REPUBLIC OF AZERBAIJAN

On the rights of the manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

OBTAINING AND STUDY OF NEW POLYFUNCTIONAL MATERIALS IN Ag_2X-Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) SYSTEMS

Speciality: 2303.01 – Inorganic chemistry

Field of science: Chemistry

Applicant: **Garay Mikayil Ashirov**

Baku – 2024

The dissertation work was carried out in the research laboratory "Thermodynamics of functional inorganic materials" of the Institute of Catalysis and Inorganic Chemistry of the Ministry of Science and Education of the Republic of Azerbaijan.

Scientific supervisor:
Ph. D. Chem. associate professor
Leyla Farhad Mashadiyeva

Scientific consultant:
D. Sci. Chem., professor, Corr.-member of ANAS
Mahammad Baba Babanly

Official opponents:
D. Sci. Chem., professor
İkhtiyar Bahram Bakhtiyarly

D. Sci. Chem., associate professor
Naghı İbrahim Yagubov

Ph. D. Chem. associate professor
Vagif Gadir Valiyev

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

Chairman of the Dissertation Council
D. Sci. Chem., Academician
Dilgam Babir Taghiyev

Scientific secretary of the Dissertation Council
Ph. D. Chem., associate professor
Ulviyya Akhmed Mammadova

Chairman of the scientific seminar
D. Sci. Chem., professor
Akif Shikhan Aliyev

GENERAL DESCRIPTION OF WORK

Actuality. The rapid development of modern science and technology requires continuous search, synthesis, and research of new inorganic functional materials with different physical and physicochemical properties. Among such inorganic materials, metal chalcogenides occupy a special place, and since the middle of the last century, these compounds have been the focus of researchers' attention as semiconductor materials[1,2].

Silver-based ternary and more complex chalcogenides are important functional materials of modern technique and technology. Many of these phases are considered promising for use in modern electronics and alternative energy conversion devices due to their optical, photoelectric, and thermoelectric properties[3].

Many of the argyrodite family compounds with the general formula A_8BX_6 (A-Cu, Ag; B-Si, Ge, Sn; X-S, Se, Te) have high ionic conductivity due to the mobility of Cu^+ (Ag^+) ions. Therefore, these compounds can be used as solid electrolytes, ion-selective electrodes, and sensors[4].

One of the main ways of creating the physicochemical basis of the search and acquisition of new multicomponent phases is the study of phase equilibria in the relevant systems. In addition to reflecting the presence of new phases in the system, the phase diagram provides important information such as their crystallization properties from the alloy, homogeneity areas, and polymorphic transformations. These data, as well as thermodynamic properties, crystal structure, and other physico-chemical properties of intermediate phases are very important for the development of their synthesis methods. What has been

---

[1] Sanghoon, X.L. Chalcogenides: From 3D to 2D and Beyond / X.L.Sanghoon, L.J.Tengfei, L.Y.Zhang // -Elsevier, -2019,- 398 p.

[2] Ahluwalia, G.K. Applications of Chalcogenides: S, Se, and Te. G.K.Ahluwalia /-Springer, -2016. – 461 p.

[3] Jin, M. Fabrication and Thermoelectric Properties of Single-Crystal Argyrodite Ag_8SnSe_6 / M.Jin, S.Lin, W.Li. // Chemistry of Materials, -2019, № 7, -p. 2603–2610.

[4] Barbara, K.H. High Electron Mobility and Disorder Induced by Silver Ion Migration Lead to Good Thermoelectric Performance in the Argyrodite Ag_8SiSe_6 / Kai, W., Yasar, K. // Materials Science and Engineering, -2017. p. 4833−4839.

mentioned shows that large-scale research in the field of physico-chemical analysis and thermodynamics of multi-component systems is relevant to the development of modern functional materials science.

One of the most convenient methods for optimizing the properties of compounds with functional properties is to obtain solid solutions based on them. Thus, it is possible to control the properties by changing the composition of solid solutions. For this reason, the physicochemical study of multicomponent systems based on A_8BX_6 compounds is important from both a scientific and a practical point of view.

The analysis of literature data shows that recently the phase diagrams of multicomponent systems formed by copper and silver with chalcogens of p^2 elements have been studied for a number of fragments and it has been determined that new phases with interesting functional properties are present in most of those systems. Ag_2X-Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) type systems studied in the thesis work can be considered interesting research objects as the formation of large solid solution areas is expected. Until our research, the complete picture of phase equilibria of these systems has not been studied.

The object and subject of the research. Taking into account the mentioned data, systems Ag_2X-Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) were taken as the research object of the dissertation. The subject of the research was the study of phase equilibria, thermodynamic properties, and ionic conductivity in those systems.

Purpose of work. The main goal of the dissertation work was to determine the nature of physico-chemical interaction in Ag_2X-Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) systems, to develop the scientific basis for the search and synthesis of new phases in them.

In order to achieve the stated goal, the following specific issues were set and resolved:

- Investigation of phase equilibria on Ag_8SiX_6-Ag_8GeX_6 cross-sections, which are border systems of Ag_2X-Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) systems, search for new intermediate phases, determining the nature of their formation, primary crystallization, and homogeneity areas;

• Construction of projections of liquidus surfaces of Ag_2X-Ag_8SiX_6-Ag_8GeX_6 systems, as well as a series of isothermal and polythermal sections of phase diagrams.

• Determination of thermodynamic functions of Ag_8SiSe_6 and Ag_8SiTe_6 compounds with solid electrolyte (Ag_4RbJ_5) EMF method.

• Investigation of the ionic conductivity of the Ag_8GeSe_6 compound, which belongs to the argyrodite family compounds.

Research methods. Differential thermal analysis (DTA), X-ray phase analysis (XRD), electromotive force (EMF), and ion conductivity measurement methods were used in the dissertation work. "NETZSCH 404 F1 Pegasus" device and multi-channel DTA device developed based on "TC-08 Thermocouple Data Logger" electronic data logger were used for differential thermal analysis. D2 Phaser and D8 ADVANCE devices of the German Bruker firm were used to take diffraction patterns of the samples and the obtained results were analyzed using the computer software of those devices. "Keithley 2100 6 1/2 Digit Multimeter" brand digital voltmeter was used in EMF measurements. The measurement of ion conductivity was carried out in the E7-25 immittance device at the Institute of Radiation Problems of ARETN.

The main provisions defended:

1. Landscapes of phase equilibria of Ag_2S-Ag_8SiS_6-Ag_8GeS_6, Ag_2Se-Ag_8SiSe_6-Ag_8GeSe_6, Ag_2Te-Ag_8SiTe_6-Ag_8GeTe_6 systems, horizontal and vertical sections of phase diagrams, projections of liquidus surfaces.

