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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

THERMODYNAMIC STUDY OF PHASE TRANSFORMATIONS OF COPPER AND SILVER ARGYRODITES AND SOME SOLID SOLUTIONS BASED ON THEM

Speciality:	2307.01 – Physical Chemistry
Field of science:	Chemistry
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GENERAL DESCRIPTION OF WORK

Relevance and degree of investigation of the topic. The development of many areas of science and technology, especially high technologies, is associated with the production and application of functional materials with unique properties, including new chalcogenide compounds and phases based on them.

In the last decade, researchers have shown a sharp increase in interest in environmentally friendly functional materials, including copper and silver-based chalcogenides. These compounds, along with their unique thermoelectric, photoelectric, optical, and other electronic properties, also have high ionic conductivity and are considered promising for applications as solid electrolytes, electrochemical sensors, and ion-selective electrodes. Currently, among the materials that are widely studied in this regard, argyrodite family compounds occupy a special place[1].

Numerous studies have shown that the application properties of these compounds can be significantly improved by changing their composition and structure[2]. A systematic and scientifically justified solution to this problem is largely due to the application of the thermodynamic approach. At the first stage of the process of creating new materials, this approach involves the study of phase equilibria in the relevant systems and the construction of their phase diagrams. The phase diagram not only shows the presence of new phases in the system but also allows us to determine the nature of their formation, areas of initial crystallization and homogeneity, phase transitions, etc. In order to optimize the technological parameters of the processes of synthesis of multicomponent phases and the growth of their single crystals, deeper thermodynamic analysis and thermodynamic

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[1] Babanly M.B., Yusibov Y. A., Imamaliyeva S.Z. Babanly D.M., Alverdiyev I.J. Phase Diagrams in the Development of the Argyrodite Family Compounds and Solid Solutions Based on Them. J. Phase Equilib. Diffus. 45, 228–255 (2024)

[2] S. Lin, W. Li, Y. Pei, Thermally insulative thermoelectric argyrodites, Mater. Today, 2021, 48, p 198-213

calculations are required. This is impossible without reliable data on the fundamental thermodynamic functions of the relevant substances. Analysis of the literature data shows that certain successes have been achieved in the study of phase equilibria in systems based on copper and silver chalcogenides, including systems containing argyrodite compoundsr[1,3]. However, there are very few studies on the fundamental thermodynamic properties of these phases, especially in the field of thermodynamics of their polymorphic transformations. Only a few compounds have been indirectly calculated by the electromotive force (EMF) method. Such studies using more precise methods such as calorimetry, including differential scanning calorimetry (DSC), are almost non-existent.

The above-mentioned shows that studies on the preparation and study of thermodynamic properties of argyrodite family compounds and various substitutional solid solutions based on them are very relevant.

Object and subject of research. The objects of research of the dissertation work are compounds of the argyrodite family and solid solutions based on them. The subject of the research was the determination of the thermodynamic functions of polymorphous transformation of these phases and the study of phase equilibria in some systems.

The aim and tasks of the study. The main goal of the dissertation work was to determine the thermodynamic functions of polymorphous transformation of compounds with the general formula $A^{I}_{8}B^{IV}X_6$ (A^{I}-Cu, Ag; B^{IV}-Si, Ge, Sn; X-S, Se) by the DSC method, as well as to obtain and thermodynamically study new argyrodite phases in the Cu_2X-Cu_8SiX_6-Cu_8GeX_6 systems.

To achieve this aim, the following specific issues were set and resolved:

- determination of the thermodynamic functions of polymorphic transformations of $A_8B^{IV}X_6$ type compounds by the DSC method;

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[3] Ivanchenko M., Jing H. Smart Design of Noble Metal–Copper Chalcogenide Dual Plasmonic Heteronanoarchitectures for Emerging Applications: Progress and Prospects. // Chemistry of Materials, 2023, v.35(12), p. 4598-4620

- determination of phase equilibria in the Cu_2X-Cu_8SiX_6-Cu_8GeX_6 systems, construction of a number of polythermal and isothermal sections of their T-x-y diagrams, as well as projections of liquidus surfaces;
- individual preparation and characterization of $Cu_8Si_{1-x}Ge_xX_6$ solid solutions in the studied systems;
- thermodynamic study of polymorphic transformations of continuous substitution solid solutions formed in the Cu_8SiS_6-Cu_8GeS_6 system.

Research methods. Thermodynamic studies of polymorphic transformations were carried out by differential scanning calorimetry (DSC). Differential thermal analysis (DTA), X-ray phase analysis (XFA), and scanning electron microscopy (SEM) were used to study phase equilibria. DSC studies of phase transitions of samples were carried out using aluminum crucibles with lids in a Linseis DSC400 differential scanning calorimeter. DTA curves were recorded in evacuated quartz ampoules in a multi-channel DTA device assembled based on an electronic data recorder "TC-08 Thermocouple Data Logger". Powder diffractograms were recorded on D8 ADVANCE and D2 Phaser devices of the German company Bruker and analyzed with their computer software. SEM images were obtained using a JEOLJSM-7600F scanning electron microscope.

Provisions submitted for defense:

- New schemes of phase equilibria in the Cu_2X-Cu_8SiX_6-Cu_8GeX_6 systems, several vertical and isothermal sections of T-x-y diagrams, and projections of liquidus surfaces.
- Substitutional solid solutions discovered in the studied systems, their initial crystallization surfaces from the alloy, homogeneity areas, and crystallographic indicators.
- Thermodynamic functions of polymorphous transformation of $A_8B^{IV}X_6$ type compounds and $Cu_8Si_{1-x}Ge_xX_6$ solid solutions.

The scientific novelty of the research. The following new scientific results were obtained in the dissertation work:

- Phase equilibria schemes of Cu-Si-Ge-X (X-S, Se) composition tetrahedra along the Cu_2X-Cu_8SiX_6-Cu_8GeX_6 solid planes were determined, a number of polythermal and isothermal sections of the T-x-y phase diagrams of both systems, as well as projections of liquidus surfaces were constructed;

- Continuous solid solution series were found between the high-temperature modifications of the initial compounds along the Cu_8SiX_6-Cu_8GeX_6 sides of the studied systems. It was found that low-temperature modifications also form continuous solid solutions in the sulfide system, and in the selenide system there are wide solubility areas based on them;
- Thermodynamic functions of polymorphic transformations of 8 compounds of the $A_8^IB^{IV}X_6$ type belonging to the argyrodite family and $Cu_8Si_{1-x}Ge_xX_6$ (x=0.2; 0.4; 0.6; 0.8) solid solutions were determined by the DSC method. It is shown that the heat and entropy of polymorph transformation of all these compounds have anomalously high values compared to the usual polymorph transformations of chalcogenides, and this is because during these transformations, unlike usual polymorph transformations, more serious changes occur in the crystal lattice and a sharp increase in order in the cation sublattice.
- It was found that the enthalpies and entropies of polymorph transformation of solid solutions vary linearly depending on the composition, that is, within the error, the heat and entropy of phase transitions of solid solutions are equal to the sum of the corresponding functions of the initial compounds. This indicates that $Si \rightarrow Ge$ substitutions in these solid solutions are athermal processes, that is, these solutions can be characterized as quasi-ideal.

The theoretical and practical significance of the research. The *new scientific results* obtained in the work, including a complex of new mutually adjusted results related to phase equilibria in the Cu_2X-Cu_8SiX_6-Cu_8GeX_6 systems, as well as the thermodynamic functions of polymorphic transformations of $A_8^IB^{IV}X_6$-type compounds and $Cu_8Si_{1-x}Ge_xS_6$ solid solutions, are a contribution to the chemistry, thermodynamics, and materials science of argyrodite family compounds. The *practical significance* of the obtained results is because the new phases discovered in the studied systems are of great interest as potentially environmentally safe functional materials. The phase diagrams, crystallographic and thermodynamic properties of compounds, and solid solutions presented in the work are necessary information for their preparation and modification. They can also be included in modern electronic databases and reference books as fundamental characteristics of substances.

According to the international electronic database "Google Scholar Citations", 10 references were made to the author's two published articles on the topic of his dissertation.

Approbation and application of the work. 17 scientific works have been published on the topic of the dissertation, including 6 articles in journals indexed in WoS and SCOPUS databases.

The main results of the thesis were discussed at the following conferences: "Müasir təbiət və iqtisad elmlərinin aktual problemləri" beynəlxalq konfrans (Gəncə, Azərbaycan, 2019, 2021, 2023); XII International conference ”Electronic Processes in organic and Inorganic Materials” (Kamianets-Podilskye, Ukraine, 2020); 9th Rostocker International Conf.: THERMAM (Rostock, Germany, 2020); “Kimyanin müasir problemləri” Respublika elmi konfransı (Sumqayıt, Azərbaycan, 2021); IX Всероссийской конференции "Физико-химические процессы в конденсированных средах и на межфазных границах" (Воронеж, Россия, 2021); Международная научная конференция "Кинетика и механизм кристаллизации. Кристаллизация и материалы нового поколения" (Иваново, Россия, 2021,2023); XXIII International Conference on Chemical Thermodynamics (Kazan, Russia, 2022); 2nd International Scientific Conference “Research Retrieval and Academic Letters” (Warsaw, Poland, 2023).

