alpha' + (SnSe)_I$	19.5	39	803
E ₂	$L \leftrightarrow \alpha' + (SnSe)_I + (Ag_8SnSe_6)_{II}$	18	40.5	820
E ₃	$L \leftrightarrow (SnSe)_I + \gamma + (Ag_8SnSe_6)_{II}$	20	51	763
E ₄	$L \leftrightarrow (SnSe)_I + \varepsilon + Sn$	~97	<1.0	493
E ₅	$L \leftrightarrow \alpha' + (Ag_8SnSe_6)_{II} + Se$	<1.0	>99	488
E ₆	$L \leftrightarrow (Ag_8SnSe_6)_{II} + SnSe_2 + Se$	<1.0	>99	490
m ₁ (m ₁ ')	$L_1 \leftrightarrow L_2 + Ag$	-	12(32)	1163
m ₂ (m ₂ ')	$L_2 \leftrightarrow L_3 + \alpha$	-	44.5(95)	890
m ₃ (m ₃ ')	$L_2 \leftrightarrow L_1 + (SnSe)_{II}$	53(84)	47(16)	1090
m ₄ (m ₄ ')	$L_2 \leftrightarrow L_3 + (Ag_8SnSe_6)_{II}$	5.5(1)	49(94)	873
M ₁ (M ₁ ')	$L_2 \leftrightarrow L_3 + \alpha' + (Ag_8SnSe_6)_{II}$	3(<1)	48(94)	850
M ₂ (M ₂ ')	$L_2 \leftrightarrow L_3 + (SnSe)_I + (Ag_8SnSe_6)_{II}$	14(2)	59(93)	728
C(C')	$L_1 + L_2 \leftrightarrow \alpha + (SnSe)_{II}$	34(21.5)	14.5(35.5)	890

Note: Greek letters indicate solid solutions based on Ag (α), high-temperature modifications of Ag_2Se (α') and $AgSnSe_2$ (γ), as well as intermediate phases of the Ag-Sn system (ξ , ε). Indices I and II indicate, respectively, low-temperature and high-temperature modifications of the compounds.

Table 3

**DTA results and crystal lattice parameters for samples of the
Cu₂SnS₃-Cu₂SnSe₃ system**

Composition, mol% Cu ₂ SnSe ₃	Thermal effects, K	Syngony, crystal lattice parameters, nm
0 (Cu ₂ SnS ₃)	1125	Monoclinic, Cc: $a=0,66581$; $b=1,1531$; $c=0,66672$; $\beta=109,39^0$
10	1100-1115	Monoclinic, Cc: $a=0,67111$; $b=1,1621$; $c=0,67204$; $\beta=109,31^0$
20	1077-1100	Monoclinic, Cc: $a=0,67642$; $b=1,1712$; $c=0,67735$; $\beta=109,24^0$
30	1063-1092	Monoclinic, Cc: $a=0,68171$; $b=1,1803$; $c=0,68266$; $\beta=109,15^0$
40	1037-1085	Monoclinic, Cc: $a=0,68697$; $b=1,1897$; $c=0,68794$; $\beta=109,07^0$
50	1030-1075	Monoclinic, Cc: $a=0,69473$; $b=1,1989$; $c=0,69324$; $\beta=108,98^0$
60	1020-1060	Two-phase sample, $\gamma_1+\gamma_2$: γ_1 -monoclinic ($a=0,69243$; $b=1,2037$; $c=0,69584$; $\beta=108,94^0$); γ_2 -cubic ($a = 0,56303$).
70	1015-1043	cubic, $a = 0,56311$
80	1000-1025	cubic, $a = 0,56535$
90	986-1004	cubic, $a = 0,56744$
100	973	cubic, $a = 0,56962$

The character of solid-phase equilibria at 300 K (Fig. 6) is somewhat different. This is because limited solid solutions are formed in the Cu₂S-Cu₂Se system at room temperature based on low-temperature modifications of the starting compounds (α_1 - and α_2 -phases). Between them, a wide (50-80 mol% Cu₂Se) two-phase field $\alpha_1+\alpha_2$ is formed. The presence of these regions leads to the formation of new two- ($\alpha_1+\text{Cu}_4\text{SnS}_4$, $\alpha_1+\gamma_1$, $\text{Cu}_4\text{SnS}_4+\gamma_1$, $\alpha_2+\gamma_2$) and three-phase ($\alpha_1+\gamma_1+\text{Cu}_4\text{SnS}_4$, $\alpha_1+\alpha_2+\gamma_1$, $\alpha_2+\gamma_1+\gamma_2$) areas in the mutual system

(Fig. 6). A characteristic feature of this system is that the regions of existence of the ternary sulfides Cu_4SnS_4 and $\text{Cu}_2\text{Sn}_3\text{S}_7$ which do not have selenium analogs are strongly limited by the $\alpha_1+\gamma_1$ and $\beta+\gamma_1$ two-phase fields.

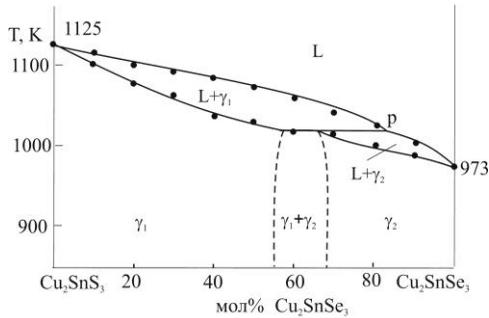


Fig.5. T-x phase diagram of the Cu_2SnS_3 - Cu_2SnSe_3 system

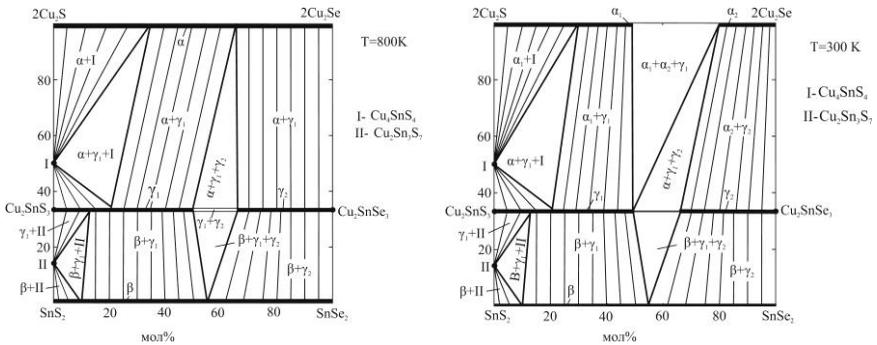


Fig.6. Isothermal sections at 800 and 300 K of the $2\text{Cu}_2\text{S}+\text{SnSe}_2 \leftrightarrow 2\text{Cu}_2\text{Se}+\text{SnS}_2$ reciprocal system

The liquidus surface consists of 6 fields corresponding to the primary crystallization of the α -, Cu_4SnS_4 , β -, γ_1 - and γ_2 - phases. Isotherms in increments of 100° reflect the curvature of the liquidus surfaces. These fields are delimited by eutectic e_1U_1 , e_2U_1 , U_1U_2 , U_2e_5 , e_3U_3 , e_4U_3 , U_3U_4 , U_4e_6 , and peritectic pU_2 , pU_4 curves, as well as points U_1 - U_4 reflecting nonvariant transition equilibrium.

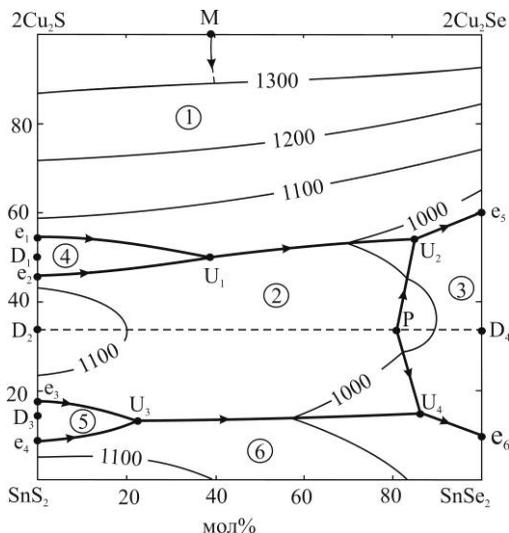


Fig. 7. The projection of the liquidus surface of the reciprocal system $2\text{Cu}_2\text{S}+\text{SnSe}_2 \leftrightarrow 2\text{Cu}_2\text{Se}+\text{SnS}_2$. Fields of primary crystallization: 1- α ; 2- γ_1 ; 3- γ_2 ; 4- Cu_4SnS_4 ; 5- $\text{Cu}_2\text{Sn}_3\text{S}_7$; 6- β . Dotted lines - quasibinary section Cu_2SnS_3 - Cu_2SnSe_3

The types and temperatures (temperature ranges) of all non- and monovariant equilibria (including for boundary quasi-binary sections) in the phase diagram of the $2\text{Cu}_2\text{S}+\text{SnSe}_2 \leftrightarrow 2\text{Cu}_2\text{Se}+\text{SnS}_2$ reciprocal system are given in Table 4.

$2\text{Ag}_2\text{S}+\text{GeSe}_2 \leftrightarrow 2\text{Ag}_2\text{Se}+\text{GeS}_2$ system has one quasibinary section Ag_8GeS_6 - Ag_8GeSe_6 (Fig. 8), which divides it into two reversibly reciprocal subsystems. In the high-temperature region ($T > 500$ K) this section is characterized by the formation of a continuous series of S \rightarrow Se substitutional solid solutions and has a phase diagram of the “cigar” type.

The formation of solid solutions sharply lowers the temperature of the polymorphic transitions of both compounds. The temperature of the polymorphic transition of the Ag_8GeS_6 in the composition range 0–30 mol% decreases from 496 to 360 K, and at composition > 40 mol% Ag_8GeSe_6 drops below room temperature. A polymorphic transition of the Ag_8GeSe_6 compound for the composition of 90

mol% Ag_8GeSe_6 was not observed even at temperatures above room temperature. These results show that the substitutional solid solutions formed in the system expand the region of existence of the high-temperature cubic phase and stabilize it at room temperature.

Table 4
Non- and monovariant equilibria in the
 $2\text{Cu}_2\text{S}+\text{SnSe}_2\leftrightarrow 2\text{Cu}_2\text{Se}+\text{SnS}_2$ system

Point or curve on the Fig.7	Equilibria	T, K
D ₁	$\text{L}\leftrightarrow\text{Cu}_4\text{SnS}_4$	1106
D ₂	$\text{L}\leftrightarrow\text{Cu}_2\text{SnS}_3$	1130
D ₃	$\text{L}\leftrightarrow\text{Cu}_2\text{Sn}_3\text{S}_7$	1080
D ₄	$\text{L}\leftrightarrow\text{Cu}_2\text{SnSe}_3$	970
M	$\text{L}\leftrightarrow\alpha$	1330
e ₁	$\text{L}\leftrightarrow\alpha+\text{Cu}_4\text{SnS}_4$	1075
e ₂	$\text{L}\leftrightarrow\gamma_1+\text{Cu}_4\text{SnS}_4$	1085
e ₃	$\text{L}\leftrightarrow\gamma_1+\text{Cu}_2\text{Sn}_3\text{S}_7$	1070
e ₄	$\text{L}\leftrightarrow\beta+\text{Cu}_2\text{Sn}_3\text{S}_7$	1063
e ₅	$\text{L}\leftrightarrow\alpha+\gamma_2$	940
e ₆	$\text{L}\leftrightarrow\beta+\gamma_2$	860
P	$\text{L}+\gamma_1\leftrightarrow\gamma_2$	1020
U ₁	$\text{L}+\text{Cu}_4\text{SnS}_4\leftrightarrow\alpha+\gamma_1$	1060
U ₂	$\text{L}+\gamma_1\leftrightarrow\alpha+\gamma_2$	980
U ₃	$\text{L}+\text{Cu}_2\text{Sn}_3\text{S}_7\leftrightarrow+\gamma_1$	1048
U ₄	$\text{L}+\gamma_1\leftrightarrow\beta+\gamma_2$	935
e ₃ U ₃	$\text{L}\leftrightarrow\gamma_1+\text{Cu}_2\text{Sn}_3\text{S}_7$	1070-1048
e ₄ U ₃	$\text{L}\leftrightarrow\beta+\text{Cu}_2\text{Sn}_3\text{S}_7$	1063-1048
U ₃ U ₄	$\text{L}\leftrightarrow\gamma_1+\beta$	1048-935
PU ₄	$\text{L}+\gamma_1\leftrightarrow\gamma_2$	1020-935
U ₄ e ₆	$\text{L}\leftrightarrow\beta+\gamma_2$	935-860