2. Nonvariant and monovariant equilibria determined during the study of phase diagrams of Ag_2X-Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) systems.

3. New solid solution areas, areas of primary crystallization of these phases from the alloy, homogeneity areas existing in the subsolidus, and crystallographic parameters of solid solutions, identified in the studied systems.

4. Partial molar functions of silver in Ag_8SiSe_6 and Ag_8SiTe_6 compounds and standard integral thermodynamic functions of those compounds.

5. Results regarding the ionic conductivity of the Ag_8GeSe_6

compound.

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

✓ In the Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) type systems, the nature of physicochemical interaction was determined, and it was established that continuous solid solutions were formed between the high-temperature modifications of the primary components of all three systems.

✓ Full sceneries of phase equilibria of Ag_2X-Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) systems were obtained, liquidus surface projections of these systems, some isothermal and polythermal sections of phase diagrams were constructed.

✓ The areas of homogeneity and primary crystallization of the solid solutions found in the investigated systems were determined, and phases with different compositions were synthesized and identified from these areas.

✓ The partial thermodynamic functions of silver in the Ag_8SiSe_6-$SiSe_2$-Se and Ag_8SiTe_6-Si_2Te_3-Te composition area were determined using the Ag_4RbI_5 superionic conductive solid electrolyte EMF method, and the standard integral thermodynamic functions of Ag_8SiSe_6, Ag_8SiTe_6 compounds were calculated based on them.

✓ Above 325 K, Ag_8GeSe_6 compound becomes superionic and Ag^+ ions act as charge carriers. Below the temperature of 300 K, conduction in localized cases occurs according to the jump mechanism.

Theoretical and practical significance of research work. In the dissertation work, the new results obtained regarding the phase equilibria landscapes in Ag_2X-Ag_8SiX_6-Ag_8GeX_6 systems, as well as the thermodynamic parameters of Ag_8SiSe_6, Ag_8SiTe_6 compounds are a contribution to the chemistry and materials science of chalcogenides. Also, these results can be used for the directional synthesis of the corresponding phases and the development of methods for single-crystal growth. These data are the main physico-chemical parameters of the substances and they can be included in relevant databases.

Based on the information taken from the international electronic database "Google Scholar Citations", 25 citations were made to the author's 4 articles published in international scientific journals based on the dissertation topic.

Approbation and application. 11 scientific works, including 6 articles (4 articles in journals indexed in Web of Sciences and Scopus databases) were published on the subject of the dissertation. The main results obtained in the dissertation work were reported and discussed at the following scientific conferences: "XI Международная научная конференция "Кинетика и механизм кристаллизации. Кристаллизация и материалы нового поколения" Кластер конференций, Иваново, Россия, 2021; 9th and 10th Rostocker International Conference: “Thermophysical Properties for Technical Thermodynamics”, Rostock, Germany, 2021, 2022; Müasir biologiya və kimyanın aktual problemləri" beynəlxalq konfransları, Ganja, Azerbaijan, 2021, 2022.

The new phases with variable composition obtained in the dissertation work are of interest as environmentally safe thermoelectric materials and mixed ion-electron conductors.

The name of the institution where the dissertation work was performed. The dissertation work was carried out at the "Inorganic Functional Materials" department of the Institute of Catalysis and Inorganic Chemistry of the Ministry of Science and Education.

The total volume of the dissertation work with the mark number, noting the separate volume of the structural sections of the dissertation. The dissertation consists of an introduction (11.150 characters), four chapters (chapter I – 41.287 characters, II – 45.989 characters, III – 22.963 characters, IV – 35.681 characters), main results (2,735 characters), a list of scientific literature used in 226 names. The total volume of the dissertation consists of 161 pages. The dissertation includes 64 pictures and 13 tables.

Thanks. The authors are deeply grateful to Professor Rauf Sardarli (AR ETN Institute of Radiation Problems) and the staff of the laboratory headed by him for their help in measuring the ionic conductivity of the Ag_8GeSe_6 compound, as well as Professor Imamaddin Amiraslanov (AR ETN Institute of Physics) and docent Vagif Gasimov (ARETN ICIC) for their help in conducting X-ray studies and interpreting the obtained results.

MAIN CONTENTS OF THE WORK

In the introduction, the relevance of the dissertation work is justified, and the purpose, scientific novelty, practical importance and main provisions of the work are given.

In the first chapter of the dissertation, literature data on phase equilibria and thermal, crystallographic and thermodynamic properties of intermediate phases of Ag-X, Ag-B-X (B-Si, Ge; X-S, Se, Te) systems are given. Also, in this chapter, a literature review on the important functional properties of argyrodite family compounds and the modern situation in the study of phase equilibria of systems composed of compounds with formula Ag_8BX_6 were investigated and the selection of the research objects of the dissertation was justified.

In the second chapter, information was given about the synthesis methods of metal chalcogenides and the DTA, XRD, EMF methods used in the study of phase equilibria and the methods used for measuring ion conductivity were explained.

The primary binary and ternary compounds of the studied systems were synthesized by co-melting stoichiometric amounts of high-purity (99.999%) elementary components belonging to the German company Alfa Aesar in quartz ampoules under vacuum conditions (~10-2 Pa). Since the saturated vapor pressure of sulfur and selenium is high at the melting temperatures of the compounds, their synthesis was carried out in a two-zone mode in an inclined furnace. The individuality of the synthesized compounds was verified by DTA and XRD methods. Using primary binary and ternary compounds, the synthesis of mixtures of all three studied systems was carried out. Samples were prepared at different cross-sections of the ternary systems, one from 5 to 10 mol% and 1 gram each. The primary binary compounds taken in a stoichiometric ratio for synthesis were filled into quartz ampoules, vacuumed, melted, and sealed, and then synthesized in a single-zone furnace at a temperature range of 950-1150^{o}C, depending on the composition of the sample. For the Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) systems, two samples of each composition were prepared, and one series of them was kept in a liquid state above the melting temperature for 3-4 hours and annealed in ice water, and the second series was gradually cooled by disconnecting the furnace from the current source. Specific synthesis conditions of the combination and samples are given in the dissertation.

In order to bring the samples to a state of thermodynamic equilibrium, 30-50°C below the solidus line, the composition was thermally treated for 4-12 weeks.

The third chapter presents the results of the study of phase equilibria in the Ag_2S-Ag_8SiS_6-Ag_8GeS_6, Ag_2Se-Ag_8SiSe_6-Ag_8GeSe_6, Ag_2Te-Ag_8SiTe_6-Ag_8GeTe_6 systems. Phase equilibria in the system Ag_2S-Ag_8SiS_6-Ag_8GeS_6. In order to determine the complete picture of phase equilibria for this system, our results on a number of internal cross-sections and literature data on external quasibinary systems were processed together. The results of these studies were published in [1, 4, 5, 10].