The results obtained in this work on phase equilibria and thermodynamic properties constitute the scientific basis for the directed synthesis of the corresponding compounds and solid solutions and can be used by specialists working in the field of materials science. The results of the work can also be used in the educational process at the master's and doctoral levels of higher education institutions of the republic.

The name of the organization in which the work was carried out. The dissertation work was carried out at the "Inorganic

Materials" Department of the Institute of Catalysis and Inorganic Chemistry named after M. Nagiyev of the Ministry of Science and Education of the Republic of Azerbaijan.

The total volume of the dissertation with a mark, indicating the volume of the structural sections of the dissertation separately. The dissertation (188697 characters) consists of an introduction (12837 characters), four chapters (first chapter – 47422 characters, second chapter – 42369 characters, third chapter - 37354 characters, fourth chapter - 48694 characters), main conclusions (2961 characters) and a list of used 228 scientific literature. The dissertation includes 61 figures and 15 tables.

MAIN CONTENT OF THE WORK

The **first chapter** of the dissertation provides and interprets literature data on the crystal-chemical, thermal, thermodynamic, etc. properties of the initial compounds of the studied systems, as well as phase equilibria in boundary quasi-binary systems. This data was used in the organization of experimental studies on the topic of the dissertation and the analysis of their results.

Here, new literature data on the functional properties of compounds of the argyrodite family are presented and analyzed, and the current state of research on multicomponent systems that form argyrodite-type phases is examined. Based on this data, the selection of research objects for the dissertation work is justified.

The **second chapter** gives a brief description of the main synthesis methods of metal chalcogenides and describes the methods and conditions for obtaining the initial compounds and alloys of the studied systems.

The initial binary and ternary compounds were synthesized by co-melting simple substances of high purity in stoichiometric ratios in quartz ampoules under vacuum conditions (10^{-2}Pa). Since the saturated vapor pressures of sulfur and selenium at the melting temperatures of the compounds are high, their synthesis was carried out in an inclined two-zone furnace. The individuality of the synthesized compounds was confirmed by XRD and DTA methods.

The alloys of the studied systems with different compositions were prepared by co-melting the synthesized and identified binary and ternary compounds in the required proportions in quartz ampoules under vacuum conditions. To bring the samples to equilibrium, they were kept at 800 K for 500 hours and gradually cooled in an oven disconnected from the current source. The samples intended for the study of high-temperature regions of the phase diagrams were additionally kept at the required temperatures for ~200 hours and then annealed by dropping the ampoules directly from the oven into ice water.

Information on the experimental research methods and relevant equipment used in the work is presented in the relevant section of the introduction to the abstract.

The **third chapter** presents the results of the study of phase equilibria and some physicochemical properties of intermediate phases in the Cu_2X-Cu_8SiX_6-Cu_8GeX_6 (X-S, Se) systems.

Phase equilibria in the Cu_2S-Cu_8SiS_6-Cu_8GeS_6 system [9, 13].

Cu_8SiS_6-Cu_8GeS_6 boundary system. Table 1 shows the results obtained from the thermal DTA curves of the samples of this system that were thermally treated at 800 K for 500 hours and then gradually cooled, and Fig.1 shows the T-x phase diagram constructed based on them. It can be seen from the figure that the system is characterized by the formation of unbounded solid solutions between both crystalline modifications of the initial compounds. Due to the incongruent melting nature of the Cu_8GeS_6 compound, this system is non-quasi-binary as a whole, and there is a small initial crystallization area of HT-Cu_2S in the phase diagram. It can be seen from the phase diagram that, despite the close polymorph transformation temperatures of the Cu_8GeS_6 (336 K) and Cu_8SiS_6 (330 K) compounds, no extremum point is observed in the $\gamma \rightarrow \delta$ phase equilibria curves. The absence of extremum points in both the liquidus and solidus curves, as well as in the polymorphic transition curves, therefore indicates that the nature of the interaction between compounds in the liquid solutions of this system, as well as in the γ- and δ- solid solutions, does not deviate sharply from ideality, and allows these solutions to be characterized as "quasi-ideal solutions".

Table 1 [1, p.9; 13, p.512]

DTA data for alloys of the Cu_8SiS_6-Cu_8GeS_6 system

Composition, mol% Cu_8GeS_6	Thermal effects, K
0 (pure Cu_8SiS_6)	336; 1460
20	335; 1415
40	334; 1374-1390
60	333; 1330-1348
80	332; 1282-1303
90	330; 1270
100	330; 1253; 1285

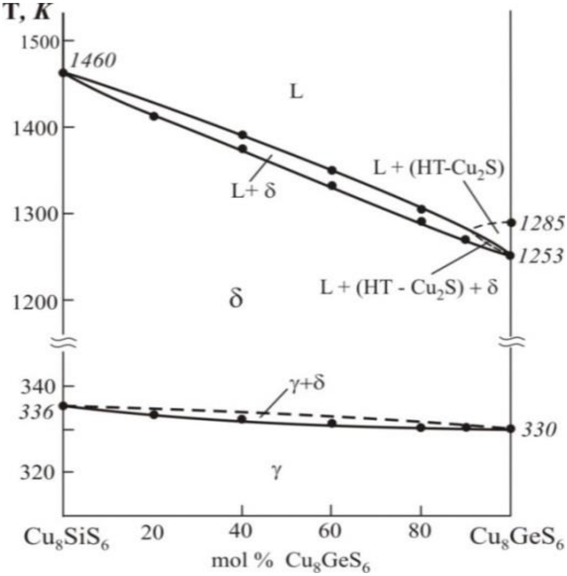


Fig.1. Phase diagram of the Cu_8SiS_6-Cu_8GeS_6 system [13, p.512]

The constructed phase diagram is fully confirmed by X-ray diffraction data. XRD analysis data confirming the formation of a continuous solid solution sequence between low-temperature modifications of the starting compounds are presented in Fig. 2.

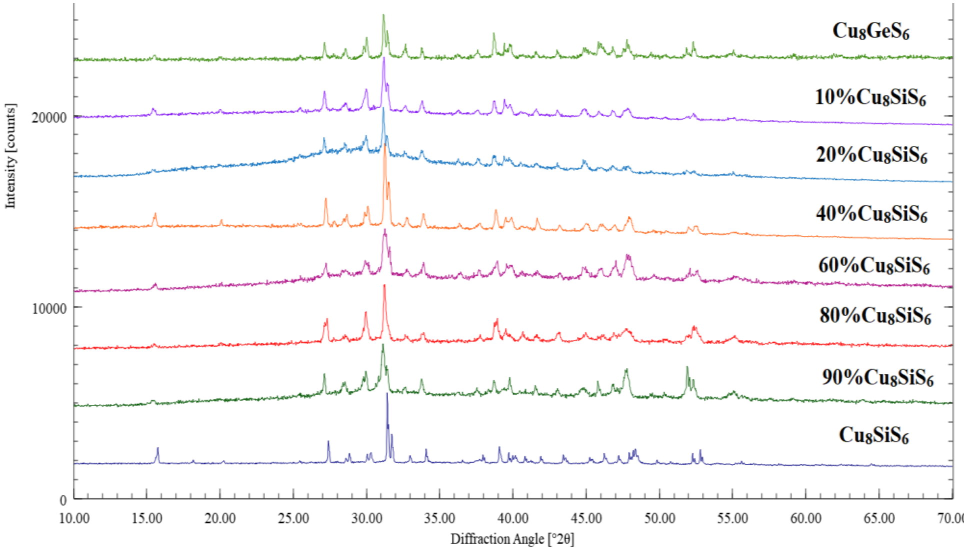


Fig. 2. Powder diffractograms of slowly cooled samples of the Cu_8SiS_6-Cu_8GeS_6 system after thermal treatment[10, p.278]

XRD analysis of heat-treated samples shows unlimited mutual solubility of high-temperature modifications. Fig.3 shows the powder diffractogram of a sample with a 60 mol% Cu_8GeS_6 composition as an example. As can be seen, the sample has a diffraction pattern characteristic of the cubic system, and all reflection lines are indexed in the cubic structure (Sp.gr. $F43m$).

Table 2 lists the crystal lattice types and parameters of solid solutions for both low-temperature and high-temperature modifications. Based on these quantities, graphs of the dependence of lattice parameters on composition were constructed (Fig. 4). It can be seen from the graphs that in both series of solid solutions, the lattice parameters are linear functions of composition, i.e., Vegard's rule is satisfied.