The XRD results (Fig. 9) confirm the phase diagram of the Ag_8GeS_6 - Ag_8GeSe_6 . As can be seen, an alloy with a composition of 20 mol% Ag_8GeSe_6 has a diffraction pattern similar to Ag_8GeS_6 . Samples with compositions of 40-80 mol% Ag_8GeSe_6 have diffraction

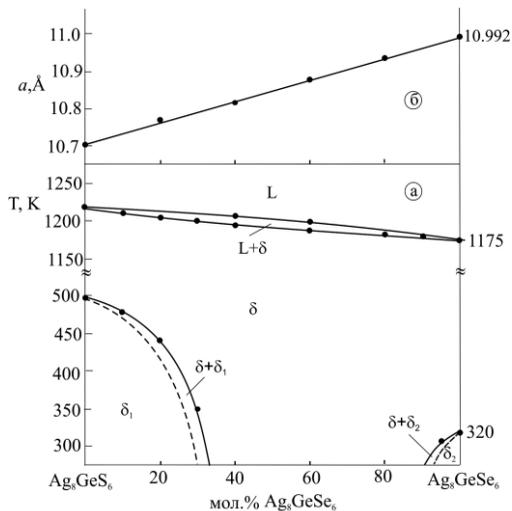


Fig. 8. Phase diagram of the Ag_8GeS_6 - Ag_8GeSe_6 (a) system and concentration dependences of the lattice parameters (b) of samples quenched from 900 K

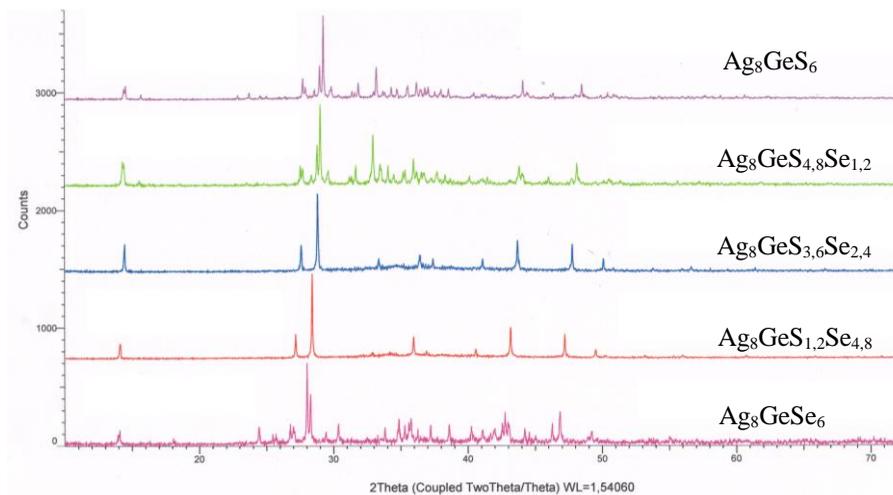


Fig. 9. X-ray powder diffraction patterns of some alloys of the Ag_8GeS_6 - Ag_8GeSe_6 system at room temperature

patterns different from the low-temperature modifications of the starting compounds. An analysis of these diffraction patterns shows that they have a pattern characteristic of cubic syngony (F.qr. F-43m), i.e. solid solutions in the range of compositions 40-80 mol% Ag_8GeSe_6 crystallize in cubic syngony.

The crystal lattice parameters of the starting compounds and solid solutions calculated using TOPAZ 3.0 computer software are shown in Table 5. A comparison of the results shows that solid solutions in the range of 40-80 mol% Ag_8GeSe_6 have a cubic lattice at room temperature and 900 K. The crystal lattice periods of high-temperature cubic solid solutions obey the Vegard rule (Fig. 8).

Table 5
Types and parameters of crystal lattices of solid solutions of the Ag_8GeS_6 - Ag_8GeSe_6 system

Composition	Room temperature			Quenching from 900K		
	Syngony Sp.Gr.	Crystal lattice parameters, Å			Syngony Sp.gr.	lattice period, Å
		<i>a</i>	<i>b</i>	<i>c</i>		
Ag_8GeSe_6	Romb. Pna2 ₁	15,129	7,4565	10,5535	Cubic, F -43m	10,705
$\text{Ag}_8\text{GeS}_{4,8}\text{Se}_{1,2}$	"_"				"_"	10,772
$\text{Ag}_8\text{GeS}_{3,6}\text{Se}_{2,4}$	Cubic F -43m	10,812	-	-	"_"	10,816
$\text{Ag}_8\text{GeS}_{2,4}\text{Se}_{3,6}$	"_"	10,875	-	-	"_"	10,879
$\text{Ag}_8\text{GeS}_{1,2}\text{Se}_{4,8}$	"_"	10,930	-	-	"_"	10,935
Ag_8GeSe_6	romb . Pmn2 ₁	7,8402	7,7322	10,912	"_"	10,992

Isothermal sections of the phase diagram at 700 and 300 K (Fig. 10). At a temperature of 700 K, the boundary Ag_2S - Ag_2Se , GeS_2 - GeSe_2 , and Ag_8GeS_6 - Ag_8GeSe_6 systems are characterized by the formation of continuous series of solid solutions (α -, β - and δ -phases, respectively), which correspond to narrow (1-2 mol% wide) homogeneity areas along the corresponding quasibinary sections. The Ag_2GeS_3 compound has a small region of homogeneity (γ -phase). The interaction of these phases leads to the formation of two-

phase regions $\alpha+\delta$, $\beta+\gamma$, $\beta+\delta$ and $\gamma+\delta$ on the phase diagram. Between the last three, there is a three-phase region $\beta+\gamma+\delta$ (Fig. 10).

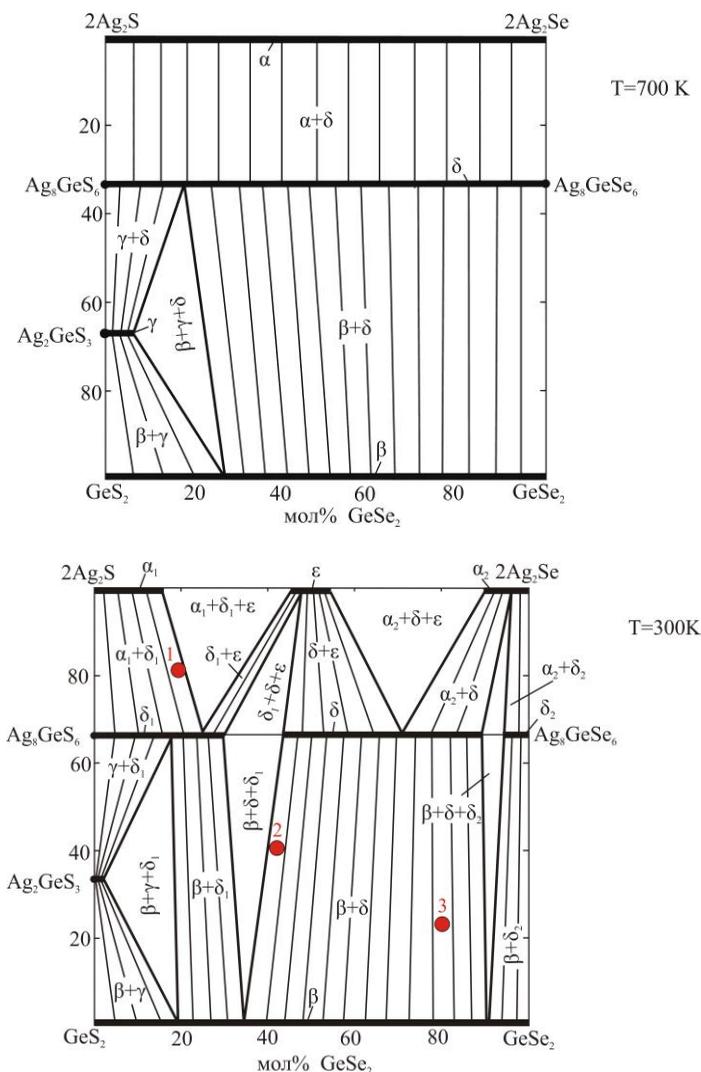


Fig. 10. Isothermal sections of the phase diagram of the $2\text{Ag}_2\text{S} + \text{GeSe}_2 \leftrightarrow 2\text{Ag}_2\text{Se} + \text{GeSe}_2$ system at 700 K and 300 K.

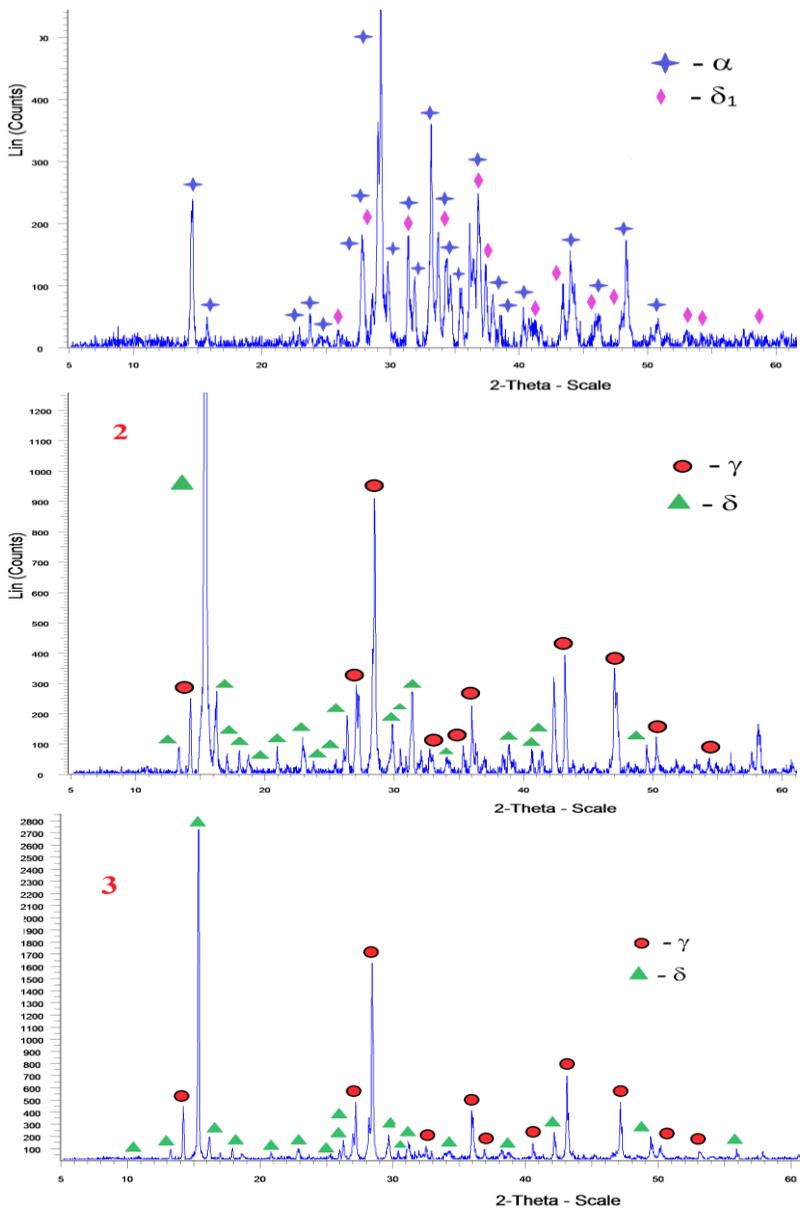


Fig. 11. Powder X-ray diffraction patterns of some alloys of the $2\text{Ag}_2\text{S} + \text{GeSe}_2 \leftrightarrow 2\text{Ag}_2\text{Se} + \text{GeS}_2$ system. 1, 2, 3 alloys indicated in fig. 10.