Ag_8SiS_6-Ag_8GeS_6 quasibinary cross section. Figure 1 shows powder diffractograms of thermally treated alloys of the Ag_8SiS_6–Ag_8GeS_6 system.

As can be seen, all intermediate alloys have qualitatively the same diffraction pattern as the starting compounds. This indicates the formation of continuous solid solutions in the Ag_8SiS_6 –Ag_8GeS_6 system over the entire solidity range between room temperature modifications of the initial compounds. A slight shift of the diffraction lines towards small angles is observed with Si→Ge substitution. This is due to the fact that the ionic radius of germanium is larger than that of silicon.

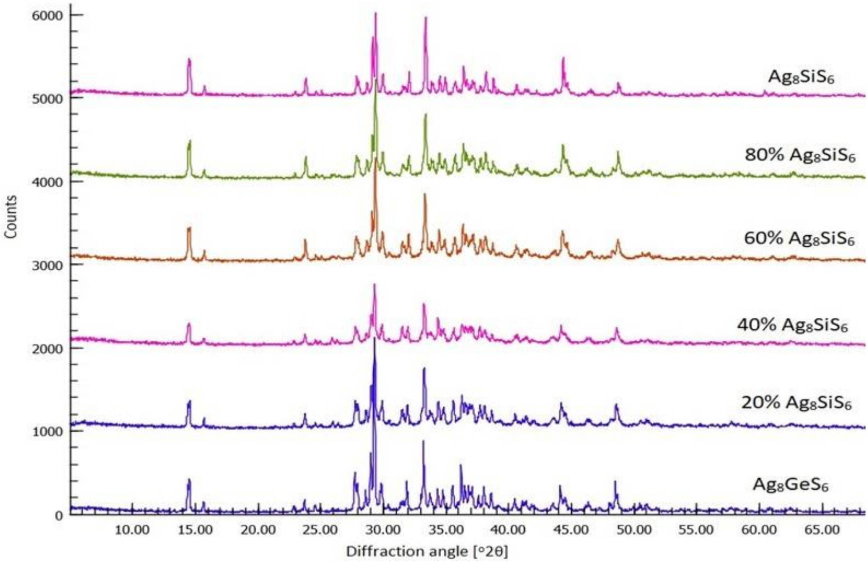

Figure 1. Powder diffraction patterns of Ag_8SiS_6–Ag_8GeS_6 alloys (room temperature) [4, 5]

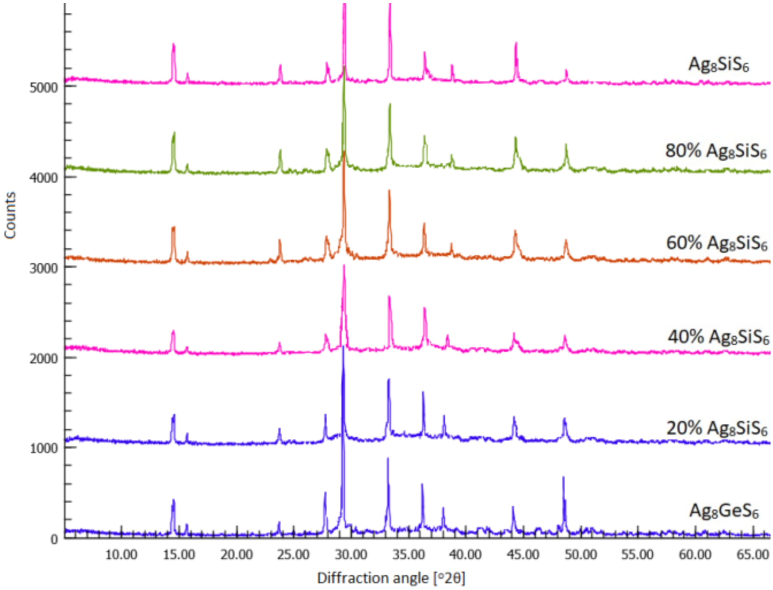

Figure 2. Powder diffraction patterns of Ag_8SiS_6 – Ag_8GeS_6 alloys (annealed from 900 K) [4]

Figure 2 shows powder XRD patterns of Ag_8SiS_6 – Ag_8GeS_6 alloys annealed at 900 K. Analysis of the XRD patterns of the annealed alloys shows that continuous series of solid solutions are formed in the entire range even between high-temperature modifications. As can be seen, the diffractograms of high-temperature alloys have a diffraction pattern characteristic of a cubic structure.

The lattice parameters of both ternary compounds and solid solutions were calculated using the TOPAS3.0 computer program and the results are given in Table.

Graphs of the dependence of crystal lattice parameters on concentration were constructed (Figure 3). As can be seen, the lattice parameters of both modifications of solid solutions increase linearly with Ge substitution, i.e., they follow Vegard's rule.

Table 1.

DTA and XRD results for Ag_8SiS_6 – Ag_8GeS_6 system

Composition, mol% Ag_8GeS_6	Effect temperatures according to DTA data, K	Lattice parameters, Å ; low-temperature phase obtained by slow cooling to 298 K, (Sp. gr. Pna21)			Lattice parameters, Å; 900 K (Sp. gr. F-43m)
		a	*b*	*c*	*a*
0 (Ag_8SiS_6)	512;1231	15.0264(2)	7.4384(3)	10.5311(7)	10.6225(2)
10	510;1229	15.0524(6)	7.4439(3)	10.5411(3)	10.6348(3)
20	506;1227	15.0751(7)	7.4412(2)	10.5429(3)	10.6436(5)
40	503;1225-1228	15.0926(1)	7.4523(7)	10.5562(9)	10.6552(9)
60	499;1223	15.0962(3)	7.4601(9)	10.5626(7)	10.6785(2)
80	497;1121	15.1265(5)	7.4694(3)	10.5774(6)	10.6935(4)
90	494;1219	15.1345(6)	7.4705(6)	10.5823(2)	10.7026(5)
100	491;1218	15.1442(8)	7.4713(5)	10.5912(4)	10.7124(7)

Based on the DTA and XRD results, the phase diagram of the Ag_8SiS_6-Ag_8GeS_6 system was constructed. As can be seen from Figure 4, continuous series of solid solutions are formed between both low (γ-phase) and high-temperature modifications (δ-phase) of the system. A special point of interest is that even though the melting temperatures (1231 and 1218 K) and polymorphic transformation temperatures (512 and 491 K) of the primary compounds are very close to each other, the extreme points on both the liquidus and solidus and δ↔γ phase transition curves not observed. This gives grounds for characterizing both the liquid solution and the δ and γ-phases formed by the mixing of ternary compounds as quasi-ideal.