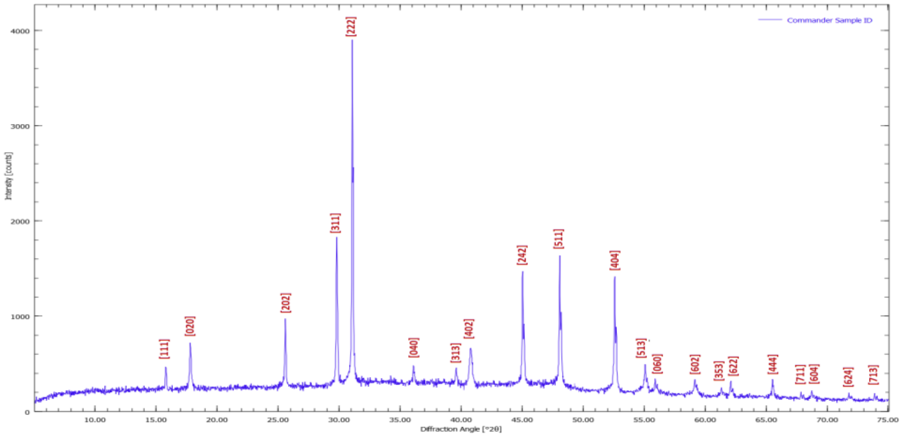


Fig. 3. Powder diffractogram of a sample with 60 mol% Cu_8GeS_6 composition annealed at 800 K. [13, p.512]

Table 2[13, p.513]
Types and parameters of the crystal lattice for $Cu_8Si_{1-x}Ge_xS$ solid solutions

Composition	Crystal lattice parameters, Å			
	LT (Ortorhombic; Sp.gr *Pmn2₁*)			HT (cubic; Sp.gr. F*43m*)
	a	*b*	*c*	*a*
Cu_8GeS_6	7.0442	6.9690	9.8726	9.9572
$Cu_8Si_{0.1}Ge_{0.9}S_6$	7.0408	6.9668	9.8691	
$Cu_8Si_{0.2}Ge_{0.8}S_6$	7.0395	6.9603	9.8603	9.9194
$Cu_8Si_{0.4}Ge_{0.6}S_6$	7.0287	6.9485	9.8378	9.8783
$Cu_8Si_{0.6}Ge_{0.4}S_6$	7.0226	6.9387	9.8296	9.8479
$Cu_8Si_{0.8}Ge_{0.2}S_6$	7.0169	6.9279	9.7990	9.8068
$Cu_8Si_{0.9}Ge_{0.1}S_6$	7.0097	6.9111	9.7732	
Cu_8SiS_6	6.9940	6.8994	9.7671	9.7615

Solid-phase equilibria at 300 K. Based on XRD and SEM-EDS data for a series of equilibrium alloys within the Cu_2S-Cu_8GeS_6-Cu_8SiS_6 composition triangle as well as phase diagrams of boundary quasi-binary systems, a solid-phase equilibria diagram at 300 K was constructed (Fig. 5).

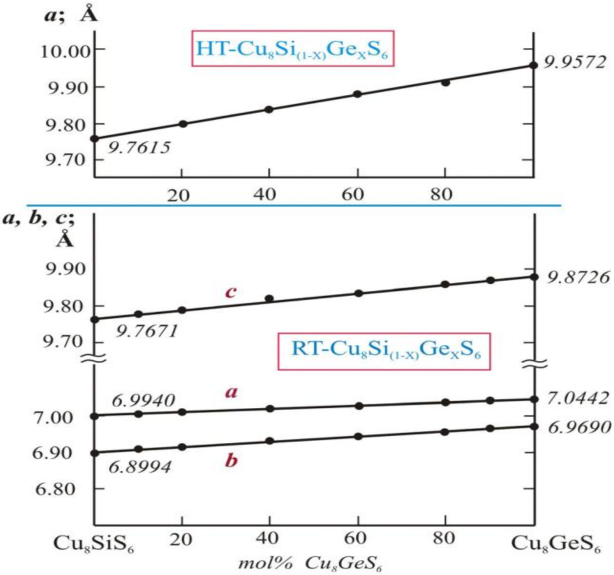


Fig. 4 Composition dependence of crystal lattice parameters of the $Cu_8Si_{1-x}Ge_xS$ solid solutions [13, p. 513]

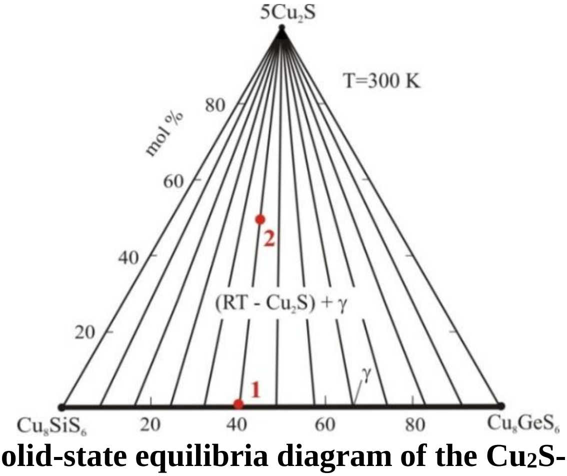


Fig. 5. Solid-state equilibria diagram of the Cu_2S-Cu_8SiS_6-Cu_8GeS_6 system at 300 K

The presence of continuous solid solutions (γ-phase) in the Cu_8SiS_6-Cu_8GeS_6 side system of the composition triangle and the absence of other phases in this triangle leads to the formation of a two-phase γ+(RT-Cu_2S) field in the system. The presence of radial tie-lines emanating from the Cu_2S vertex of the composition triangle was confirmed by the XRD method. Fig.6 shows the powder diffractograms of the alloys 1-($Cu_8Si_{0.6}Ge_{0.4}S_6$) və 2-($0.5Cu_8Si_{0.6}Ge_{0.4}S_6+Cu_2S$) shown in the phase diagram (Fig.5). As can be seen, the diffraction pattern of sample 1 reflects the diffraction lines of the Cu_8SiS_6 compound, which are characteristic of solid solutions (γ-phase) and have a certain shift. The diffractogram of alloy 2 consists of the sum of the diffraction reflection lines of the low-temperature modification of the Cu_2S compound and the γ-phase. It should be noted that the crystal lattice parameters of this sample, calculated by us in the orthorhombic system, coincide with the crystal lattice parameters of the solid solution sample with composition $Cu_8Si_{0.6}Ge_{0.4}S_6$. This is experimental evidence of the radial character of the tie-lines in the Cu_2S+γ two-phase field.

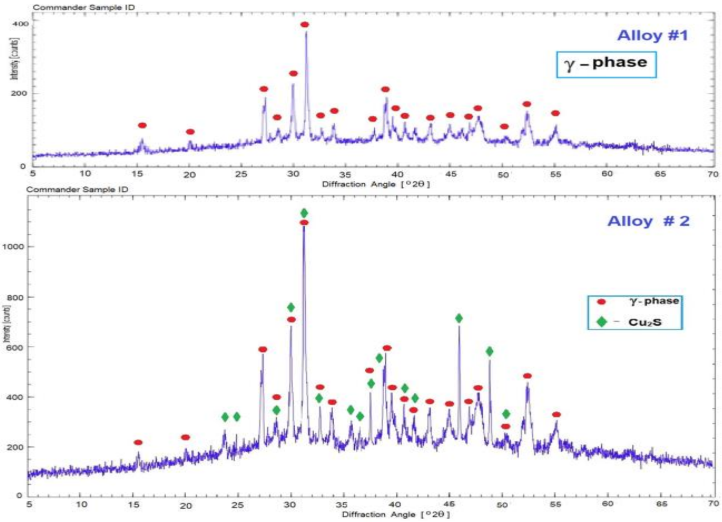
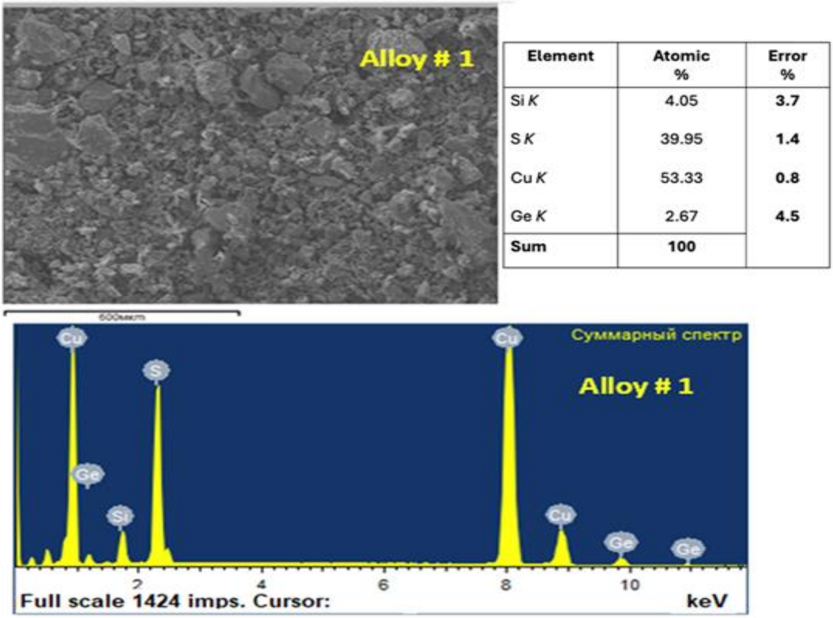


Fig. 6. Powder diffractograms of alloys 1-($Cu_8Si_{0.6}Ge_{0.4}S_6$) və 2-($0.5Cu_8Si_{0.6}Ge_{0.4}S_6+Cu_2S$) on the phase diagram (Fig. 5) [13, p.514]

SEM-EDS analysis of various samples of the Cu_8SiS_6-Cu_8GeS_6 system confirmed their single-phase nature. For example, Fig. 7 shows an SEM image of a phase containing 40 mol% Cu_8GeS_6 (sample 1). As can be seen, the sample is single-phase, and its elemental composition corresponds to the formula $Cu_8Ge_{0.39}Si_{0.61}S_6$ i.e., it practically coincides with the nominal composition of the sample.