The isothermal section at 300 K (Fig. 10) qualitatively differs from that at 700 K. This is because at 300 K in the boundary Ag_2S - Ag_2Se system there are limited solid solutions based on low-temperature modifications of the starting compounds (α_1 and α_2 -phases) and intermediate ε - phase. Also, in the Ag_8GeS_6 - Ag_8GeSe_6 quasibinary system, partial decomposition of the high-temperature phase occurs with the formation of limited δ_1 - and δ_2 - solid solutions based on low-temperature modifications of the starting ternary compounds. These changes lead to the formation of numerous new phase regions in the system: 8 two-phase and 7 three- numerous new phase regions in the system: 8 two-phase and 7 three-phase. A comparison of the isothermal sections at 700 and 300 K shows that at 300 K only two two-phase fields ($\beta+\gamma$ and $\beta+\delta$) exist at 700 K.

In conclusion, it should be noted that the existence of all phase regions and their extent are determined by the methods of XRD and SEM. As an example, Fig. 11 shows the powder diffraction patterns of some alloys from various heterogen regions.

The projection of the liquidus surface (Fig. 12) consists of the six fields of primary crystallization. Region 1 corresponds to the crystallization of the α' -phase based on the high-temperature modification of Ag_2S in the Ag_2S - Ag_2Se system. The literature data on the transition of this phase to the medium temperature α -phase (continuous solid solutions between Ag_2S and Ag_2Se) are confirmed. Region 2 corresponds to the primary crystallization of the α' -phase. The presence of a minimum point (M) in the phase diagram of the boundary Ag_2S - Ag_2Se system leads to the separation of the crystallization field of the α -phase into two parts.

The widest fields of primary crystallization (fields 3 and 5) belong to the δ - and β - phases. The ternary compound Ag_2GeS_3 , or rather the γ -phase based on it, has a narrow region of crystallization (4).

The above fields of primary crystallization of phases are separated by a series of curves of monovariant equilibria and points of invariant equilibria. These equilibria and temperatures of their establishment are given in Table 6.

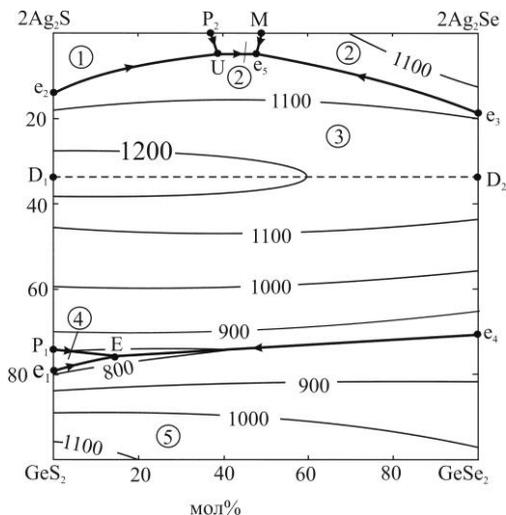


Fig.12. The projection of the liquidus surface of the system $2\text{Ag}_2\text{S}+\text{GeSe}_2\leftrightarrow 2\text{Ag}_2\text{Se}+\text{GeS}_2$. Primary crystallization fields: 1- α' ; 2- α ; 3- δ ; 4- γ ; 5- β . Dot lines – quasi-binary section $\text{Ag}_8\text{GeS}_6\text{-Ag}_8\text{GeSe}_6$.

The curves emanating from the eutectic point e_2 and the peritonic point P_2 converge at point U and a transitional equilibrium is established in the system (Table 6), resulting in a two-phase mixture $\alpha+\delta$. A similar two-phase eutectic mixture crystallizes along the Ue_5 and e_3e_5 curves. Point e_5 corresponds to the minimum point (1030 K) of non-invariant crystallization according to the eutectic scheme $L\leftrightarrow\alpha+\beta$.

It can be noted that the quasibinary section $\text{Ag}_8\text{GeS}_6\text{-Ag}_8\text{GeSe}_6$ divides the $2\text{Ag}_2\text{S}+\text{GeSe}_2\leftrightarrow 2\text{Ag}_2\text{Se}+\text{GeS}_2$ system into two sub-systems: $\text{Ag}_2\text{S-Ag}_2\text{Se-Ag}_8\text{GeS}_6\text{-Ag}_8\text{GeSe}_6$ and $\text{Ag}_8\text{GeS}_6\text{-Ag}_8\text{GeSe}_6\text{-GeSe}_2\text{-GeS}_2$. The second subsystem is characterized by the crystallization of the triple eutectics (E). Similar triple eutectics, when two of the three curves converging at point E, two come from neighboring non-invariant points of one side system are rarely encountered in practice. The implementation of this option, in this case, can be explained by the fact that the primary crystallization fields of thermally and thermodynamically more stable β - and δ -

phases strongly limit the crystallization region of the γ - phase based on Ag_2GeS_3 .

Table 6
Non- and monovariant equilibria in the system
 $2\text{Ag}_2\text{S}+\text{GeSe}_2\leftrightarrow 2\text{Ag}_2\text{Se}+\text{GeS}_2$

Point or curve on Fig. 12	Equilibria	Temperature, K
D ₁	$\text{L}\leftrightarrow(\text{Ag}_8\text{GeS}_6)_{\text{II}}$	1120
D ₂	$\text{L}\leftrightarrow(\text{Ag}_8\text{GeSe}_6)_{\text{III}}$	1180
P ₁	$\text{L}+(\text{Ag}_8\text{GeS}_6)_{\text{II}}\leftrightarrow\text{Ag}_2\text{GeS}_3$	895
P ₂	$\text{L}+\alpha'\leftrightarrow\alpha$	1108
M	$\text{L}\leftrightarrow\alpha$	1030
e ₁	$\text{L}\leftrightarrow\text{Ag}_2\text{GeS}_3+\text{GeS}_2$	780
e ₂	$\text{L}\leftrightarrow(\text{Ag}_2\text{S})_{\text{II}}+(\text{Ag}_8\text{GeS}_6)_{\text{II}}$	1080
e ₃	$\text{L}\leftrightarrow(\text{Ag}_2\text{Se})_{\text{II}}+(\text{Ag}_8\text{GeSe}_6)_{\text{II}}$	1083
e ₄	$\text{L}\leftrightarrow(\text{Ag}_8\text{GeSe}_6)_{\text{II}}+\text{GeSe}_2$	833
e ₅	$\text{L}\leftrightarrow\alpha+\delta$	1015
U	$\text{L}\leftrightarrow\alpha+\delta$	1035
E	$\text{L}\leftrightarrow\beta+\delta+\gamma$	763
e ₂ U	$\text{L}\leftrightarrow\alpha'+\delta$	1080-1035
P ₂ U	$\text{L}+\alpha'\leftrightarrow\alpha$	1108-1035
Ue ₅	$\text{L}\leftrightarrow\alpha+\delta$	1035-1015
Me ₅	$\text{L}\leftrightarrow\alpha$	1030-1015
e ₃ e ₅	$\text{L}\leftrightarrow\alpha+$	1083-1015
P ₁ E	$\text{L}+\delta\leftrightarrow\gamma$	895-763
e ₁ E	$\text{L}\leftrightarrow\beta+\gamma$	780-763
e ₄ E	$\text{L}\leftrightarrow\beta+\delta$	833-763

Note: α' - solid solutions based on high temperature modification of the Ag_2S ; α , β , γ , δ - solid solutions $\text{Ag}_2\text{S}_{1-x}\text{Se}_x$, $\text{Ag}_2\text{GeS}_{3-y}\text{Se}_y$, $\text{Ag}_8\text{GeS}_{6-z}\text{Se}_z$. The indices in the formulas of the compounds indicate crystalline modifications, starting from low temperatures.

At the end of Chapter V, the results on phase equilibria in the studied quasiternary and reciprocal systems are generalized and some of their features are noted.

An analysis of the features of phase equilibria and phase formation in $A^I-B^{IV}-X$ ternary systems (A^I -Cu, Ag; B^{IV} -Si, Ge, Sn; X-S, Se, Te) shows that the most characteristic ternary compounds in them are $A^I_8B^{IV}X_6$ and $A^I_2B^{IV}X_3$. Compounds of the first type are characterized by polymorphism. Their high-temperature modifications have a cubic structure, while the structural types of other lower-temperature modifications are diverse. Among the compounds of both types, there are both congruent and incongruent melting compounds.

The aforementioned and other features of the most typical ternary compounds allowed us to expect the realization of distinctive patterns of phase equilibria along the quasi-ternary and reciprocal planes of the corresponding quaternary systems. The obtained experimental data sets confirmed this and made it possible to identify some features of phase equilibria and phase formation in them as a whole and in sections that connect the above isoformula compounds.

Quasibinary and quasi-stable sections. An analysis of the phase diagrams shows that in quasi-ternary and reciprocal systems, sections connecting isoformula compounds of types $A^I_8B^{IV}X_6$ or $A^I_2B^{IV}X_3$ are either quasi-binary or quasi-stable (stable below solidus) and are characterized by the formation of wide or continuous solid solutions.

Systems composed of $A^I_8B^{IV}X_6$ type compounds, depending on the substitution character, can be divided into 3 groups:

I. Anion substituted $A^I_8B^{IV}X_6$ - $A^I_8B^{IV}X'_6$ (X, X'- various chalcogens);

II. A^I -cation substituted - $Cu^I_8B^{IV}X_6$ - $A^I_8B^{IV}X'_6$;

III. B^{IV} - cation substituted - $A^I_8GeX_6$ - $A^I_8SnX'_6$

Figs. 13 and 14 show T-x diagrams of all the studied polythermal sections of the indicated types so far. A comparative analysis of these phase diagrams allows us to highlight the following features:

- all silver-containing systems of groups I and III, i.e. all systems whose initial compounds melt congruently are quasibinary (Fig. 13), and copper-containing sections of groups I and II are quasi-stable, i.e. in general, they are not quasibinary due to the incongruent melting of $Cu^I_8B^{IV}X_6$ compounds, but are stable below solidus;

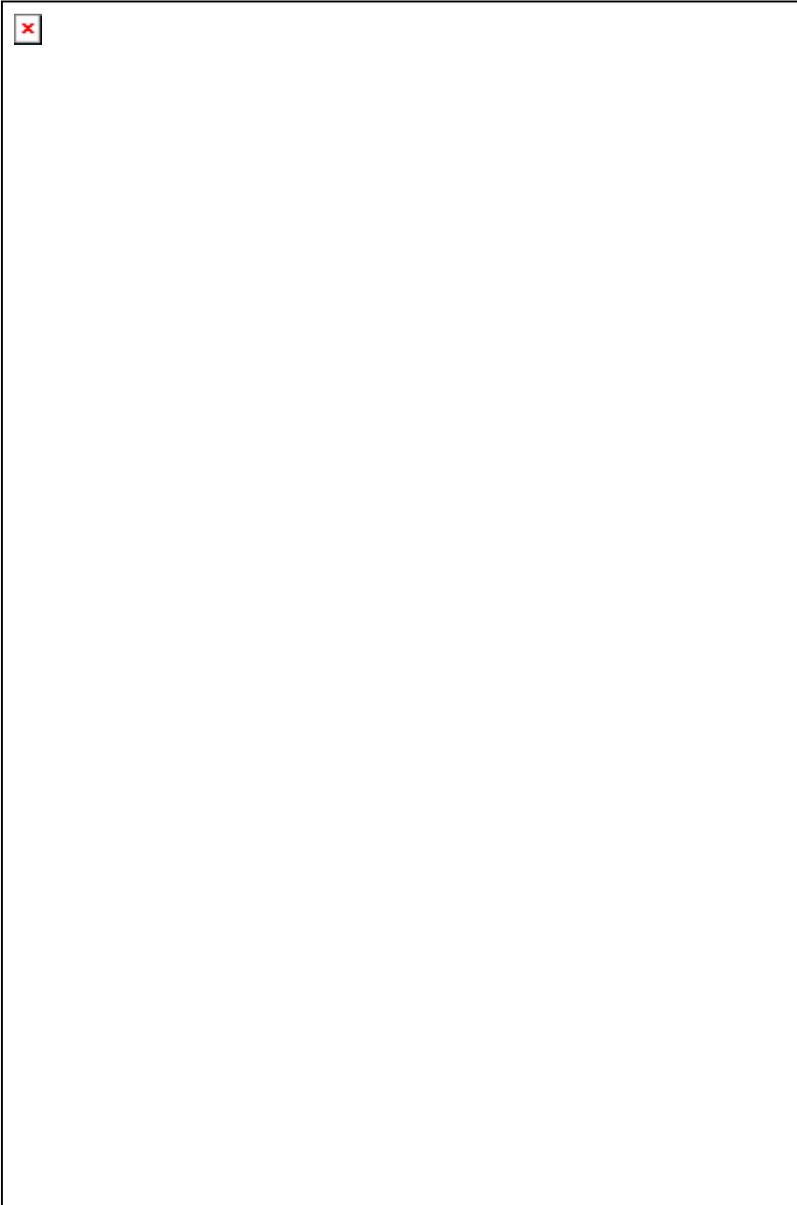


Fig. 13. Comparison of phase diagrams of systems composed of ternary compounds of $A_8B^{IV}X_6$ type.