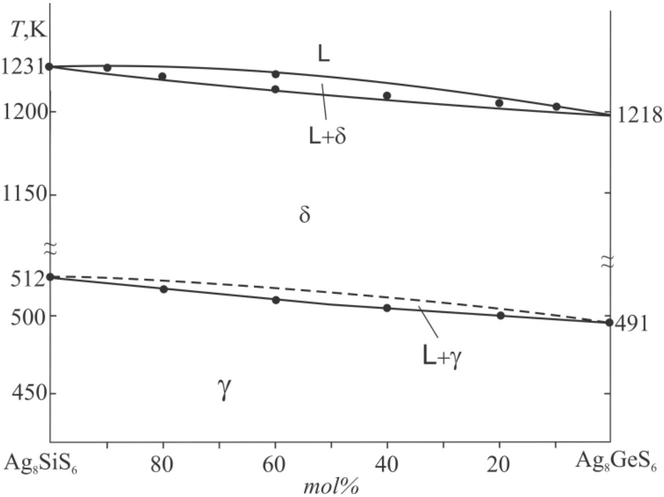

Figure 3. Phase diagram of Ag_8SiS_6-Ag_8GeS_6 system [4, 10]

Based on the XRD results of a number of equilibrium alloys within the Ag_2S–Ag_8GeS_6–Ag_8SiS_6 solidity triangle and the phase diagrams of borderline quasi-binary systems, a diagram of the solid phase equilibria of this system at 300 K was constructed (Fig. 4). In the Ag_8GeS_6–Ag_8SiS_6 side system, the formation of the γ-phase and the absence of other phases in the solidity triangle lead to the formation of a two-phase α'+γ field (where α' is a solid solution formed based on low-temperature Ag_2S). Connode lines are formed between α' and γ-phases. The phase composition of room temperature alloys of Ag_2S–Ag_8GeS_6–Ag_8SiS_6 system was determined by XRD. Figure 4 shows the investigated vertical sections and the composition of the alloys. For example, the diffraction patterns and phase compositions of mixtures 1 and 2 shown in Fig. 4 are shown in Fig. 5. As can be seen, the diffraction patterns of both alloys consist of the sum of the diffraction lines of the low-temperature modification of Ag_2S and the γ-phase. Based on the α' and γ-phases in the system, the solubility areas are up to ~1-2 mol%.

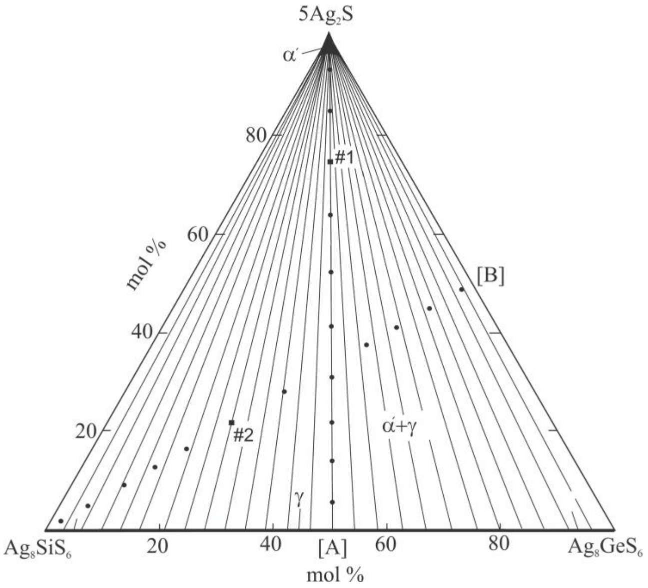

Figure 4. Diagram of solid phase equilibria of the Ag_2S–Ag_8GeS_6–Ag_8SiS_6 system at 300K. Dots indicate the composition of the studied samples [10]

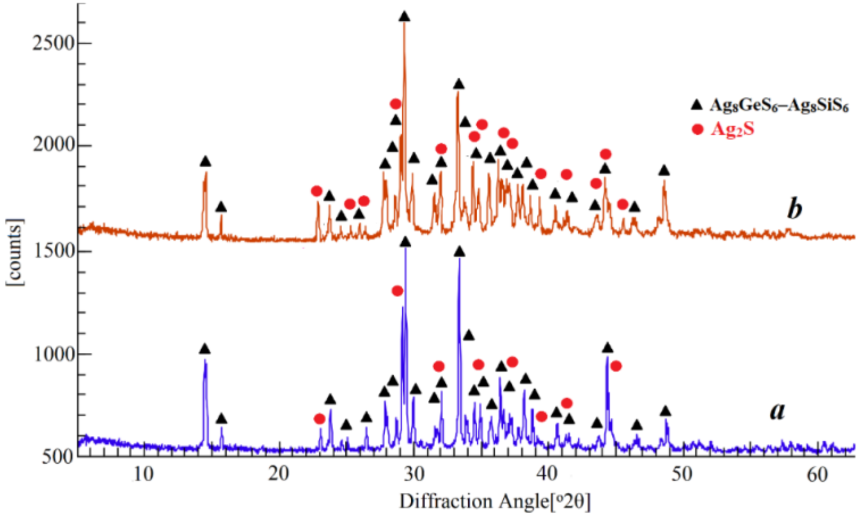

Figure 5. Powder diffractograms of Ag_2S-Ag_8SiS_6 – Ag_8GeS_6 alloys: (a)-alloy #1, (b)-alloy #2 (300 K, see Fig. 4) [10]

Liquidus surface projection. Figure 6 shows the projection of the liquid surface of the Ag_2S–Ag_8GeS_6–Ag_8SiS_6 system onto the solidity triangle. It can be seen from the figure that this quasi-ternary system is an independent subsystem of the Ag-Si-Ge-S four-component system. The projection of the liquidus surface of this system consists of two areas. One of them corresponds to the initial crystallization of α solid solutions based on high-temperature modification of the Ag_2S compound, and the second area corresponds to the initial crystallization of δ solid solutions. These areas are bounded by the e_1e_2 monovariant eutectic curve. Equilibrium for reaction (1) exists on this curve in the temperature range of 1085-1080 K.

$$L \leftrightarrow \alpha+\delta \tag{1}$$

In the solidity triangle and also on various polythermal sections, the solidities are expressed in such a way that the number of atoms (moles) is equal for all compositions. This, in turn, facilitates the comparison of T-x-y diagrams with polythermal sections.