Element	Atomic %	Error %
Si *K*	4.05	**3.7**
S *K*	39.95	**1.4**
Cu *K*	53.33	**0.8**
Ge *K*	2.67	**4.5**
Sum	**100**	

Fig. 7. Results of SEM-EDS analysis of the 1-($Cu_8Si_{0.6}Ge_{0.4}S_6$) sample on the phase diagram (Fig.5)[13, p.515]

Projection of the liquidus surface. The projection of the liquidus surface of the Cu_2S-Cu_8SiS_6-Cu_8GeS_6 system (Fig. 8) consists of 2 areas corresponding to the initial crystallization of δ- and α- solid solutions based on the HT- $Cu_8Si_{1-x}Ge_xS_6$ and HT-Cu_2S phases. These areas are bounded by a monovariant eutectic ($L\leftrightarrow\alpha+\delta$) eK curve, at the K transition point the eutectic equilibrium passes into the peritectic equilibrium ($L+\alpha\leftrightarrow\delta$). After this transition point, the peritectic curve extends to the peritectic point of the Cu_8GeS_6

compound in the Cu_2S-GeS_2 system. However, since this part of the curve is located outside the studied composition triangle, it is not reflected in Fig. 8.

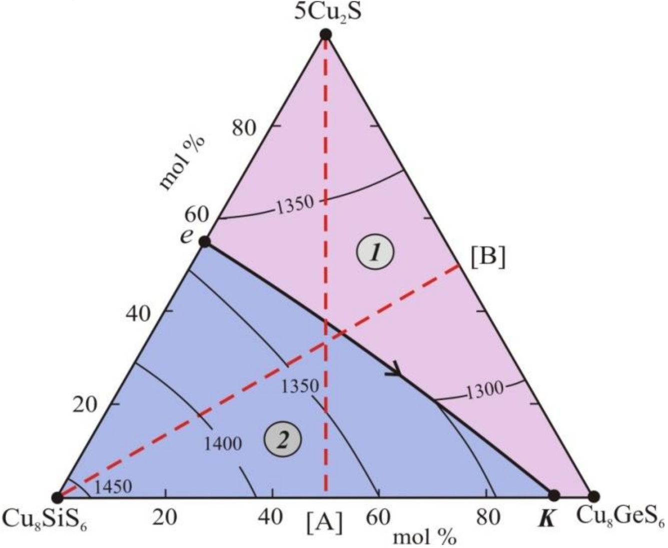


Fig. 8. Projection of the liquidus surface of the Cu_2S-Cu_8SiS_6-Cu_8GeS_6 system. Initial crystallization areas: 1- α; 2- δ [13, p. 515]

Thus, although the Cu_2S-Cu_8SiS_6-Cu_8GeS_6 system is stable over a wide range of concentrations, it is not quasi-ternary as a whole. This is due to the absence of the composition of one of the phases (α-phase) in equilibrium on the Cu_8SiS_6-Cu_8GeS_6 cross-section to the right of the transition point K on that cross-section.

Isothermal sections of the phase diagram at 1300 and 1350 K. Isothermal sections of the volume phase diagrams allow us to determine the homogeneity regions of the phases at given temperatures and their compositions in heterogeneous regions where they are in equilibrium with each other, including the location of tie-lines in two-phase regions. This information is of great importance, especially for the growth of single crystals of solid solutions with a given composition, where the directions of the connodes are given, from a liquid solution by the method of directional crystallization.

The isothermal sections presented below were constructed using the corresponding isotherms on the projection of the liquidus surface of the Cu_2S-Cu_8SiS_6-Cu_8GeS_6 system, as well as the phase diagram of the studied Cu_8SiS_6-Cu_8GeS_6 boundary system and the vә Cu_2S-[A] and Cu_8SiS_6-[B] polythermal sections

The isothermal cross section at 1350 K (Fig. 9) consists of a wide liquid region, as well as two-phase regions where the liquid phase is in equilibrium with the α-phase based on HT-Cu_2S and with the δ-phase based on HT-Cu_8SiS_6. As can be seen from Fig. 9, the homogeneity region of the α-phase covers the concentration interval of 2-3 mol% near the Cu_2S vertex of the concentration triangle. The homogeneity region of the δ-phase based on the argyrodite compound is in the form of a strip with a thickness of 1-2 mol% along the Cu_8SiS_6-Cu_8GeS_6 boundary system. The direction of the tie-lines in the L+δ two-phase region allows us to determine the compositions of the liquid and solid solutions in equilibrium. For example, the endpoints of the tie-line *ls* in the figure correspond to the compositions of the liquid phase (*l*) and the solid phase (*s*) in equilibrium with it. These data allow us to choose the composition of the liquid solution for growing solid solution crystals of the required composition.

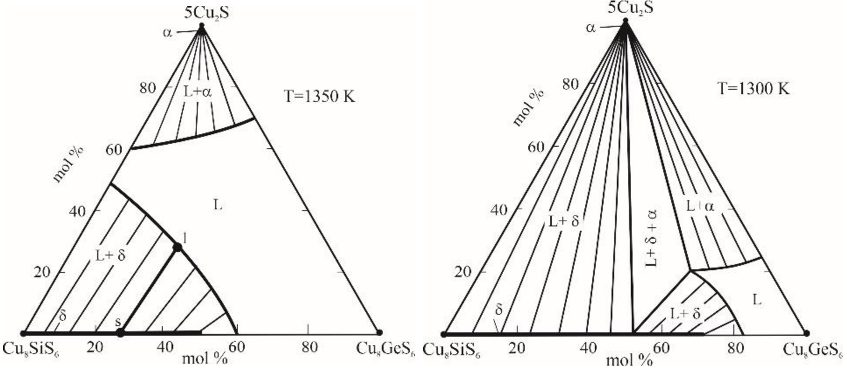


Fig 9. Isothermal sections of the phase diagram at 1300 and 1350 K

The isothermal section at 1300 K (Fig. 9). A decrease in temperature by only 50^0 leads to a sharp change in the character of phase equilibria in the system. As can be seen from the diagram, the homogeneous liquid area has decreased many times compared to 1350 K. Accordingly, the isotherms showing the composition of the liquid phase in the $L \leftrightarrow \alpha$ and $L \leftrightarrow \delta$ equilibria have also decreased significantly and merged. The intersection point of these isotherm curves reflects the $L \leftrightarrow \alpha+\delta$ equilibrium. Since the temperature is constant, this equilibrium is nonvariant. The three-phase area $L+\alpha+\delta$ on the phase diagram corresponds to it. The other two vertices of this elementary triangle indicate the compositions of the α- and δ- solid solutions in equilibrium with the liquid phase. More than 50% of the total area of the composition triangle of the phase diagram is occupied by the $\alpha+\delta$ two-phase area in the system. This area reflects the subsolidus area of the system.

Phase equilibria in the Cu_2Se-Cu_8SiSe_6-Cu_8GeSe_6 system

Cu_8SiSe_6-Cu_8GeSe_6 boundary system. The phase diagram constructed based on the DTA results of the equilibrated samples of this system is given in Fig.10. The system is characterized by the formation of continuous solid solutions (δ-phase) based on high-temperature modifications of the initial compounds. Wide solubility ranges are observed based on low-temperature modifications of the initial compounds. At room temperature, the solubility is ~50 mol% (γ_1-phase) based on the Cu_8SiSe_6 compound, and 15 mol% (γ2-phase) based on the Cu_8SiSe_6 compound. Due to the incongruent melting of the latter compound, the system is non-quasi-binary as a whole.