- all of the above sections (Fig. 13) are characterized by the formation of continuous series of solid solutions of the corresponding type of substitution between high-temperature cubic modifications of the starting ternary compounds;
- the formation of solid solutions based on ternary compounds in all systems of groups I and II (except for $\text{Ag}_8\text{SnS}_6\text{-Ag}_8\text{SnSe}_6$) is accompanied by a sharp decrease in the temperatures of their polymorphic phase transitions, which leads to an expansion of the temperature range of the existence of the cubic phase with high ionic conductivity to room temperature and lower. By the nature of the phase equilibria in the subsolidus part, the above 4 systems of groups I and II, can be attributed to the eutectoid type with eutectoid equilibria at temperatures below room temperature;
- In the $\text{Ag}_8\text{GeX}_6\text{-Ag}_8\text{SnX}_6$ systems, the formation of continuous series of solid solutions is observed, both between high-temperature and low-temperature modifications, which is associated with isostructurality, in addition to high-temperature, and also low-temperature modifications of ternary compounds. In the $\text{Ag}_8\text{SnS}_6\text{-Ag}_8\text{SnSe}_6$ system, the formation of solid solutions is accompanied by the peritectoid equilibrium $\delta+\delta_1\leftrightarrow\delta_2$ (Fig. 13).
- The polythermal section $\text{Cu}_8\text{GeSe}_6\text{-Cu}_8\text{SnSe}_6$ is also shown in Fig. 13. This is the case when one of the ternary compounds of the $\text{A}_8\text{B}^{\text{IV}}\text{X}_6$ exists. This section, like all similar sections, is non-quasibinary and passes through various phase fields. However, the formation of wide regions of solid solutions based on both modifications of Cu_8GeSe_6 is also observed here.
- Phase equilibria in such systems involving silicon compounds have not yet been studied, but taking into account the above features of such systems, it can be assumed that wide (or continuous) regions of solid solutions and regions of existence of cubic phases with high ionic density will also be revealed in systems involving A_8SiX_6 compounds conductivity will cover temperatures below room temperature.

Systems composed of compounds of $\text{A}_2\text{B}^{\text{IV}}\text{X}_3$ type. These systems (Fig. 14), as well as the previous ones (based on

AI8BIVX6), can be divided into 3 groups. We note some features of phase equilibria in them:

- three ($\text{Cu}_2\text{GeS}_3\text{-Cu}_2\text{GeSe}_3$, $\text{Cu}_2\text{SnS}_3\text{-Cu}_2\text{SnSe}_3$, $\text{Cu}_2\text{GeSe}_3\text{-Cu}_2\text{SnSe}_3$) of the seven sections of this type studied to present time are quasibinary. The $\text{Cu}_2\text{GeS}_3\text{-Cu}_2\text{GeSe}_3$ system with isostructural starting compounds is characterized by the formation of continuous solid solutions and has a phase diagram of the Rozeboom type I, and the other two are of the peritectic type with wide regions of solid solutions based on the starting compounds;
- polythermal section $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$, one of the starting compounds of which melts with decomposition as a whole, is not quasi-binary, but stable below solidus. This section, as well as quasibinary systems of a similar type, is characterized by the formation of wide areas of solid solutions based on the starting compounds;
- polythermal sections of this type with one existing ternary compound, despite instability in the subsolidus as a whole, are characterized by the formation of significant areas of solid solutions based on $\text{A}_2\text{B}^{\text{IV}}\text{X}_3$ compounds;
- no phases are formed on the polythermal section connecting the compositions of the nonexistent " Ag_2GeSe_3 " and " Ag_2SnSe_3 " compounds, which could be attributed to solid solutions based on compounds of the $\text{A}_2\text{B}^{\text{IV}}\text{X}_3$ type.

Solid-state equilibrium diagrams. Fig. 15 shows solid-phase equilibria diagrams of quasiternary, and Fig. 16 - reciprocal systems. The right columns show phase diagrams at room temperature and the left columns- at 700-800 K.

It follows from Figs. 15 and 16 that the most common feature of the solid-phase equilibria diagrams of all the studied systems is the formation of broad fields of solid solutions along some of their boundary components and internal sections. These solid solutions make a decisive contribution to the formation of general patterns of phase equilibria in both quasi-ternary and reciprocal systems. This leads to the fact that among the considered systems there is not one that has stable cross-sections with the participation of the original

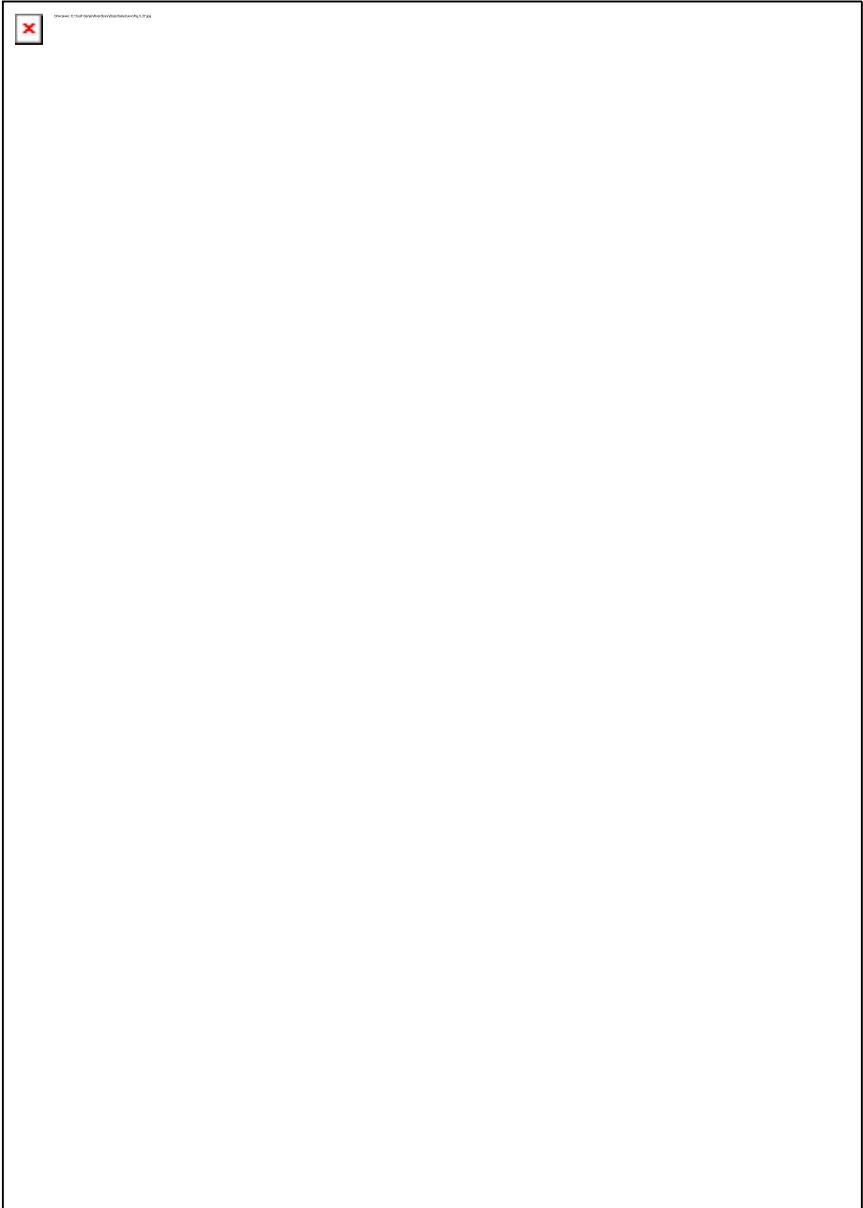


Fig. 14. Comparison of phase diagrams of systems composed $A_2B^{IV}X_3$ ternary compounds

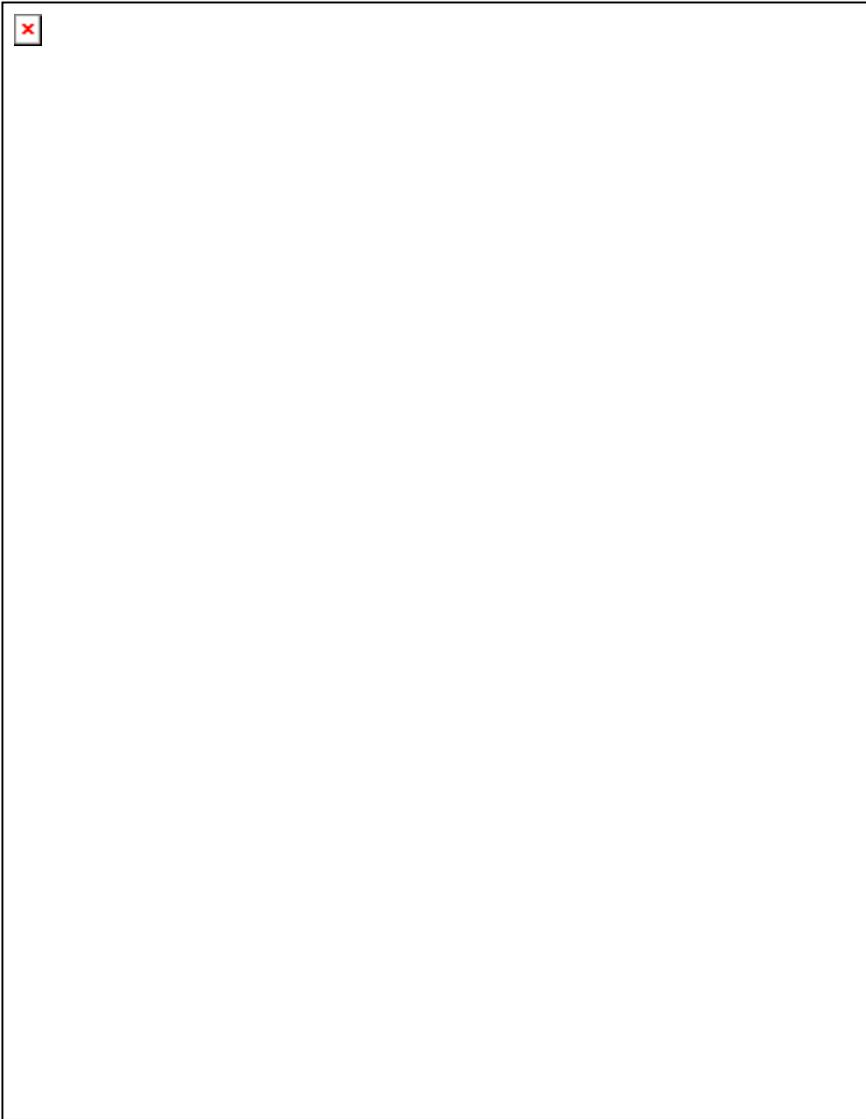


Fig. 15. Comparison of the diagrams of solid-phase equilibria of some quasi-ternary systems composed of chalcogenides of copper, silver, germanium, and tin.