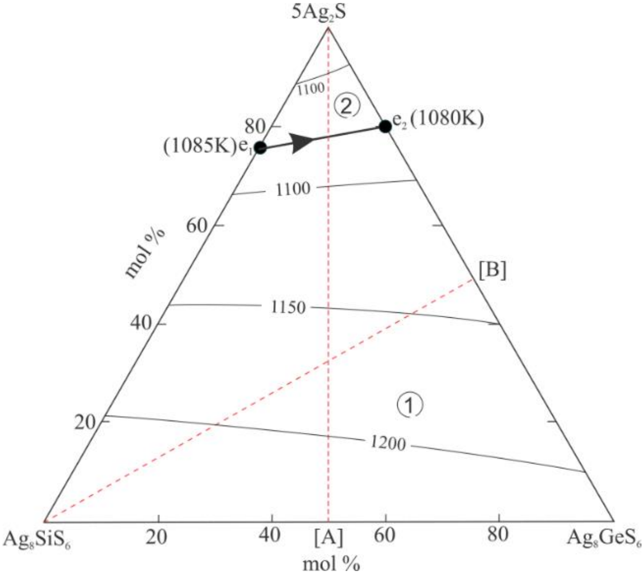

Figure 6. Projection of the liquidus surface of the Ag_2S–Ag_8GeS_6–Ag_8SiS_6 system. Primary crystallization areas: 1-δ, 2-α. Broken lines are internal cross-sections under study [10]

Some polythermal sections of the phase diagram. The Ag$_2$S Ag$_8$GeS$_6$–Ag$_8$SiS$_6$ system was studied on two internal polythermal sections, thanks to which the crystallization process was more visually described and monitored.

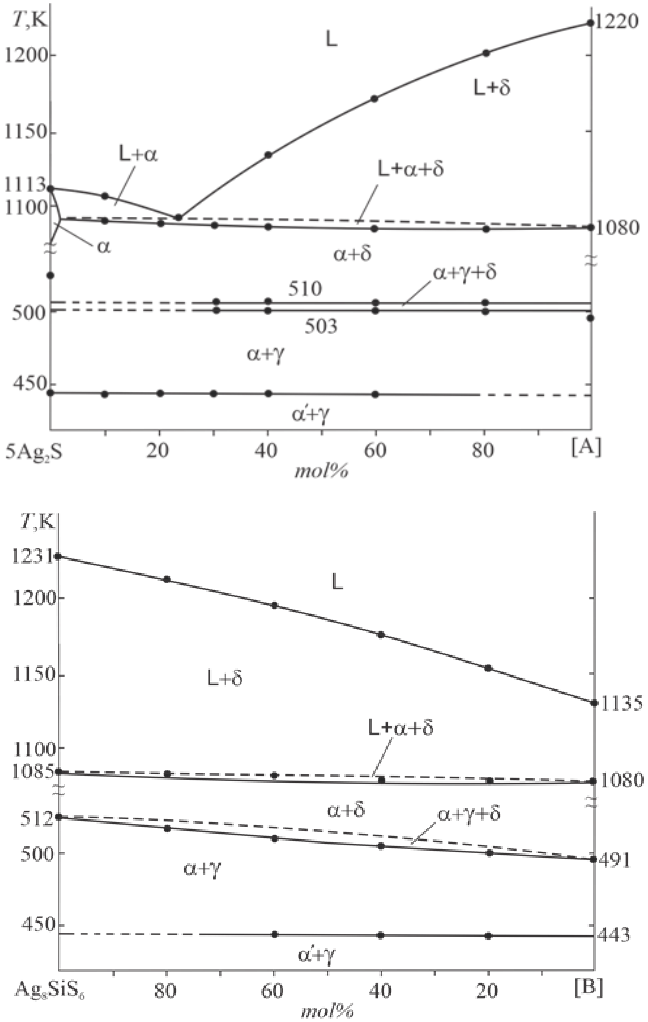

Figure 7. Isolepth sections Ag$_2$S-[A] and Ag$_8$SiS$_6$-[B] section [10]

Ag$_2$S-[A] cross-section. These correspond to the initial crystallization of solid solutions α and δ. Crystallization ends with the formation of the two-phase domain α and δ. Below the liquidus, crystallization (1) proceeds according to the eutectic reaction. Since the temperatures of e_1 and e_2 eutectic equilibria on Ag_2S–Ag_8SiS_6 and Ag_2S–Ag_8GeS_6 sides differ little (Fig. 5), the temperature interval of this monovariant eutectic equilibrium is very small (2-3°). Therefore, in Figure 8, the L+α+δ three-phase area is delimited by a dotted line. Thermal effects in the range 503-510 K correspond to monovariant equilibrium δ↔α+γ.

Based on the high-temperature modification of Ag_2S, no more than 5% solubility is available. The horizontal line at 510 K corresponds to the monovariant equilibrium δ↔γ. The horizontal line at 443 K corresponds to the polymorph transformation of α' solid solutions based on a high-temperature modification of Ag_2S compound.

Cross-section of Ag_8SiS_6-[B] (alloy containing 50%mol Ag_8GeS_6 in the [B]-$5Ag_2S$-Ag_8GeS_6 system). This section is entirely located in the primary crystallization area of the δ-phase (Fig. 9.) and initially, δ-solid solutions crystallize from the liquid phase. Then the crystallization (1) continues according to the monovariant eutectic reaction and ends with the formation of two-phase mixtures α+δ. Then δ↔α+γ monovariant eutectoid reaction (512-491) and polymorphic transformation of Ag_2S compound (443 K) take place.

Phase equilibria in the system Ag_2Se-Ag_8SiSe_6-Ag_8GeSe_6. Ag_2Se-Ag_8SiSe_6 and Ag_2Se-Ag_8GeSe_6 boundary systems belonging to this subsystem are both quasibinary and belong to the eutectic type. The phase diagram of the Ag_8SiSe_6-Ag_8GeSe_6 section, which is the third edge system of this subsystem, was constructed by us and determined to be quasibinary. The results obtained during the study of the Ag_2Se-Ag_8SiSe_6-Ag_8GeSe_6 system were published in [2, 7, 9].

Ag_8SiSe_6-Ag_8GeSe_6 quasibinary cross-section. Based on the DTA and RFA results, the phase diagram of the Ag_8SiSe_6-Ag_8GeSe_6 system was constructed (Fig. 8).