The constructed phase diagram was confirmed by XRD analysis. Fig.11 presents powder diffractograms of some alloys of the Cu_8SiSe_6-Cu_8GeSe_6 system after thermal treatment at 800 K. As can be seen, the diffraction patterns of alloys with a content of 20 and 40 mol% Cu_8GeSe_6 are qualitatively identical to the diffraction pattern of the Cu_8GeSe_6 compound. On the other hand, the diffraction pattern of the alloy with a content of 90 mol% Cu_8GeSe_6 is almost identical to that of the Cu_8GeSe_6 compound. The diffraction peaks of intermediate alloys (40 and 60 mol% Cu_8GeSe_6) consist of the sum of the reflection spectra of the initial compounds. With an increase in the concentration of silicon in the alloys, a slight shift of the diffraction peaks towards larger angles is observed. This is due to a decrease in the values of their lattice parameters.

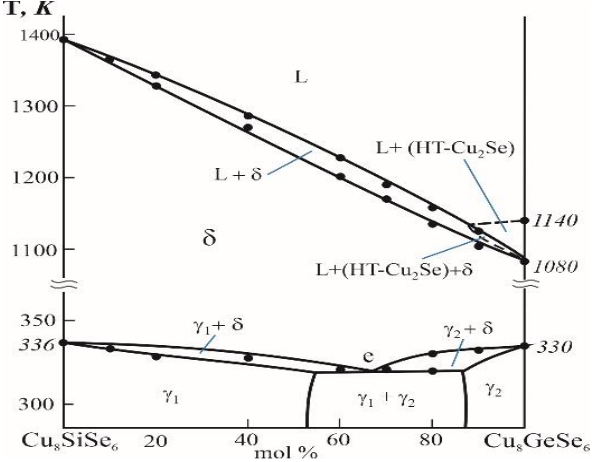


Fig.10.Phase diagram of the Cu_8SiSe_6-Cu_8GeSe_6 system {6, p.1613]

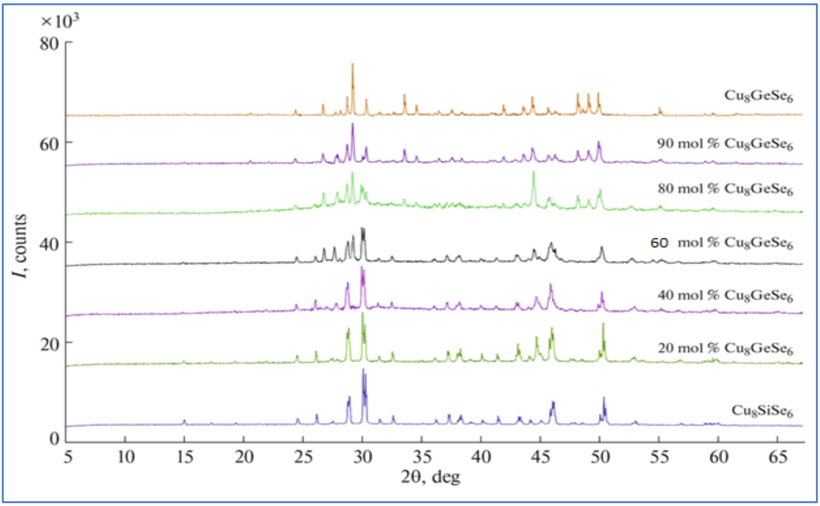


Fig. 11. Powder diffractograms of slowly cooled samples of the Cu_8SiSe_6-Cu_8GeSe_6 system after thermal treatment.[6, p.1614]

XRD of alloys quenched from 800 K confirms the unlimited mutual solubility of high-temperature modifications of the initial compounds.

Based on the XRD data, the crystallographic parameters of the initial compounds and $Cu_8Si_{1-x}Ge_xSe_6$ solid solutions for both modifications were calculated (Table 3). Analysis of the powder diffraction patterns of the alloys of the low-temperature modification showed that the reflection lines of the alloys with a content of 20 and 40 mol% Cu_8GeSe_6 are fully indexed in the orthorhombic structure of the initial RT- Cu_8GeSe_6 phase (Sp.gr. *Pmn*21). The diffractogram of the alloy with a content of 90 mol% Cu_8GeSe_6 is fully indexed in the hexagonal structure of pure RT- Cu_8GeSe_6 (Sp. gr. *P*63*mcm*). For alloys with intermediate compositions, diffraction lines of both hexagonal and orthorhombic (γ_2) phases are observed. It should be

Table 3[6, p.1616]

Crystal lattice types and parameters of the $Cu_8Si_{1-x}Ge_xSe_6$ solid solutions

Phase	Crystal lattice parameters, Å				
	Room temperature modification				Quenched from 800 K, cubic singony, Sp.gr. *F43m*
	Singony, Sp.gr.	*a*	*b*	*c*	*a*, Å
Cu_8GeSe_6	Heksaqon $P6_3mcm$	12.6428(5)		11.7549(4)	10.2103(5)
$Cu_8Si_{0.1}Ge_{0.9}Se_6$	Heksaqon *P63mcm*	12.6395(2)		11.7517(7)	
$Cu_8Si_{0.2}Ge_{0.8}Se_6$	Ikifazalı qarışıq $\gamma_1+\gamma_2$				10.2031(1)
$Cu_8Si_{0.4}Ge_{0.6}Se_6$	Ikifazalı qarışıq $\gamma_1+\gamma_2$				10.1957(3)
$Cu_8Si_{0.6}Ge_{0.4}Se_6$	Ortoromb $Pmn2_1$	7.2870(1)	7.2156(8)	10.2172(3)	10.1868(7)
$Cu_8Si_{0.8}Ge_{0.2}Se_6$	Ortoromb $Pmn2_1$	7.2818(5)	7.2107(2)	10.2111(5)	10.1812(1)
Cu_8SiSe_6	Ortoromb $Pmn2_1$	7.2769(4)	7.2056(5)	10.2052(6)	10.1753

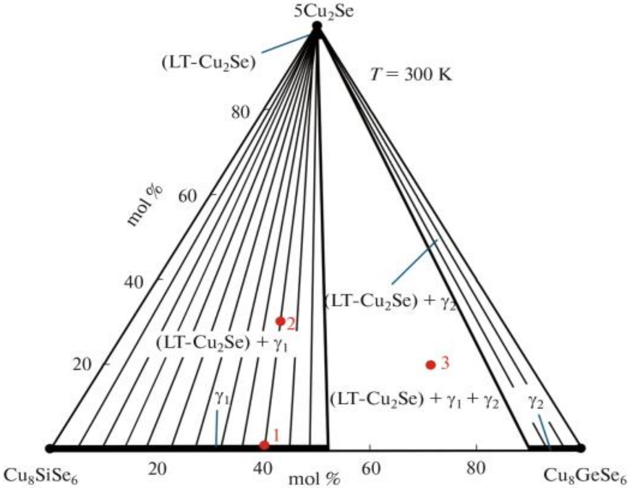


Fig. 12. Solid-state equilibria diagram at 300 K of the Cu_2S-Cu_8SiSe_6-Cu_8GeSe_6 system[12, p.1615]

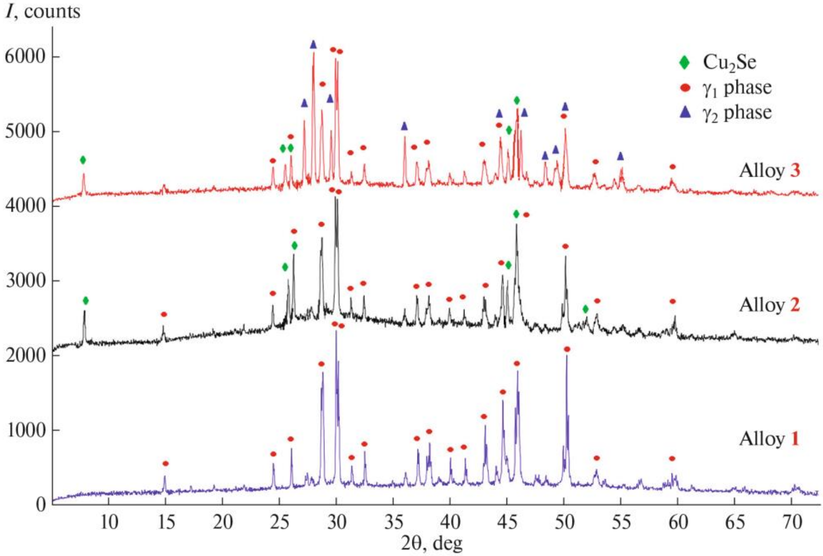


Fig. 13. Powder diffractograms of alloys No. 1, 2, and 3 are shown in the phase diagram (Fig. 12) [12, p.1616]

noted that it is difficult to use lattice parameter plots as a function of composition to determine the homogeneity regions of these phases since the lattice parameters change very little during Si↔Ge substitutions.

Solid-phase equilibria at 300 K. Based on the XRD and SEM-EDS data for several equilibrium alloys from the Cu_2Se-Cu_8SiSe_6-Cu_8GeSe_6 composition triangle and the phase diagrams of the boundary quasi-binary systems, a solid-state equilibria diagram of the Cu_2S-Cu_8SiSe_6-Cu_8GeSe_6 system at 300 K was constructed (Fig. 12).