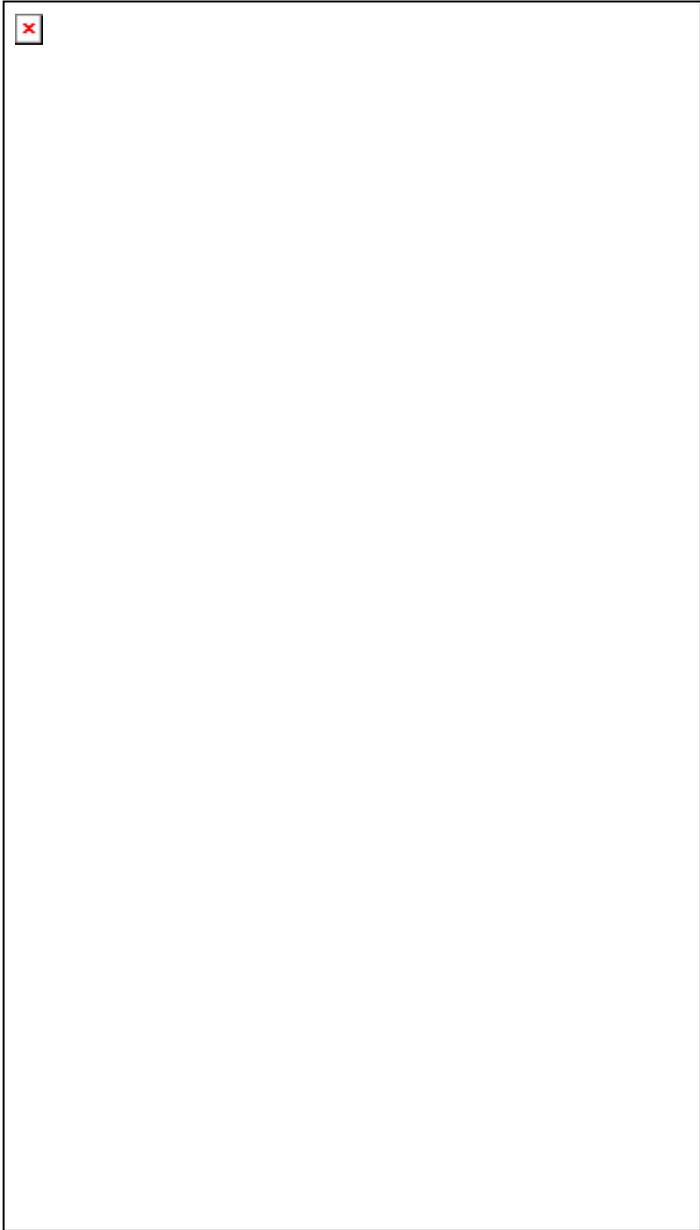


Fig.16. Comparison of the solid-phase equilibria diagrams of reciprocal systems $2A^I_2S-B^{IV}Se_2 \leftrightarrow 2A^I_2Se-B^{IV}S_2$

binary systems. Also, $A_2^I X$ and $A_8^I B^{IV} X_6$ compounds and solid solutions based on them undergo polymorphic transformations at relatively low temperatures (320-500 K), which is accompanied by a significant change in the phase equilibrium patterns at high temperatures (> 500 K) compared to room temperature.

Let's consider in more detail the quasiternary and reciprocal systems.

Quasi-ternary systems. A comparative analysis of the solid-phase equilibria diagrams of these systems reveals the following features:

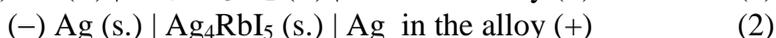
- stable cross-sections of the Cu_8GeX_6 - Ag_8GeX_6 , Ag_8GeX_6 - Ag_8SnX_6 , Cu_2GeS_3 - Ag_2GeS_3 and Cu_2GeSe_3 - Cu_2SnSe_3 types divide the Cu_2S - Ag_2S - GeS_2 system into three, the remaining quasiternary systems into two independent subsystems. All of these subsystems are characterized by the presence of wide two-phase regions;
- all reciprocal subsystems, for example, $4Cu_2S + Ag_8GeS_6 \leftrightarrow 4Ag_2S + Cu_8GeS_6$ and $Cu_8GeS_6 + 4Ag_2GeS_3 \leftrightarrow Ag_8GeS_6 + 4Cu_2GeS_3$, are reversibly reciprocal, which is the result of the dominant role in the formation of phase regions non compounds but solid solutions;
- for high-temperature ($T > 500$ K) (left column) isothermal sections, continuous series of solid solutions are characteristic along the boundary systems between compounds of the $A_2^I X$ (α - phase) and along the section between the ternary compounds of the $A_8^I B^{IV} X_6$ type (δ -phase) and continuous two-phase fields $\alpha + \delta$. At room temperature, these fields are split and more complex phase equilibrium patterns are formed containing various two- and three-phase fields;
- in the case where only one of the two possible ternary compounds of a certain type exists in the system, for example, Cu_2GeSe_3 or Cu_8GeSe_6 , this compound has a relatively narrow homogeneity region in the direction of "formula stoichiometry" and does not form a stable cross-section.

Triple reciprocal systems (Fig. 16). The most common feature of all these systems is their reversibly reciprocal character, i.e. lack of a

stable diagonal. They are divided into simpler subsystems not by stable diagonals, but by stable sections connected ternary compounds - formula analogs, namely compounds of $A_8^I B^{IV} X_6$ and $A_2^I B^{IV} X_3$ types. The aforementioned regularities of the nature of phase equilibria in the quasiternary systems are also characteristic of reciprocal systems. For example, the reciprocal nature of all subsystems, the complication of the picture of phase equilibria at room temperature, etc.

The sixth chapter presents the results of a thermodynamic study of sulfides and selenides of copper (silver) with germanium and tin, as well as solid solutions based on them, using the electromotive forces method (EMF). At the beginning of the chapter (subsections 6.1-6.3), the fundamentals of the EMF method are briefly described, its most widely used modifications are noted, especially the EMF method with solid electrolyte used in this work.

To conduct thermodynamic experiments by the EMF method with a solid electrolyte, we assembled the concentration cells of the following types:



In cells of types (1) and (2), the reference electrodes were metallic copper or silver, and the right electrodes were equilibrium alloys from various phase regions of the studied systems, the compositions of which were selected based on phase diagrams. Alloys were obtained from pre-synthesized and identified binary and ternary compounds, as well as high purity elemental chalcogen by fusion in evacuated ($\sim 10^{-2}$ Pa) quartz ampoules at temperatures $30\div 50^\circ$ above the temperature of the liquidus. Taking into account that the state of electrode alloys should be as close to equilibrium as possible, cast non-homogenized samples were subjected to long-time stepwise thermal annealing at various temperatures. The phase compositions of the annealed alloys were controlled by XRD. Then, the annealed alloys were ground into powder, pressed into tablets weighing 0.5-1 g and used as anodes in the cell of types (1) and (2).

Solid superionic conductors $\text{Cu}_4\text{RbI}_3\text{Cl}_2$ and Ag_4RbI_5 , which have high ionic conductivity at room temperature, used as electrolytes. Moreover, the level of their electronic conductivity is negligible.

The dissertation describes in detail the methods of synthesis of alloys-electrodes, electrolytes, assembly of electrochemical cells and EMF measurements.

EMF measurements were carried out in the temperature ranges 300-380 K (sulfide systems) and 300-450 K (selenide systems) using a high-resistance digital voltmeter B7-34A.

For alloys - electrodes, one of the phases of which undergoes a polymorphic transformation in the temperature range of the thermodynamic experiment, we first measured the EMF in the temperature range of the existence of the high-temperature modification, and then the low-temperature one. The first equilibrium values were obtained after holding the cell at ~ 370 K, and the subsequent ones every 3-4 hours after a certain temperature was established. The values of EMF, which during repeated measurements at a given temperature differed from each other by no more than 0.5 mV, regardless of the direction of temperature change, were taken as equilibrium.

Measurements showed that the nature of the concentration dependences of the EMF cells are in accordance with the solid-phase equilibria diagrams of the studied systems. At a constant temperature within each three-phase region, the EMF values were constant, independently of the total composition of the alloy — the anode, and upon transition from one region to another, they changed stepwise. In the regions of homogeneity and two-phase fields, the EMF values were continuous functions of the composition. According to the condition of thermodynamic equilibrium, the EMF values of cells of types (1) and (2) cannot decrease with decreasing copper (silver) content along the radial lines from Cu (Ag) vertices of the concentration triangles. Our experimental data satisfy this requirement.

The experiments also showed the linearity of the temperature dependences of the EMF cells of types (1) and (2). In this case, for electrode alloys containing $\text{A}_8\text{B}^{\text{IV}}\text{X}_6$ compounds with polymorphic transitions, these dependencies had the form of two straight lines

with a breakpoint at the polymorphic transformation temperature. As an example, Fig. 17 shows the temperature dependences of the emf of the concentration chains (1) for compounds Cu_8GeS_6 and Cu_8GeSe_6 .

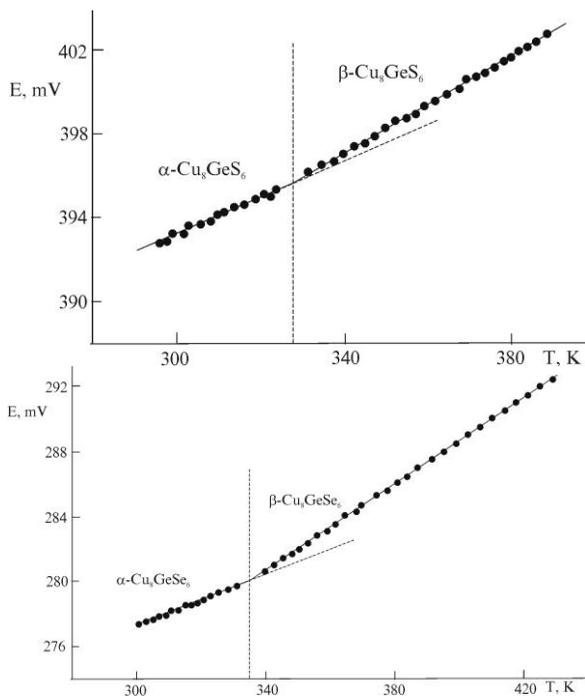


Fig. 17. Dependence of the EMF of concentration chains of type (1) for Cu_8GeS_6 and Cu_8GeSe_6 compounds

To calculate the thermodynamic functions of the phases of the studied systems, the results of the EMF measurements were processed by the least square method in approximating the linear dependence of the EMF on temperature and are presented in the form of equations of the type:

$$E = a + bT \pm t \left[\frac{S_E^2}{n} + S_b^2 (T - \bar{T})^2 \right]^{1/2} \quad (3)$$

Table 7
Temperature dependences of the EMF of concentration cells of types (1) and (2) for alloys of the A^I-B^{IV}-X (A^I-Cu, Ag; B^{IV}-Ge, Sn; X-S, Se) systems