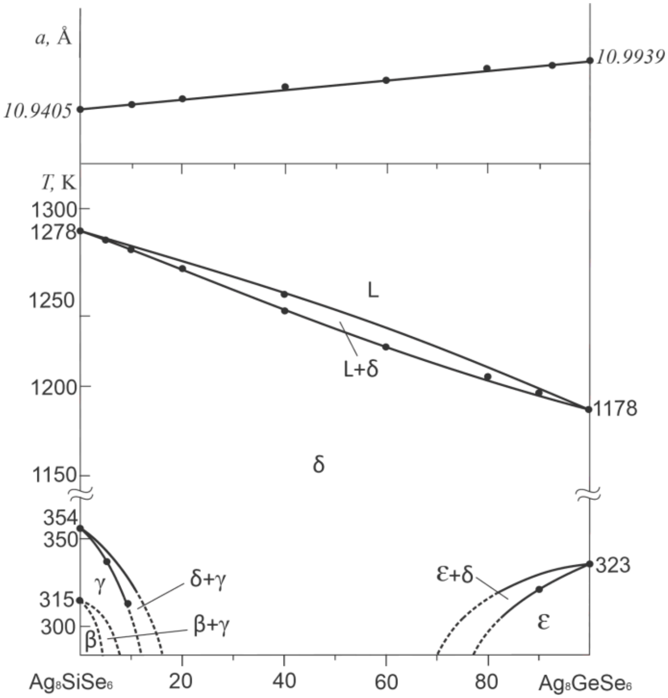

Figure 8. Phase diagram of Ag_8SiSe_6-Ag_8GeSe_6 system and composition dependence of crystal lattice parameters of HT-$Ag_8Si_{1-x}Ge_XSe_6$ solid solutions. [7, 9]

As can be seen, in this system there is a continuous solid solution sequence (δ-phase) between the high-temperature modifications of the initial compounds. Based on the low-temperature (β) and medium-temperature (γ) modifications of the Ag_8SiSe_6 compound, as well as the low-temperature modification (ε) of the Ag_8GeSe_6 compound, limited solid solution areas are formed. It can be seen from the phase diagram that the formation of solid solutions is accompanied by a decrease in the polymorphic transformation temperatures of the primary compounds. This leads to the widening of the temperature range in which the high-temperature ion-conducting δ-phase exists and its stability at room temperature and below in the range of 20-70 mol% Ag_8GeSe_6.

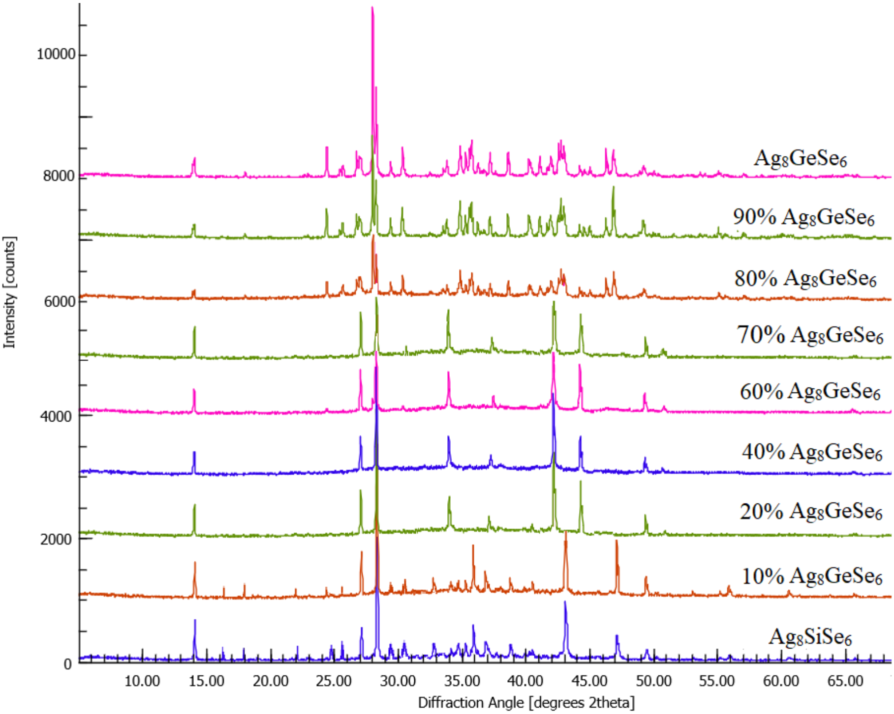

Figure 2. X-ray diffraction patterns of Ag_8SiSe_6-Ag_8GeSe_6 system alloys (room temperature) [7, 9]

XRD results of samples annealed from 900 K are shown in Figure 3. It is clear that the diffractograms of the initial compounds and all intermediate samples are qualitatively the same and have a characteristic diffraction pattern for cubic syngonia. This confirms the formation of continuous δ-solid solutions in the system.

Solid phase equilibria of the Ag_2Se–Ag_8GeSe_6–Ag_8SiSe_6 system. In Figure 4, the solid solutions formed in the Ag_8GeSe_6–Ag_8SiSe_6 system are in tie-line contact with RT-Ag_2Se (α-phase) and with each other. Boundary tie lines divide the system into 10 heterogeneous areas. 7 of them are two-phase and three are three-phase fields.

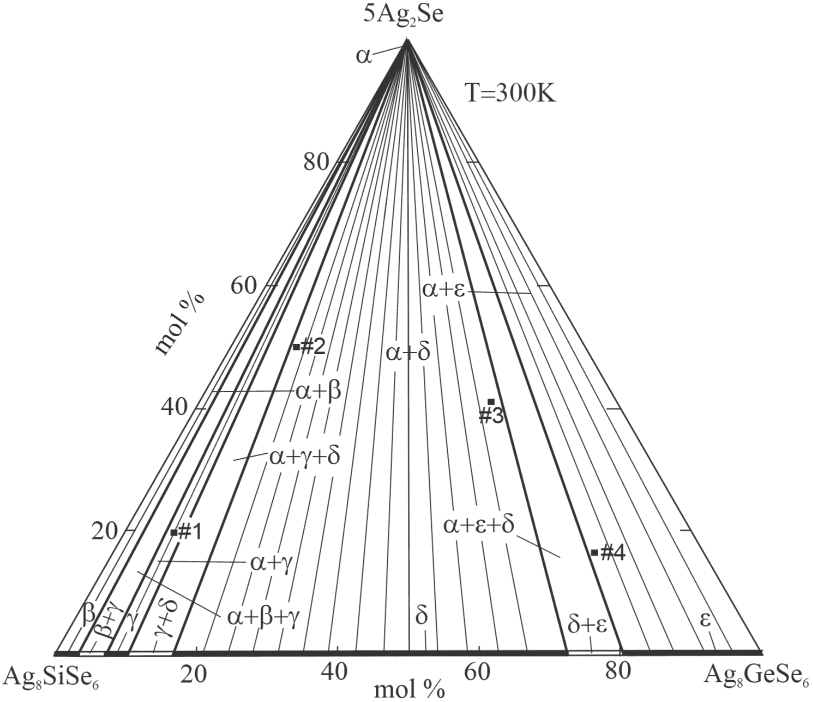

Figure 10. Diagram of solid phase equilibria at 300 K of the Ag_2Se–Ag_8GeSe_6–Ag_8SiSe_6 system. Dots indicate the composition of the studied samples [9]

The noted phase fields were confirmed by the XRD method. Thus, the powder diffractograms of the samples selected in Figure 10 are given in Figure 11. From the analysis of these XRD results, it can be seen that the X-ray pattern of sample #1 consists of α phase and γ phase, the X-ray pattern of samples #2 and #3 consists of α phase and δ phase, and the X-ray pattern of sample #4 consists of the sum of diffraction lines of α phase and ε phase. This confirms the solid phase equilibrium given in Figure 10 at a temperature of 300 K.