The presence of γ_1- and γ_2-solid solutions in the Cu_8SiSe_6-Cu_8GeSe_6 side system and the absence of other phases in the studied composition triangle lead to the formation of two-phase (RT-Cu_2Se)+γ_1 and (RT-Cu_2Se)+γ_2 fields. These fields are bordered by the (RT- Cu_2Se)+γ_1+γ_2 three-phase field. As can be seen from Fig.12, γ_1- and γ_2-solid solutions have a tie-line with the phase based on RT-Cu_2Se. All phase fields of the system were confirmed by the XRD method. Fig. 13 shows the powder diffraction patterns of alloys No. 1, 2, and 3 shown in the solid-phase equilibria diagram (Fig. 12). As can be seen, the mentioned diffraction pattern of alloy No. 1 is characteristic of solid solutions (γ_1-phase) and reflects the diffraction peaks of the Cu_8SiSe_6 compound with a certain shift. The diffraction pattern of alloy No. 2 consists of a set of diffraction lines of the γ_1-phase and RT-Cu_2Se, while the diffractogram of alloy No. 3 consists of the sum of the diffraction lines of the RT-Cu_2Se, γ_1- and γ_2 -phases.

The phase compositions of the alloys of the studied system were also confirmed by SEM analysis. For example, Fig.14 shows SEM images for alloys of the two- and three-phase regions of the studied system (alloys No. 2 and 3 in Fig.12, respectively).

To determine the chemical composition of the phases, the samples were studied by EDS analysis. For example, Fig.15 shows the results of EDS analysis of the γ_1-phase with a content of 20 mol % Cu_8GeSe_6. The analysis shows that its elemental composition corresponds to the formula $Cu_{8.02}Si_{0.78}Ge_{0.22}Se_{5.98}$. This is very close to the nominal composition of the sample ($Cu_8Si_{0.8}Ge_{0.2}Se_6$).

Projection of the liquidus surface. The liquidus surface of the Cu_2Se-Cu_8SiSe_6-Cu_8GeSe_6 system (Fig. 16) consists of 2 areas corresponding to the initial crystallization of the α-phase and the $Cu_8Si_{1-x}Ge_xS_6$ solid solutions (δ-phase) based on HT-Cu_2Se. These areas are bounded by the monovariant eutectic equilibrium (L↔(HT-Cu_2Se)+δ) curve (eK). Taking into account the peritectic nature of the formation of the Cu_8GeSe_6 compound, it can be assumed that this curve transforms into the peritectic equilibrium (L+(HT-Cu_2Se)↔δ) at the K transition point.

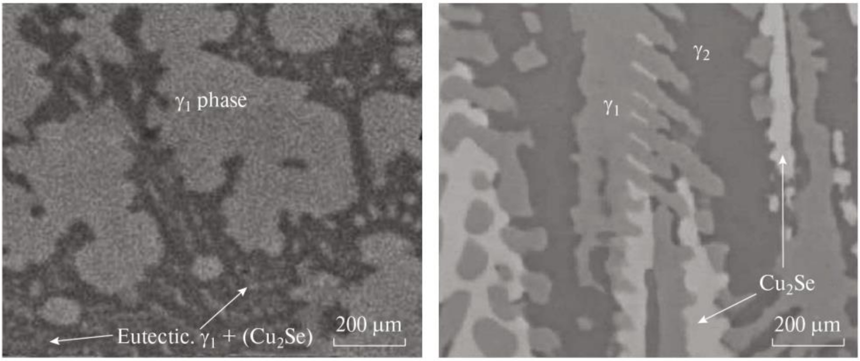
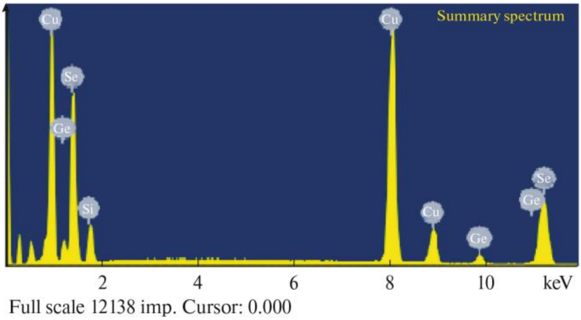


Fig. 14. SEM images of alloys No. 2 and 3 shown in the phase diagram (Fig. 12) [6, p.1616]



Element	Atomic %	Error %
Si*K*	4.05	3.8
Se*K*	39.95	1.2
Cu*K*	53.33	0.9
Ge*K*	2.67	4.6
Sum	100	

Fig. 15. EDS analysis results for the $Cu_8Si_{0.8}Ge_{0.2}Se_6$ alloy [12, p.1617]

As can be seen from Fig.16, the new δ-phase we discovered in this system crystallizes directly from the liquid alloy over a wide composition and temperature range. This creates good opportunities for obtaining its samples with different compositions in single crystals using directional crystallization.

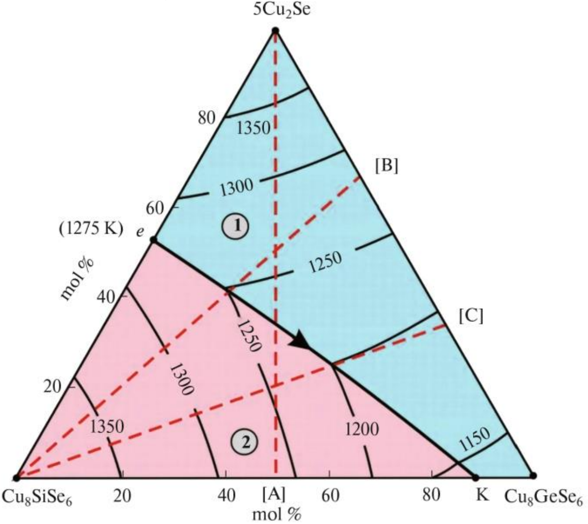


Fig. 16. Projection of the liquidus surface of the Cu_2Se-Cu_8SiSe_6-Cu_8GeSe_6 system. Primary crystallization regions: 1 – (HT-Cu_2Se); 2 –δ-phase. Red broken lines are the studied internal sections.[12, p.1617]

Isothermal sections of the phase diagram at 1200 and 1300 K (Fig. 17). It is known that isothermal sections of the T-x-y phase diagrams of the studied systems allow us to determine the boundaries of the homogeneity regions of the phases existing at given temperatures and their compositions in heterogeneous regions reflecting their equilibrium with each other, as well as the directions of the tie-lines in two-phase regions. These data, in particular the directions of the tie-lines, are of great importance in terms of obtaining crystals of solid solutions of a given composition from a liquid alloy by directional crystallization.

The isothermal sections presented below were constructed using the phase diagram of the studied Cu_8SiSe_6-Cu_8GeSe_6 boundary system and the Cu_2Se-[A], Cu_8SiSe_6-[B] and Cu_8SiSe_6-[C] vertical sections and the corresponding isotherms on the projection of the liquidus surface of the Cu_2Se-Cu_8SiSe_6-Cu_8GeSe_6 system.

The isothermal section at 1300 K (Fig. 17). This isothermal section consists of a large liquid region, as well as two-phase regions where the liquid phase is in equilibrium with the α-phase based on HT-Cu_2Se and with the δ-phase based on HT-Cu_8SiSe_6. As can be seen from Fig.17, the homogeneity region of the α-phase covers a very small (2-3 mol%) concentration interval near the vertex of the concentration triangle corresponding to the Cu_2Se compound. The homogeneity region of the δ-phase based on the HT- Cu_8SiSe_6 compound is in the form of a strip with a width of 1-2 mol % along the Cu_8SiSe_6-Cu_8GeSe_6 boundary system. Determination of the directions of the tie-lines in the L+δ two-phase field allows us to determine the compositions of the liquid and solid solutions in equilibrium. For example, the endpoints of the *ls* connode line shown in the figure indicate the compositions of the liquid solution (*l*) and the solid phase in equilibrium with it (*s*). This information can be used to select the composition of the liquid solution for growing solid solution crystals with the required composition

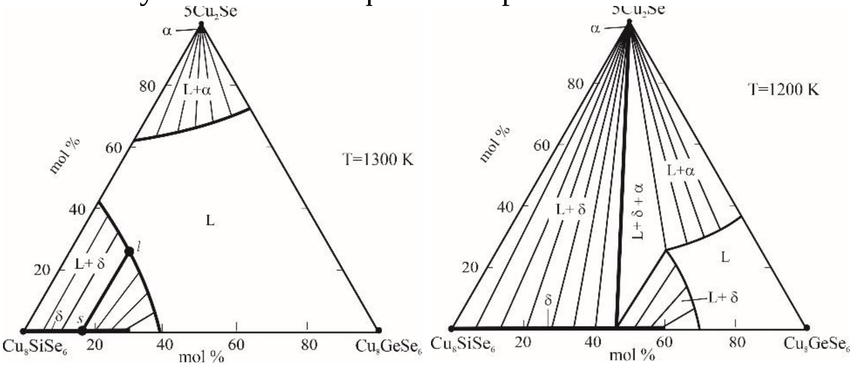


Fig.17. Isothermal sections of the phase diagram at 1200 and 1300 K

The isothermal section at 1200 K. It can be seen from the phase diagram that the homogeneous liquid area in the system at 1200 K has sharply decreased compared to 1300 K. As a result, the isotherms reflecting the compositions of the liquid phase involved in the L↔α vә L↔δ equilibria have also decreased significantly and merged. Their intersection point reflects the L↔α+δ equilibrium in the system. Since this equilibrium is nonvariant, the compositions of the phases in equilibrium are constant and an elementary triangle corresponds to the L+α+δ three-phase area on the phase diagram. The α+δ two-phase area in the system occupies about 50% of the total area of the triangle. This area reflects the solid-phase equilibria in the system.