Phase area	E, mV=a+bT+t·S _E (T)
Cu ₂ GeS ₃ + GeS ₂ + S	$436,2 + 0,024T \pm 2 \left[\frac{6,3}{28} + 5,9 \cdot 10^{-5} (T - 339,3)^2 \right]^{1/2}$
α - Cu ₈ GeS ₆ + Cu ₂ GeS ₃ + S	$366,6 + 0,089T \pm 2,2 \left[\frac{0,04}{15} + 2,9 \cdot 10^{-5} (T - 307,7)^2 \right]^{1/2}$
β - Cu ₈ GeS ₆ + Cu ₂ GeS ₃ + S	$357,8 + 0,116T \pm 2 \left[\frac{0,45}{24} + 6,2 \cdot 10^{-5} (T - 360,5)^2 \right]^{1/2}$
α - Cu ₈ GeSe ₆ + Cu ₂ GeSe ₃ + Se	$254,8 + 0,075T \pm 2,2 \left[\frac{0,02}{15} + 9,1 \cdot 10^{-6} (T - 314,4)^2 \right]^{1/2}$
β - Cu ₈ GeSe ₆ + Cu ₂ GeSe ₃ + Se	$234,3 + 0,136T \pm 2 \left[\frac{0,21}{24} + 1,3 \cdot 10^{-5} (T - 378,0)^2 \right]^{1/2}$
Cu ₂ SnSe ₃ + SnSe ₂ + Se	$325,34 + 0,1305T \pm 2 \left[\frac{0,86}{24} + 1,81 \cdot 10^{-5} (T - 377,7)^2 \right]^{1/2}$
α - Ag ₈ GeSe ₆ + GeSe ₂ + Se	$237,7 + 0,092T \pm 2,2 \left[\frac{0,06}{15} + 4 \cdot 10^{-5} (T - 306,9)^2 \right]^{1/2}$
β - Ag ₈ GeSe ₆ + GeSe ₂ + Se	$218,2 + 0,153T \pm 2 \left[\frac{0,18}{24} + 8,1 \cdot 10^{-6} (T - 371,4)^2 \right]^{1/2}$
α - Ag ₈ SnSe ₆ + SnSe ₂ + Se	$253,5 + 0,089T \pm 2,2 \left[\frac{0,58}{15} + 1,1 \cdot 10^{-5} (T - 328,2)^2 \right]^{1/2}$
β - Ag ₈ SnSe ₆ + SnSe ₂ + Se	$233,6 + 0,145T \pm 2 \left[\frac{0,66}{24} + 1,3 \cdot 10^{-5} (T - 397,5)^2 \right]^{1/2}$
AgSnSe ₂ + SnSe ₂	$210,1 + 0,127T \pm 2 \left[\frac{1,07}{24} + 2,2 \cdot 10^{-5} (T - 381,7)^2 \right]^{1/2}$
Ag _{0,84} Sn _{1,16} Se ₂ + SnSe ₂ + SnSe	$209,8 + 0,168T \pm 2 \left[\frac{0,89}{24} + 1,8 \cdot 10^{-5} (T - 377,2)^2 \right]^{1/2}$

Table 8

**Partial molar thermodynamic functions of copper (silver)
in alloys of A^I-B^{IV}-X systems**

Phase area	T, K	$-\overline{\Delta G}_{\text{Cu(Ag)}}$	$-\overline{\Delta H}_{\text{Cu(Ag)}}$	$\overline{\Delta S}_{\text{Cu(Ag)}}$ J·K ⁻¹ ·mol ⁻¹
		kJ·mol ⁻¹		
Cu ₂ GeS ₃ + GeS ₂ + S	298	42,778±0,110	42,09±0,51	2,32±1,49
α- Cu ₈ GeS ₆ +Cu ₂ GeS ₃ +S	298	37,925±0,013	35,37±0,32	8,56±1,04
β-Cu ₈ GeS ₆ +Cu ₂ GeS ₃ +S	400	-39,00±0,098	34,52±0,55	11,19±1,52
α-Cu ₈ GeSe ₆ +Cu ₂ GeSe ₃ +Se	298	26,735±0,009	24,59±0,19	7,20±0,59
β-Cu ₈ GeSe ₆ +Cu ₂ GeSe ₃ +Se	400	27,856±0,059	22,61±0,27	13,12±0,70
Cu ₂ SnSe ₃ + SnSe ₂ + Se	298	-35,15±0,07	-31,39±0,31	12,59±0,82
α- Ag ₈ GeSe ₆ – GeSe ₂ – Se	298	25,582±0,014	22,93±0,38	8,88±1,23
β- Ag ₈ GeSe ₆ – GeSe ₂ – Se	400	26,968±0,043	21,05±0,21	14,76±0,55
α-Ag ₈ SnSe ₆ -SnSe ₂ -Se	298	27.01±0.05	24.46±0.24	8.57±0.70
β-Ag ₈ SnSe ₆ -SnSe ₂ -Se	400	28.14±0.08	22.54±0.30	13.99±0.71
AgSnSe ₂ -SnSe ₂	298	23.93±0.09	20.27±0.35	12.25±9.91
Ag _{0.84} Sn _{1.16} Se ₂ -SnSe ₂ -SnSe	298	25.08±0.07	20.24±0.31	16.21±0.82

where n is the number of pairs of values of E and T; S_E and S_b are the dispersions of individual measurements of EMF and b - coefficient; \overline{T} - average absolute temperature; t – student test. At a confidence level of 95% and the number of experimental points n≥20, Student's test t≤2.

From the temperature dependences of the EMF using the relations

$$\Delta \overline{G}_{\text{Cu(Ag)}} = -zFE \quad (4)$$

$$\Delta \overline{H}_{\text{Cu(Ag)}} = -z \left[E - T \left(\frac{\partial E}{\partial T} \right)_P \right] = -zFa \quad (5)$$

$$\Delta \overline{S}_{\text{Cu(Ag)}} = zF \left(\frac{\partial E}{\partial T} \right)_P = zFb \quad (6)$$

(F is the Faraday number, z is the charge of a mobile ion) the relative partial molar functions of copper (silver) in the alloys are calculated. For compounds A^I₈B^{IV}X₆, 2 equations were obtained that relate to

their two crystalline modifications (Table 7).

According to the phase diagrams of the corresponding systems, these functions relate to certain potential-forming reactions. As an example, we consider potential-forming reactions for Cu-B^{IV}-X systems. From the solid-phase equilibria diagrams of these systems, it follows that the partial molar functions of copper in various phase regions are thermodynamic functions of the following potential-forming reactions (all substances are in a crystalline state)



According to reaction (7), the Gibbs free energy and the enthalpy of formation of the Cu₂GeS₃ compound can be calculated by the relation

$$\Delta_f Z(\text{Cu}_2\text{GeS}_3) = 2\Delta_f \bar{Z}_{\text{Cu}} + \Delta_f Z(\text{GeS}_2) \quad (12)$$

Z ≡ G, H, while the entropy

$$S^0(\text{Cu}_2\text{GeS}_3) = 2[\Delta_f \bar{S}_{\text{Cu}} + S^0(\text{Cu})] + S^0(\text{S}) + S^0(\text{GeS}_2) \quad (13)$$

Similarly, the standard integral thermodynamic functions for the other compounds were calculated. The calculation results are given in Table 9. Errors are calculated by the accumulation of errors.

From the obtained thermodynamic data for two modifications of compounds of the A₈B^{IV}X₆ type, we calculated the thermodynamic functions of their polymorphic transformations.

Since the heats of formation of A₈B^{IV}X₆ compounds are almost constant in the temperature ranges of EMF measurements, we can write

$$\Delta H_{\text{n.tr.}} = \Delta_f H^0(\beta) - \Delta_f H^0(\alpha) \quad (14)$$

where ΔH_{ph.tr.} are the heats of polymorphic transformations of A₈B^{IV}X₆ compounds, Δ_fH⁰(β) and Δ_fH⁰(α) are the heats of formation of their two modifications. On the other hand, from the relations of potential-forming reactions (8) and (10), it follows that the contri-

butions of the binary GeS_2 and GeSe_2 compounds to the enthalpy of formation of both modifications of these ternary compounds are the same. Therefore, the $\Delta H_{\text{ph.tr.}}$ the calculation can be carried out by the relation ratio

Table 9

**Integral Thermodynamic Functions of Chalcogenides of Copper
(Silver) - Germany (Tin)**

Phase	T, K	$-\Delta_f G^0$	$-\Delta_f H^0$	S^0 J·K ⁻¹ ·mol ⁻¹
		kJ·mol ⁻¹		
Cu_2GeS_3	298	211.3±2,4	213.7±2,3	190.3±5,5
$\alpha\text{-Cu}_8\text{GeS}_6$	298	438.9±2,5	425.9±4,2	536.3±13,1
$\beta\text{-Cu}_8\text{GeS}_6$	400	445.3±3,1	420.8±5,6	552.1±15,8
$\alpha\text{-Cu}_8\text{GeSe}_6$	298	341.1±3,3	327.4±4,5	596.7±11,6
$\beta\text{-Cu}_8\text{GeSe}_6$	400	348.1±3,7	315.6±5,0	632.3±12,5
Cu_2SnSe_3	298	189.5±2.6	187.5±4.8	251.6±5.0
	298	198.4±0.6 [ref]	198.5±2.9 [ref]	237±5 [ref]
	298		180.5 [ref]	
$\alpha\text{-Ag}_8\text{GeSe}_6$	298	306,0±3,1	285,7±5,7	694,0±19,2
$\beta\text{-Ag}_8\text{GeSe}_6$	400	316,6±3,4	270,7±4,2	740,9±13,8
		249,0 [ref]	240,9 [ref]	
$\alpha\text{-Ag}_8\text{SnSe}_6$	298	335.3±2.9	320.4±6.4	695.5±10.5
$\beta\text{-Ag}_8\text{SnSe}_6$	298	342.4±3.2*	305.0±6.8	738.8±10.6
	298	352.5±1.9 [ref]	323.1±1.6 [ref]	
	298	347.6±27.2 [ref]	336.2±19.2 [ref]	
AgSnSe_2	298	144.1±2.6	145.0±4.8	172.8±4.1
	298	133.9±1.6 [ref]	124.9±1.3 [ref]	-
$\text{Ag}_{0.84}\text{Sn}_{1.16}\text{Se}_2$	298	152.0±2.3	152.0±4.7	182.7±6.0

* **Note:** the thesis contains a detailed comparison of the results we have obtained and the literature data.

$$\Delta H_{\text{n.t.}} = 8[\Delta \bar{H}_{\text{Cu(Ag)}}(\beta) - \Delta \bar{H}_{\text{Cu(Ag)}}(\alpha)]. \quad (15)$$

These relations do not include the values and errors of the heat of formation of GeS_2 and GeSe_2 , which allows us to reduce the errors of the final data.

The entropies of polymorphic transformations are calculated using

the relations

$$\Delta S_{n.n.} = \Delta H_{n.n.} / T_{n.n.} \quad (16)$$

The obtained values of the thermodynamic functions of the phase transition of $A^I_8B^{IV}X_6$ compounds are given in table 10.

Relatively high errors in the data obtained are because in the EMF method the partial enthalpy and entropy are calculated indirectly from the coefficient of the temperature dependence of the EMF.

Table 10
Temperatures and thermodynamic functions of phase transitions of $A^I_8B^{IV}X_6$ compounds

Compound	$T_{ph.tr.}$	$\Delta H_{ph.tr.}, kJ \cdot mol^{-1}$	$\Delta S_{n.n.}, J \cdot mol^{-1} \cdot K^{-1}$
Cu_8GeS_6	328	$5,1 \pm 2,4$	$15,5 \pm 7,5$
Cu_8GeSe_6	335	$11,9 \pm 2,8$	$35,5 \pm 8,4$
Ag_8GeSe_6	320	15.4 ± 4.7	46.9 ± 14.8
Ag_8SnSe_6	355	15.4 ± 4.3	43.4 ± 12.1

We also used EMF measurements of concentration cell of types (1) and (2) with solid electrolyte to control and refine the solid-phase equilibria diagrams considered in the dissertation of quasiternary and reciprocal systems and to determine the thermodynamic functions of solid solutions from stable sections consist of ternary compounds - formula analogs. The results obtained showed their reproducibility and high sensitivity of the EMF method to changes in both the phase compositions of alloys and the elemental composition of solid solutions.

As an example, let's consider the results of a thermodynamic study of solid solutions along the Cu_2GeS_3 - Ag_2GeS_3 section from the EMF measurements of concentration cells of type (1).