The projection of the liquidus surface of this system consists of two areas (Fig. 12). One of them corresponds to the initial crystallization of the α' solid solution and the second to the δ solid solution based on the high-temperature modification of the Ag_2Se compound. These areas are bounded by the e_1e_2 curve, which reflects the monovariant eutectic equilibrium.

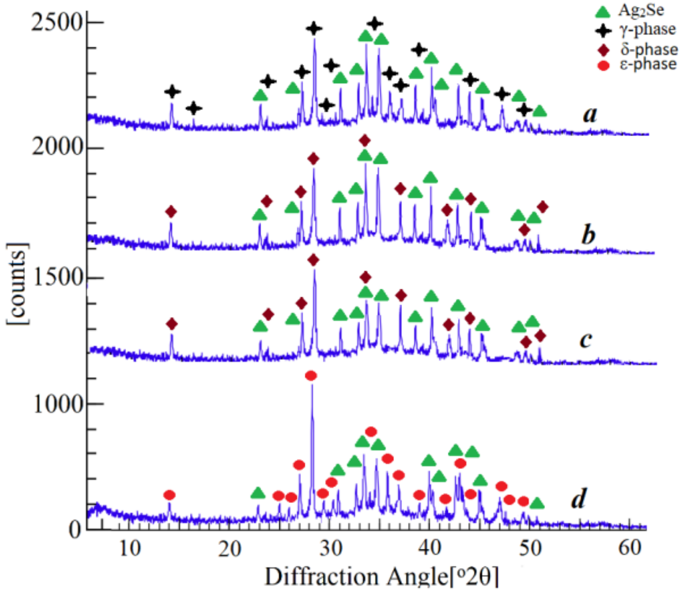

Figure 11. XRD views of samples (a) - #1, (b) -#2, (c) -#3 and (d) -#4 in the Ag_2Se-Ag_8SiSe_6 – Ag_8GeSe_6 solids triangle (look Fig. 10) [9]

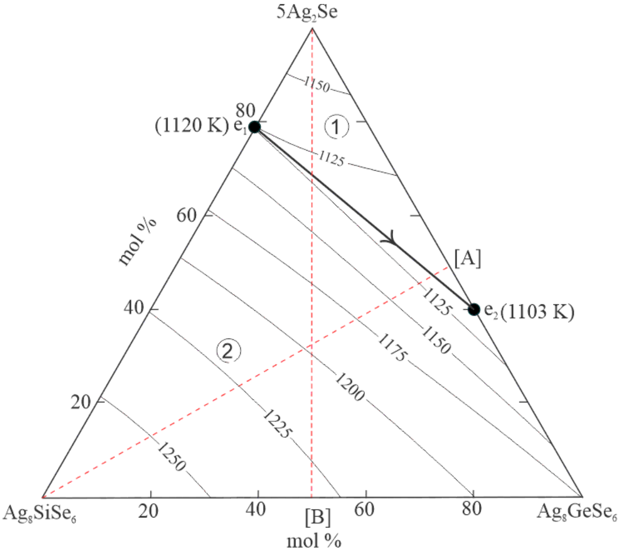

Figure 12. Projection of the liquidus surface and studied polythermal sections of the Ag_2Se–Ag_8GeSe_6–Ag_8SiSe_6 system. Primary crystallization area: 1-α', 2 -δ. Broken lines indicate the vertical sections studied [9]

Phase equilibria in the Ag_2Te-Ag_8SiTe_6-Ag_8GeTe_6 system.

The Ag_2Te-Ag_8SiTe_6 outer boundary system of this subsystem is quasibinary and belongs to the eutectic state diagram. Ag_2Te-Ag_8GeTe_6 boundary system is a peritectic type. The Ag_8SiTe_6–Ag_8GeTe_6 boundary system was studied by us and determined to be quasibinary. The results of these studies were published in [3, 6].

Ag_8SiTe_6-Ag_8GeTe_6 system. The melting nature of Ag_8GeTe_6 compound has been shown to be congruent in some literatures and incongruent in some literature. Ag_8GeTe_6 compound was synthesized by us and DTA analysis revealed that this compound melts incongruently.

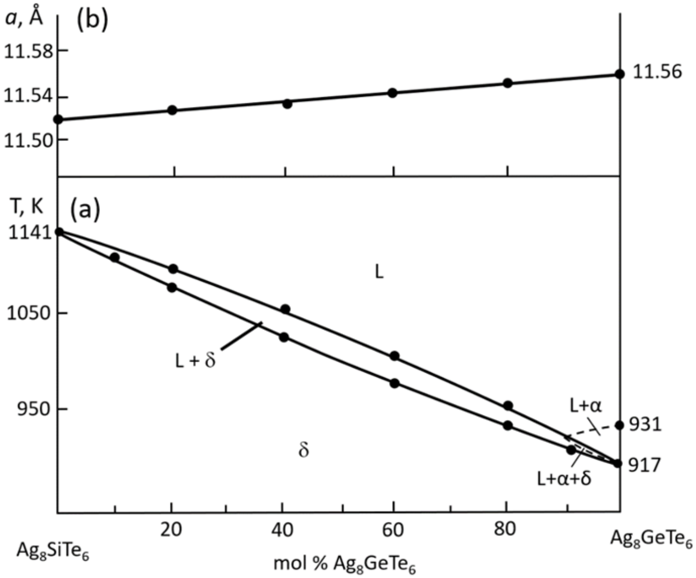

Figure 13. Ag_8SiTe_6–Ag_8GeTe_6 system phase diagram (a) and lattice parameter (b) composition dependence graph [3, 6]

Based on TOPAZ 3.0 computer program, the crystal lattice parameters were calculated from the X-ray images of primary compounds and solid solutions and it was determined that the lattice parameters in solid solutions change linearly depending on the composition (Fig. 13b). The formation of continuous solid solutions in the Ag_8SiTe_6 – Ag_8GeTe_6 system was also confirmed by DTA and XRD results (Figure 13a). Due to the incongruent melting of the Ag_8GeTe_6 compound, the α-phase crystallizes first on Ag_2Te from the liquid in the region containing >90 mol% Ag_8GeTe_6. The crystallization process ends with the formation of the δ-phase. Since no heating effect is observed in this area, the corresponding part of the diagram is constructed theoretically and is therefore marked with broken lines. Alloys of the Ag_2Te–Ag_8GeTe_6–Ag_8SiTe_6 system were prepared by melting the mixtures of the primary compounds in different proportions in vacuumed quartz ampoules. To bring the samples to equilibrium, they were thermally treated for a long time (500 h) at 900 K.