The analysis of the isothermal and polymetric sections presented in the dissertation work shows that they both fully correspond to the projection of the liquidus surface, and also agree well with each other and correctly reflect the nature of phase equilibria in the subsolidus part of the phase diagram.

The obtained new solid solutions open up new opportunities for purposeful modification of both the thermoelectric properties and ionic conductivity of high-temperature modifications of the initial compounds, and the photoelectric indicators of their low-temperature modifications. The constructed phase diagrams are the scientific basis for the synthesis and growth of crystals of solid solutions with a given composition and structure.

Chapter IV presents the results of the study of the thermodynamic functions of polymorphous phase transitions of argyrodite family compounds and some variable composition phases based on them [1-9, 14, 16].

Study of the phase transition of the Cu_8SiS_6 compound by the DSC method. DSC study of the Cu_8SiS_6 compound was carried out in an aluminum crucible with a lid. Considering that the object of study is in a solid polycrystalline state, the sample was ground into powder before measurement to ensure the maximum possible contact area between the studied sample and the bottom of the crucible. The DSC measurements regime was selected taking into account the phase transition temperature of the studied compound. The heating rate was 3°/min.

To increase the accuracy of the study, two samples of the Cu_8SiS_6 compound with a mass of 29.13 and 36.15 mg were used. For each sample, three DSC heating curves were recorded in the dynamic mode from room temperature to 395 K. As a result, a total of six DSC curves were drawn for two different mass samples of one compound. It should be noted that in the first experiment, the ternary compound (in this experiment, the Cu_8SiS_6 sample) was heated to 415 K. This was done to check that the studied compound was pure, i.e., there was no binary Cu_2X admixture. Binary copper chalcogenides Cu_2S and Cu_2Se undergo polymorphic transitions at 376 K and 393 K, respectively.

Then the DSC curves were processed using the Linseis TA Evaluation V2.3.1 software and the values of the peak onset (T_{onset}) and end (T_{end}) temperatures, as well as the phase transition enthalpy ($\Delta H_{ph.t.}$) per 1 mole of the substance were determined. Fig. 17 shows one of the DSC heating curves for a sample with a mass of 29.13 mg. All the results for the six DSC curves (for two different mass samples) drawn for the Cu_8SiS_6 compound are shown below:

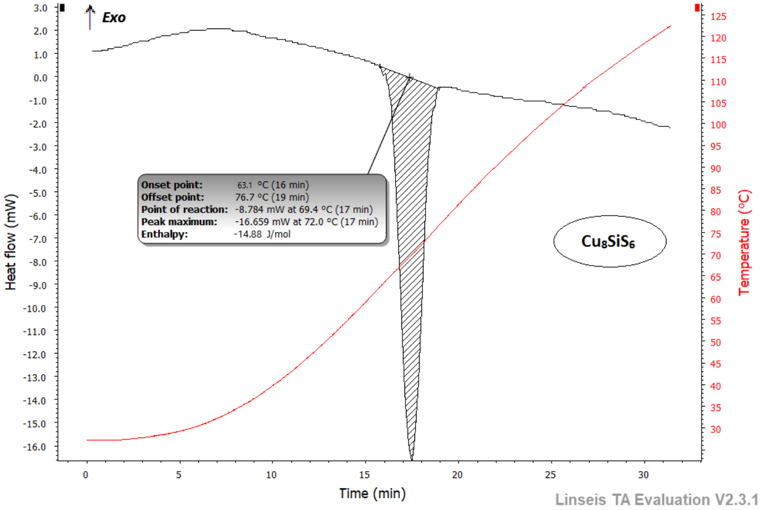


Fig 17. DSC heating curve of a 29.13 mg sample of the Cu_8SiS_6 compound (experiment 1)

<u>Sample I, weight 29.13 mg</u>

Experiment 1: phase transition temperature $T_{ph.t.}$=336.25 K; phase transition enthalpy -$\Delta H_{ph.t.}$=14.88 kC/mol (Fig. 17).

Experiment 2: phase transition temperature $T_{ph.t.}$==336.0 K; phase transition enthalpy -$\Delta H_{ph.t.}$=14.86 kC/mol.

Experiment 3: phase transition temperature $T_{ph.t.}$=336.1 K; phase transition enthalpy -$\Delta H_{ph.t.}$=14.84 kC/mol.

<u>Sample II, weight 36.15 mg</u>

Experiment 1: phase transition temperature $T_{ph.t.}$=336.0 K; phase transition enthalpy -$\Delta H_{ph.t.}$=14.84 kC/mol

Experiment 2: phase transition temperature $T_{ph.t.}$=336.0 K; phase transition enthalpy $-\Delta H_{ph.t.}$=14.85 kC/mol.

Experiment 3: phase transition temperature $T_{ph.t.}$=336.0 K; phase transition enthalpy $-\Delta H_{ph.t.}$=14.83 kC/mol.

Then, the average value of the phase transition enthalpy was calculated from the experimental data of the two studied samples:

$$-\Delta H_{ph.t.}=14.85 \text{ kC/mol.}$$

The average value of the phase transition temperature was taken as the most repeated $T_{ph.t.}$=336.0 K during the experiment.

The Gibbs-Helmholtz equation ($\Delta G=\Delta H-T\cdot\Delta S$) was used to calculate the entropy of the phase transition. Since $\Delta G_\alpha=\Delta G_\beta$ for the first type of phase transitions ($\alpha\leftrightarrow\beta$), the change in Gibbs free energy in the Gibbs-Helmholtz equation is equal to zero ($\Delta G=0$):

$$\Delta G_{ph.t.}=\Delta H_{ph.t.}- T_{ph.t.}\cdot\Delta S_{ph.t.};\ \Delta G_{ph.t.}=0$$

Then for the first type of phase transition we can write:

$$\Delta H_{ph.t} =T\cdot\Delta S_{ph.t}$$

From this equation, we can calculate the entropy of the phase transition:

$$\Delta S_{ph.t.}= \frac{\Delta H_{ph.t.}}{T_{ph.t.}}.$$

Using the last equation, the phase transition enthalpy of the compound obtained from the DSC curve, and the peak onset temperature (336 K), the phase transition entropy of the studied compound was calculated.

$$\Delta S_{ph.t.}= \frac{\Delta H_{ph.t.}}{T_{ph.t.}}. = \frac{14.85\frac{kC}{mol}*1000}{336.0\ K} = 44.20\ \frac{C}{mol\cdot K}$$

As can be seen, the values obtained in the DSK curves as a result of experiments almost coincide and do not differ by more than 2%. In such cases, the error in determining the thermal effects does not exceed ±4%. Based on this, the error of the thermodynamic functions of the phase transition was calculated as 4%:

$\Delta H_{ph.t.}$ xətası = 14.85 кC/mol · 0.04 = 0.59 кC/mol ;

$\Delta S_{ph.t.}$ xətası = 44.20 C/(mol·К) · 0.04 = 1.77 C/(mol·К) .

Thus, the thermodynamic functions of the phase transition of the Cu_8SiS_6 compound take values: $-\Delta H_{ph.t.}$ = 14.85±0.59 кC/mol;

$\Delta S_{ph.t.}$= 44.20±1.77 C/(mol·К).

The thermodynamic transformation functions for all other compounds were calculated in the same way (Table 4).

Table 4[9, p.188; 14, p.399]

Thermodynamic data of phase transitions of argyrodite family compounds based on copper and silver

Compound	**T** $_{\text{ph.t.}}$**, К**	$\Delta H_{\text{ph.t..}}$**,** **кC/mol**	$\Delta S_{\text{ph.t..}}$**,** **C/(mol·К)**
Cu_8SiS_6	336	14.85±0.59	44.20±1.77
Cu_8SiSe_6	325	14.73±0.59	45.32±1.81
Cu_8GeS_6	330	15.54±0.62	47.09±1.88
		*12.4±5.1	*37.8±14.1
Cu_8GeSe_6	330	11.23±0.45	34.03±1.36
		*11.9±2.8	*35.5±8.4
Ag_8GeS_6	495	9.46±0.38	19.11±0.76
Ag_8GeSe_6	321	16.95±0.68	52.80±2.11
		*15.0±4.7	*46.9±14.8
Ag_8SnS_6	446	8.77±0.3	19.66±0.79
Ag_8SnSe_6	355	19.67±0.6	55.41±2.22
		*15.4±4.3	*43.4±12.1

Note: Quantities marked with * are literature data calculated using the EMF method.