The compositions of the right electrodes were selected based on the arrangement of phase regions in the quaternary Cu-Ag-Ge-S system (Fig. 18). According to this scheme, the lines of radiation from the top of Cu (dotted lines) crossing the Cu_2GeS_3 - Ag_2GeS_3 section (squares) passing through the concentration tetrahedron reach the

lateral Ag-Ge-S ternary system in the three-phase region $\text{Ag}_2\text{GeS}_3+\text{GeS}_2+\text{S}$ (triangles in the darkened area). Given this, in cells (1), equilibrium alloys along the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ section prepared with a small excess of GeS_2 and S were used as right electrodes.

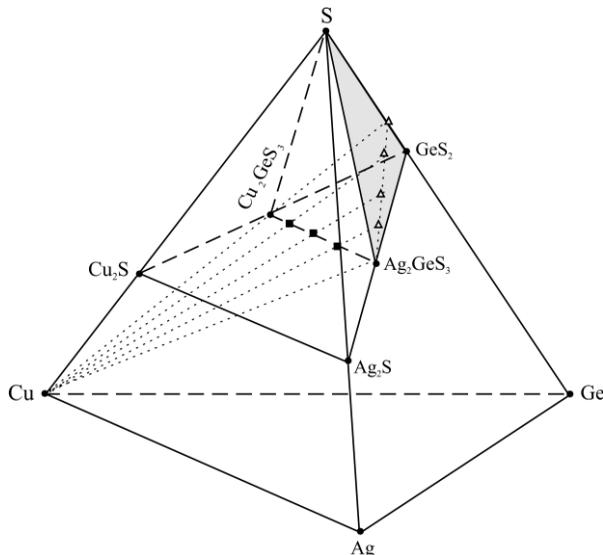


Fig. 18. Concentration tetrahedron Cu-Ag-Ge-S at experimental temperatures (300-380K). The darkened plane is the $\text{Ag}_2\text{GeS}_3+\text{GeS}_2+\text{S}$ three-phase region.

EMF measurements showed that in the regions of compositions <30 and >75 mol% Ag_2GeS_3 , the EMF isotherms at 300 and 380 K have the form of monotonic curves, and in the intermediate region they are horizontal (Fig. 19). This agrees with our data on the formation of wide regions of solid solutions based on the starting components in the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ system.

An analysis showed that the temperature dependences of the EMF that for all samples studied are almost linear. Therefore, the results of EMF measurements were processed in the approximation of their linear temperature dependence by the least square method and linear equations of the type (3) were obtained.

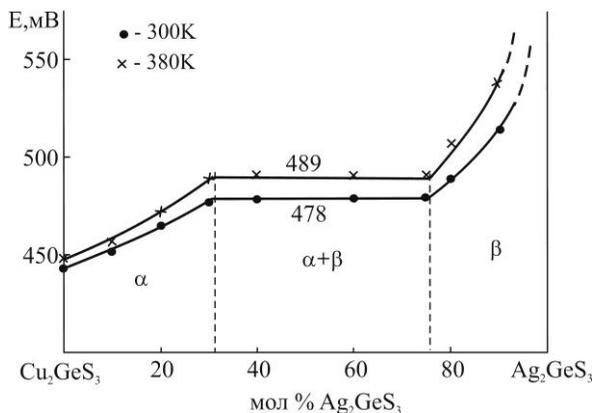


Fig. 19. Composition dependence of the EMF of concentration cells of type (1) at 300 and 380K for the alloys of the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ system

Table 11

Temperature dependences of EMF of concentration chains of type (1) for the alloys of the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ system ($T=300\text{-}380\text{K}$)

Composition, mol% Ag_2GeS_3	$E, \text{ mV} = a + bT + t \cdot S_E(T)$
Cu_2GeS_3	$436.2 + 0.024T \pm 2 \left[\frac{6.3}{28} + 5.9 \cdot 10^{-5} (T - 339.3)^2 \right]^{1/2}$
10	$436.6 + 0.051T \pm 2 \left[\frac{1.4}{24} + 3.4 \cdot 10^{-5} (T - 338.1)^2 \right]^{1/2}$
20	$438.1 + 0.085T \pm 2 \left[\frac{1.7}{24} + 4.3 \cdot 10^{-5} (T - 338.7)^2 \right]^{1/2}$
30	$438.0 + 0.129T \pm 2 \left[\frac{0.9}{24} + 3.0 \cdot 10^{-5} (T - 340.3)^2 \right]^{1/2}$
40-70	$438.8 + 0.131T \pm 2 \left[\frac{1.2}{24} + 3.2 \cdot 10^{-5} (T - 340.9)^2 \right]^{1/2}$
80	$433.2 + 0.192T \pm 2 \left[\frac{1.5}{24} + 3.5 \cdot 10^{-5} (T - 337.8)^2 \right]^{1/2}$
90	$443.4 + 0.234T \pm 2 \left[\frac{1.2}{24} + 3.1 \cdot 10^{-5} (T - 339.4)^2 \right]^{1/2}$

From the obtained equations of the temperature dependences of the EMF (Table 11), according to relations (4) - (6), the relative partial thermodynamic functions of copper in alloys at 298 K were calculated (Table 12).

Table 12

Relative partial molar functions of copper in the alloys of the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ system at 298 K

Composition, mol % Ag_2GeS_3	$-\overline{\Delta G}_{\text{Cu}}$	$-\overline{\Delta H}_{\text{Cu}}$	$\overline{\Delta S}_{\text{Cu}}$
	$\text{kJ}\cdot\text{mol}^{-1}$		$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Cu_2GeS_3	42.78±0.11	42.09±0.51	2.32±1.48
10	43.59±0.07	42.13±0.39	4.92±1.13
20	44.72±0.08	42.27±0.43	8.20±1.27
30	45.97±0.06	42.26±0.36	12.45±1.06
40-70	46.11±0.06	42.34±0.37	12.64±1.09
80	47.32±0.07	41.80±0.40	18.53±1.14
90	49.51±0.06	42.78±0.37	22.58±1.08

The concentration dependences of these functions at 298 K (Fig. 20) have the form characteristic for systems with the formation of limited solid solutions based on the starting compounds. Within the homogeneity region of α - and β -solid solutions based on Cu_2GeS_3 and Ag_2GeS_3 , respectively, the partial molar functions of copper are monotonic composition functions, and in the heterogeneous region $\alpha+\beta$ have constant values, since the compositions of the coexisting phases are almost constant.

With an increase in the silver content in solid solutions, a decrease in the Gibbs partial free energy and enthalpy and an increase in the partial entropy of copper occur.

Analysis of the concentration tetrahedron Cu-Ag-Ge-S (Fig. 18) allows one to determine potential-forming reactions for the ternary compound Cu_2GeS_3 and individual compositions of solid solutions $\text{Cu}_{2-x}\text{Ag}_x\text{GeS}_3$

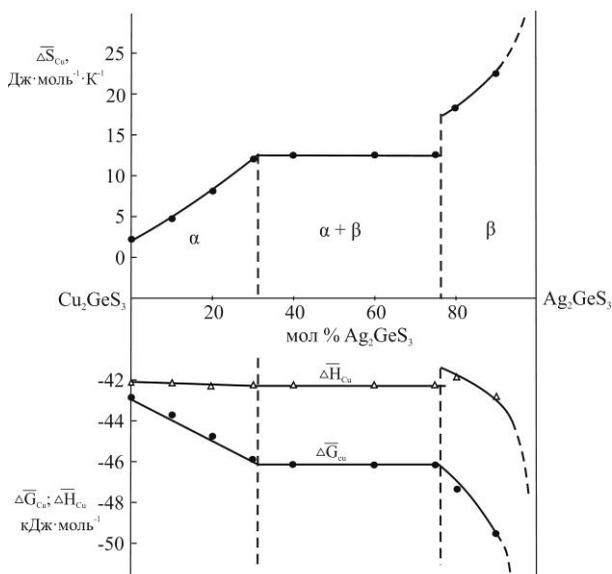
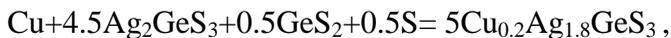


Fig. 20. Composition dependences of the partial thermodynamic functions of copper on composition in the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ system at 298 K.

It can be seen from Fig. 18 that the rays from Cu at the top of the tetrahedron passing through the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ section reach the concentration plane of the boundary ternary system Ag-Ge-S in the three-phase region $\text{Ag}_2\text{GeS}_3+\text{GeS}_2+\text{S}$. Therefore, the total potential-forming reaction for $\text{Cu}_{2-x}\text{Ag}_x\text{GeS}_3$ solid solutions should contain the phases of the indicated three-phase region and elemental copper. For example, for a solid solution of the composition $\text{Cu}_{0.2}\text{Ag}_{1.8}\text{GeS}_3$, the potential formation reaction has the form



and the relations for calculating its integral thermodynamic functions are

$$\Delta_f Z^0=0.2\overline{\Delta Z}_{\text{Cu}}+0.9\Delta_f Z^0(\text{Ag}_2\text{GeS}_3)+0.1\Delta_f Z^0(\text{GeS}_2)$$

$$S^0=0.2\overline{\Delta S}_{\text{Cu}}+0.2S^0(\text{Cu})+0.9S^0(\text{Ag}_2\text{GeS}_3)+0.1S^0(\text{GeS}_2)+0.1S^0(\text{S})$$

In a similar way, the integral thermodynamic functions of $\text{Cu}_{2-x}\text{Ag}_x\text{GeS}_3$ solid solutions were calculated for compositions $x = 0.4$;

0.6; 1.6; 1.8. Deviations were found by the accumulation of errors. The results are presented in the Table.13.

Table 13

Standard thermodynamic functions of formation and with standard phase entropies in the $\text{Cu}_2\text{GeS}_3\text{-Ag}_2\text{GeS}_3$ system

Composition	$-\Delta_f G^0(298\text{K})$	$-\Delta_f H^0(298\text{K})$	$S^0(298\text{K})$
	$\text{kJ}\cdot\text{mol}^{-1}$		$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
GeS_2 [лит]	125.7±2.0	127.9±1.3	87.45±2.09
Cu_2GeS_3	211.3±2.4	213.7±2.3	190.3±5.5
$(\text{Cu}_2\text{GeS}_3)_{0.9}(\text{Ag}_2\text{GeS}_3)_{0.1}$	212.2±2.1	210.7±2.2	199.9±5.2
$(\text{Cu}_2\text{GeS}_3)_{0.8}(\text{Ag}_2\text{GeS}_3)_{0.2}$	213.3±2.1	209.6±2.2	209.4±5.7
$(\text{Cu}_2\text{GeS}_3)_{0.7}(\text{Ag}_2\text{GeS}_3)_{0.3}$	214.0±2.1	208.2±2.2	219.1±5.8
$(\text{Cu}_2\text{GeS}_3)_{0.2}(\text{Ag}_2\text{GeS}_3)_{0.8}$	208.9±2.1	200.7±2.2	235.8±8.0
$(\text{Cu}_2\text{GeS}_3)_{0.1}(\text{Ag}_2\text{GeS}_3)_{0.9}$	207.4±2.1	199.6±2.2	238.3±8.3
Ag_2GeS_3 [лит]	206.0±2.1	198.0±2.2	239.1±8.8

In the calculations, we used the literature data on the corresponding standard integral thermodynamic functions of the Ag_2GeS_3 and GeS_2 compounds (Table 13) as well as the standard entropies of elemental copper and sulfur.

Table 14

Thermodynamic mixing functions during the formation of solid solutions from ternary compounds ($T = 298\text{ K}$)

Composition	$-\Delta G_m$	$-\Delta G_{\text{см}}^{\text{ид.р-р}}$	$-\Delta H_m$
	$\text{kJ}\cdot\text{mol}^{-1}$		
$(\text{Cu}_2\text{GeS}_3)_{0.9}(\text{Ag}_2\text{GeS}_3)_{0.1}$	1.96	0.81	-1.43
$(\text{Cu}_2\text{GeS}_3)_{0.8}(\text{Ag}_2\text{GeS}_3)_{0.2}$	3.06	1.24	-0.96
$(\text{Cu}_2\text{GeS}_3)_{0.7}(\text{Ag}_2\text{GeS}_3)_{0.3}$	4.29	1.51	-0.79
$(\text{Cu}_2\text{GeS}_3)_{0.2}(\text{Ag}_2\text{GeS}_3)_{0.8}$	1.84	1.24	-0.44
$(\text{Cu}_2\text{GeS}_3)_{0.1}(\text{Ag}_2\text{GeS}_3)_{0.9}$	0.87	0.81	0.0

By comparing the standard thermodynamic functions of the formation of solid solutions and the starting compounds Cu_2GeS_3 and Ag_2GeS_3 (Table 13), the Gibbs free energy of mixing and the heat of

mixing during the formation of solid solutions from ternary compounds are estimated (Table 14).

As can be seen from Table 14, the Gibbs free energy of mixing the starting ternary compounds during the formation of solid solutions has deeper negative values than the ideal binary solution, and the heat of mixing is close to zero.

At the end of chapter VI, some important results of thermodynamic research are presented:

- Our experiments showed that subject to well-known requirements for the EMF method, measurements lead to reproducible results. This is expressed in accordance of E-x diagrams with the nature of solid-phase equilibria diagrams: within the regions of phase homogeneity, the EMF is continuous compositional functions and in two-phase regions remain constant regardless of the total composition of the alloy;
- for all equilibrium samples, the temperature dependences are linear in the temperature ranges of EMF measurements. This confirms the constancy of phase compositions and compositions of coexisting phases in these temperature ranges and shows the validity of thermodynamic calculations based on them;
- for $A^I_8B^{IV}X_6$ compounds undergoing polymorphic transformations, the E-T dependences are two straight lines with a breakpoint at the transformation temperature. This made it possible to calculate the thermodynamic functions of polymorphic transitions of these compounds from the EMF data;
- The studied systems can be divided into 2 groups: 1) systems whose initial compounds contain only copper (or silver); 2) systems with Cu→Ag substitutions. In systems of the first type, the Gibbs partial free energy of the mobile component monotonically changes between the values for the initial compounds, and in systems of the second type, it increases with decreasing concentration of the mobile component and tends to infinity. This is in accordance with the provisions of the thermodynamics of solutions;

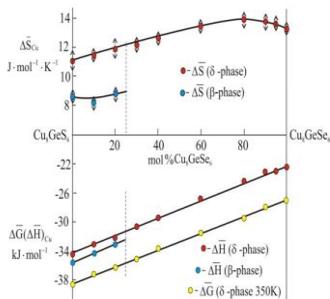
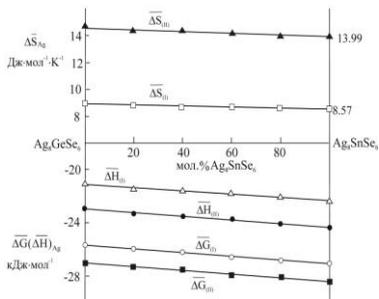
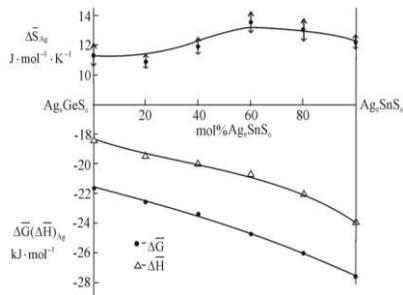
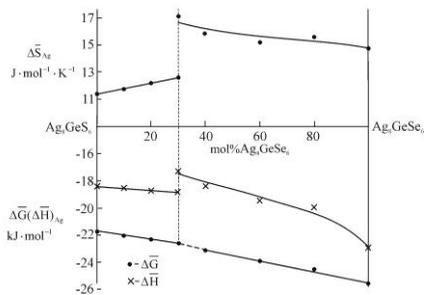
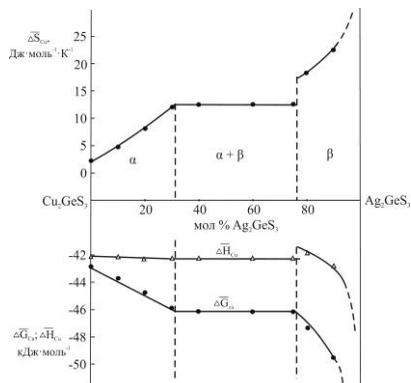
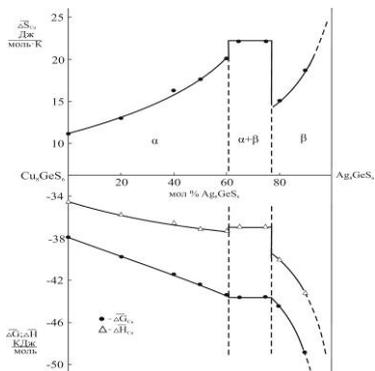


Fig.21. Comparison of the concentration dependences of PTF over various stable sections of the studied systems

- a comparative analysis of the curves of the concentration dependences of PTFs for various stable cross-sections (Fig. 21) shows their complete correspondence with phase diagrams. In systems with continuous series of solid solutions, all three PTFs are continuous compositional functions, and in systems, with limited solid solutions, they continuously change within the regions of phase homogeneity and remain constant in heterogeneous regions. At the boundaries of the phase regions, an abrupt change in the partial enthalpy and entropy is observed. This is especially pronounced for a structurally sensitive function — partial entropy.

MAIN RESULTS AND CONCLUSIONS

1. By the introduction of the EMF method with a solid cationic electrolyte into the traditional complex of experimental methods of physicochemical analysis, new complexes of mutually consistent data on phase equilibria and thermodynamic properties of the A', B^{IV}|| S, Se and Cu-Ag-Ge-X (A'-Cu, Ag; B^{IV}-Ge, Sn; X-S, Se) systems are obtained.
2. In the frame of the study of the above quaternary systems, phase equilibria in the Cu-Ge-Se and Ag-Ge-Se ternary systems were re-studied and some poly-thermal sections and isothermal sections of phase diagrams at room temperature were constructed, as well as projections of the liquidus surface. The fields of primary crystallization of phases, types, and coordinates of non- and monovariant phase equilibria are determined. The diagrams of the Cu₂X-GeX₂ quasi-binary systems are also refined.
3. For the first time, the character of the physicochemical interaction was established and complete schemes of phase equilibria were obtained, including a series of vertical and horizontal sections of phase diagrams and projections of liquidus surfaces, types and parameters of non- and monovariant equilibria for quasi-ternary Cu₂S-Ag₂S-GeS₂, Cu₂Se-Ag₂Se-GeSe₂, and ternary reciprocal systems $2\text{Cu}_2\text{S} + \text{GeSe}_2 \leftrightarrow 2\text{Cu}_2\text{Se} + \text{GeS}_2$, $\text{Cu}_2\text{S} + \text{SnSe}_2 \leftrightarrow 2\text{Cu}_2\text{S} + \text{SnS}_2$, $2\text{Ag}_2\text{S} + \text{GeSe}_2 \leftrightarrow 2\text{Ag}_2\text{Se} + \text{GeS}_2$.

4. It is shown that all four studied ternary reciprocal systems are reversibly reciprocal. Quasibinary or stable in the subsolidus are all of their sections between the isoformula compounds Cu_8GeS_6 - Cu_8GeSe_6 , $\text{Ag}_8\text{B}^{\text{IV}}\text{S}_6$ - $\text{Ag}_8\text{B}^{\text{IV}}\text{Se}_6$ and $\text{Cu}_2\text{B}^{\text{IV}}\text{S}_3$ - $\text{Cu}_2\text{B}^{\text{IV}}\text{Se}_3$. Quasiternary systems Cu_2X - Ag_2X - GeX_2 do not have the quasibinary sections. The sections between ternary compounds-analogs Cu_8GeX_6 - Ag_8GeX_6 and Cu_2GeS_3 - Ag_2GeX_3 stable below solidus. All of the above sections are characterized by the formation of continuous or wide areas of solid solutions.
5. It was established that the formation of solid solutions in the Cu_8GeX_6 - Ag_8GeX_6 and $\text{Ag}_8\text{B}^{\text{IV}}\text{S}_6$ - $\text{Ag}_8\text{B}^{\text{IV}}\text{Se}_6$ systems is accompanied by a significant decrease in the temperatures of polymorphic transitions of the starting compounds, which leads to stabilization of high-temperature ion-conducting cubic phases at room temperature.
6. Using the obtained data on phase equilibria, the solid solutions of a given composition were synthesized from the above sections, the types of their crystal structures were determined by powder x-ray diffraction, and the unit cell parameters were calculated. It is shown that changes in the lattice parameters of solid solutions obey Vegard's rule.
7. EMF measurements of concentration cells of types

$$(-) \text{Cu (s.)} | \text{Cu}_4\text{RbI}_3\text{Cl}_2 \text{ (s.)} | \text{Cu in the alloy (+)} \quad (1)$$

$$(-) \text{Ag (s.)} | \text{Ag}_4\text{RbI}_5 \text{ (s.)} | \text{Ag in the alloy (+)} \quad (2)$$
 for the above ternary and quaternary systems, allow calculating the partial molar Gibbs free energy, the enthalpy and entropy of copper or silver in alloys and, in particular, in solid solutions. An analysis of the concentration dependences of these functions graphs showed that they are in good agreement with the general scheme of the phase equilibria in the studied systems and made it possible to clarify the boundaries of phase regions on the solid-phase equilibrium diagrams over stable sections.
8. Based on the partial molar functions of copper and silver as well as the phase diagrams of the corresponding systems, the standard thermodynamic formation functions are calculated and the stand-

ard entropies of ternary compounds Cu_2GeS_3 , Cu_2GeSe_3 , Cu_2SnS_3 , AgSnSe_2 , Cu_8GeS_6 , Cu_8GeSe_6 , Ag_8GeSe_6 , and Ag_8SnSe_6 are calculated.

9. A procedure for calculations of the integral thermodynamic functions for four-component solid solutions from data on partial molar functions and a schematic phase diagram was developed, with the help of which mutually agreed sets of values of these functions for solid solutions are obtained for the stable sections of studied quaternary systems.
10. Based on the analysis of the obtained complexes of data on phase equilibria in the studied systems and literature data on similar systems, a number of schemes of the phase equilibria and phase formation in them are revealed. It was shown that in the reciprocal $\text{A}^{\text{I}}, \text{B}^{\text{IV}}\|\text{S}, \text{Se}$ and quasi-ternary $\text{Cu}_2\text{X}-\text{Ag}_2\text{X}-\text{GeX}_2$, $\text{A}_2^{\text{I}}\text{X}-\text{GeX}_2-\text{SnX}_2$ systems, sections composed of the isoformula $\text{A}_8^{\text{I}}\text{B}^{\text{IV}}\text{X}_6$ and $\text{A}_2^{\text{I}}\text{B}^{\text{IV}}\text{X}_3$ compounds are quasibinary or quasi-stable. The former are characterized by the formation of continuous solid solutions between high-temperature cubic modifications of the starting compounds and the different nature of the interaction between their low-temperature modifications. Continuous or wide areas of solid solutions are also formed in systems composed of $\text{A}_2^{\text{I}}\text{B}^{\text{IV}}\text{X}_3$ compounds. The presence of wide areas of solid solutions along the above-mentioned internal sections and a number of boundary quasibinary components play a main role in the formation of phase regions in the studied systems: all reciprocal systems are reversible, not diagonal sections are stable in them, but sections of types $\text{A}_8^{\text{I}}\text{B}^{\text{IV}}\text{S}_6-\text{A}_8^{\text{I}}\text{B}^{\text{IV}}\text{Se}_6$ and $\text{Cu}_2\text{B}^{\text{IV}}\text{S}_3-\text{Cu}_2\text{B}^{\text{IV}}\text{Se}_3$, dividing them into two subsystems that also do not have a stable diagonal. Similar sections connecting isoformule ternary compounds divide quasiternary systems into independent subsystems, the concentration trapezoid of which is also adiabonal. In all the studied systems, the concentration regions of primary crystallization and the existence of ternary compounds that do not have formula analogues in the system are strongly limited by phases of variable composition and heterogeneous regions formed by them.

The main results of the thesis are published in the following works:

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