As can be seen from Table 4, the entropies of the phase transitions of the Cu_8SiS_6 and Cu_8GeS_6 compounds are very close to each other. The same situation is observed for sulfide compounds based on silver. This is because these quantities refer to the same type of changes in the crystal structure during the phase transition (from orthorhombic lattice to cubic lattice or from hexagonal lattice to cubic lattice). A similar picture is observed for selenides.

Note that the values of $\Delta H_{\text{ph.t.}}$ previously obtained by the EMF method for the Ag_8GeSe_6 and Ag_8SnSe_6 compounds differ from our results by up to 22% (Table 4), which is within the error interval of the EMF method.

Analysis of literature data on the thermodynamic functions of phase transitions of chalcogenides shows that for our research objects the values of these functions are significantly higher than the values characteristic of the thermodynamic functions of phase transitions of the first type. This indicates a more serious ordering in the crystal structures of the argyrodite family compounds during the phase transition. It is known that during the transitions of argyrodite compounds of the $Ag_8B^{IV}X_6$ type to high-temperature modifications, many vacant cation positions are formed in the rigid anion framework of the crystal lattice, as a result of which copper or silver cations acquire mobility. This leads to a further increase in entropy.

The dissertation also determined the thermodynamic functions of phase transitions of $Cu_8Si_{(1-X)}Ge_XS_6$ solid solutions (Table 5).

Table 5[13,p.513]

Thermodynamic functions of phase transitions of Cu_8SiS_6 və Cu_8GeS_6 compounds and $Cu_8Si_{(1-X)}Ge_XS_6$ solid solutions

Phase	**T ph.t., K**	**ΔH ph.t., кC/mol**	**ΔS ph.t., C/(mol·K)**
Cu_8GeS_6	330	15.54±0.62	47.09±1.88
$Cu_8Si_{0.2}Ge_{0.8}S_6$	330	15.35±0.61	46.51±1.86
$Cu_8Si_{0.4}Ge_{0.6}S_6$	330	15.16±0.61	45.83±1.83
$Cu_8Si_{0.6}Ge_{0.4}S_6$	332	15.06±0.6	45.52±1.82
$Cu_8Si_{0.8}Ge_{0.2}S_6$	334	14.95±0.6	44.77±1.79
Cu_8SiS_6	336	14.85±0.59	44.20±1.77

Based on Table 5, graphs of the composition dependence of the thermodynamic functions of the $Cu_8Si_{(1-X)}Ge_XS_6$ solid solutions were constructed (Fig.18).

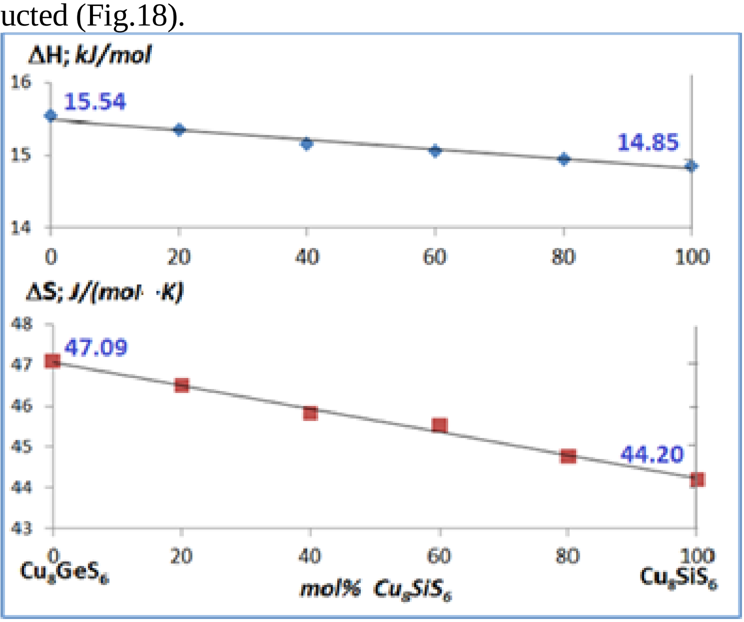


Fig. 18. Composition dependences of thermodynamic functions of phase transitions of the $Cu_8Si_{1-x}Ge_xS_6$ solid solutions[13,p.513]

As can be seen, these dependences for both functions are practically linear, i.e., within the error, the heats and entropies of phase transitions of solid solutions are equal to the sum of the corresponding functions of the initial compounds. This fact, as well as the absence of extremum points in the $\delta\leftrightarrow\gamma$ equilibrium curves of the phase diagram of the Cu_8SiS_6-Cu_8GeS_6 system (Fig. 1), indirectly indicate that $Si\leftrightarrow Ge$ substitutions in γ- and δ-solid solutions are athermal processes, i.e., these solid solutions can be characterized as quasi-ideal.

RESULTS

1. The temperatures and enthalpies of polymorphic transformations of the Cu_8SiX_6, Cu_8GeX_6, Ag_8GeX_6 və Ag_8SnX_6 (X-S, Se) compounds belonging to the argyrodite family were determined by differential scanning calorimetry, and the polymorphic transformation entropies were calculated based on them. It was shown that the polymorphic transformation heat and entropy of all the studied compounds have anomalously high values compared to the values characteristic of metal chalcogenides. Based on the structural features of various crystallinity modifications of the argyrodite family compounds, it was determined that this is because during these transformations, unlike ordinary polymorphic transformations, more serious changes occur in the crystal lattice and a sharp increase in disorder in the cation sublattice [1-9,14, 16].
2. To obtain new phases with variable composition based on copper argyrodites, Cu-Si-Ge-X (X-S, Se) concentration tetrahedrons were comprehensively studied on the Cu_2X-Cu_8SiX_6-Cu_8GeX_6 composition planes by differential thermal analysis, X-ray diffraction analysis and scanning electron microscopy methods, and mutually adjusted schemes of phase equilibria were obtained in them. Several polythermal and isothermal sections of the

volume phase diagram of both systems, including diagrams of solid-phase equilibria at 300 K, as well as projections of liquidus surfaces were constructed. It was shown that these systems are partially quasi-ternary due to the incongruent melting of Cu_8GeX_6 compounds and belong to the monovariant eutectic type [10, 12, 13]

3. It was found that the Cu_2S-Cu_8SiS_6-Cu_8GeS_6 system is characterized by the formation of continuous solid solution series between both high-temperature cubic and low-temperature orthorhombic modifications of the initial ternary compounds along the Cu_8SiS_6-Cu_8GeS_6 side of the composition triangle [10,13].
4. In the Cu_8SiSe_6-Cu_8GeSe_6 boundary system of the Cu_2Se-Cu_8SiSe_6-Cu_8GeSe_6 concentration triangle, continuous solid solution series between high-temperature cubic modifications of the initial ternary compounds were also found. However, it was found that polymorphic transformations of the compounds are accompanied by the formation of eutectoid equilibrium in the system and the formation of limited solid solution regions based on low-temperature modifications [12].
5. The solid solution samples found in both studied systems were synthesized and characterized in a homogeneous state. It was shown that the dependences of the lattice parameters of solid solutions on the composition are linear [10,12,13].
6. It was found that the polymorphic transformations of the $Cu_8Si_{1-x}Ge_xS_6$ (x=0.2; 0.4; 0.6; 0.8) solid solutions are practically isothermal processes, like the corresponding transformations of individual compounds. Based on this, the polymorphic transformation enthalpies of these solid solutions were determined by the DSC method, and their entropies were calculated based on the $\Delta S_{ph.t.} = \Delta H_{ph.t.}/T_{ph.t}$ expression [13, 15, 17].
7. It has been shown that the polymorphic transition enthalpies and entropies of the $Cu_8Si_{1-x}Ge_xS_6$ solid solutions vary linearly depending on the composition, i.e., within the error, the heats and entropies of phase transitions of solid solutions are equal to the sum of the corresponding functions of the initial compounds. This indicates that Si→Ge substitutions in these solid solutions are athermal processes, i.e., the considered phases can be characterized as quasi-ideal solutions [13, 15, 17].

The results of the dissertation work have been published in the following scientific works:

1. Bayramova Ü.R., Məşədiyeva L.F., Alverdiyev İ.C., Əliyeva Z.M., Yusibov Y.Ə. $Cu_8B^{IV}X_6$ (B^{IV}-Si, Ge, Sn; X-S, Se, Te) tipli birləşmələrin ərimə xarakteri və faza çevrilmələri / "Müasir təbiət və iqtisad elmlərinin aktual problemləri" Beynəlxalq elmi konfrans, Gəncə, 2019, s.7-10
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