Solid phase equilibria of the Ag_2Te–Ag_8GeTe_6–Ag_8SiTe_6 system. The formation of the δ-phase in the Ag_8GeTe_6–Ag_8SiTe_6 side system and the absence of other phases in the solidity triangle lead to the formation of a two-phase RT (Ag_2Te)+δ field. The phase composition of room temperature alloys of Ag_2Te–Ag_8GeTe_6–Ag_8SiTe_6 system was determined by XRD.

Liquidus surface projection. The projection of the liquidus surface of this system consists of three areas. One of them corresponds to the initial crystallization of the α solid solution, the second to the α' solid solution, and the third to the δ solid solution based on the high-temperature modification of the Ag_2Te compound (Fig. 14b). These areas are bounded by eK_2 monovariant eutectic curve and K_2P monovariant peritectic curve. The K_1P^* curve is shown by broken lines. Point K_2 indicates the transition from monovariant eutectic equilibrium to monovariant peritectic equilibrium. In Fig. 14b, the studied polythermal sections are indicated by broken lines. $5Ag_2Te$–[A] and Ag_8SiTe_6–[B] sections (where [A]–$Ag_8Si_{0.5}Ge_{0.5}Te_6$ solid solution; [B]–Ag_2Te $0.2Ag_8GeTe_6$ section biphasic alloy with 50 mol% Ag_2Te) were studied to determine the crystallization order of the phases and the exact position of the monovariant line eK_2 and liquidus surface of the system.

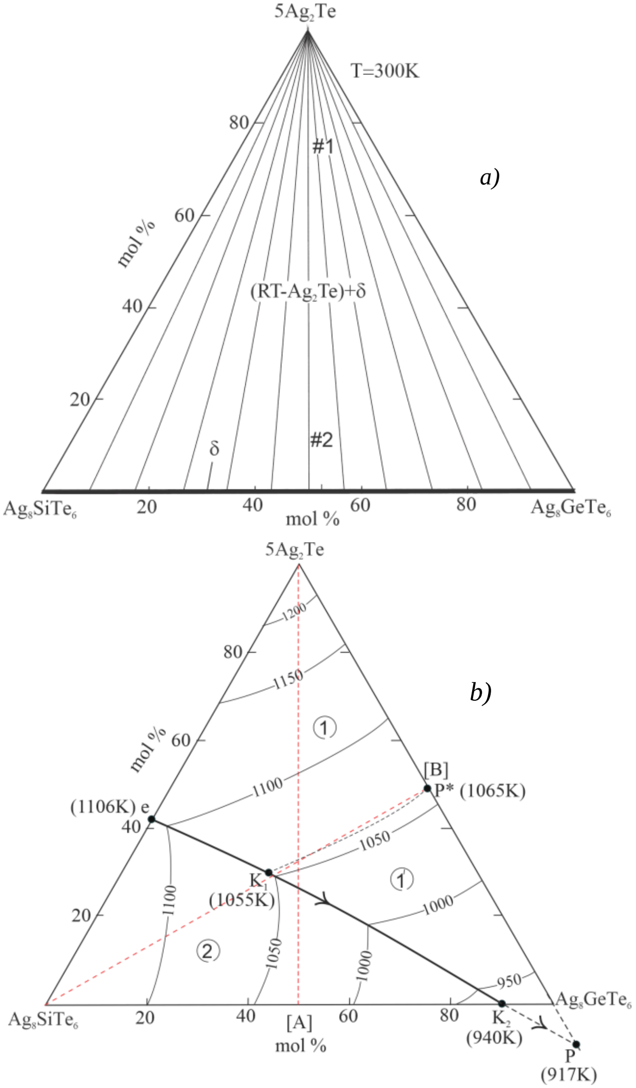

Figure 14. Solid phase equilibria diagram (a) and liquidus surface projection (b) of Ag_2Te–Ag_8GeTe_6–Ag_8SiTe_6 system at 300 K temperature. Primary crystallization sites: 1-RT-Ag_2Te, 2-δ. Broken lines indicate internal cross-sections studied [6]

The fourth chapter is dedicated to the study of the partial molar and standard integral thermodynamic functions of silver in Ag_8SiSe_6,

Ag_8SiTe_6 compounds and the study of the ionic conductivity of Ag_8GeSe_6 compound by EMF method. The results of these studies were published in [8, 11]. Calculation of thermodynamic properties of some compounds of the argyrodite class with the formula Ag_8BX_6. For the thermodynamic study of silver-silicon selenide (telluride), a solidification circuit of the type given below was designed.

(-) Ag (solid) | solid electrolyte, Ag+| (in Ag alloy) (solid) (+)

For EMF measurements, silver metal was selected as the left electrode in the hardness circuit, and alloys from the Ag_8SiSe_6-$SiSe_2$-Se (Ag_8SiTe_6-Si_2Te_3-Te) component of the Ag-Si-Se(Te) system were selected as the right electrode (Fig. 15). In Figure 15, XRD analyzes were performed to identify the mixtures marked with numbers 1, 2, 3 and 4. In the diffraction pattern of the mixture marked with numbers 1 and 2, the diffraction lines of Ag_8SiSe_6, $SiSe_2$ and free selenium are observed. The diffraction pattern of alloys No. 3 and 4 consists of the sum of the diffraction lines of Ag_8SiTe_6, Si_2Te_3 and free tellurium.

During the measurements, it was determined that EMF values change linearly depending on the temperature. The results also show that the EMF values are stable within the heterogeneous areas, and fluctuate at the boundaries of these areas. The linearity of EMF-temperature dependence makes it possible to process the results in a computer program by the method of least squares. As a result, linear equations of the following type were obtained:

$$E=a+bT\pm2\cdot\left[(S_E^2/n)+S_b^2(T_i-\overline{T})^2\right]^{1/2} \tag{2}$$

where n is the number of pairs of E and T values; SE – the dispersion of individual EMF measurements, and S_b – the constant b; $\overline{T}$ – is the average temperature. Based on linear equations of type (2) obtained for Ag-Si-Se(Te) systems (Table 2) and using the following thermodynamic expressions, the relative partial molar functions of silver at 300 K were calculated (Table 3):

$$\Delta\overline{G}_{Ag}=-zFE \tag{3}$$

$$\Delta\overline{H}_{Ag}=-z\left[E-T\left(\frac{\partial E}{\partial T}\right)_P\right]=-zFa \tag{4}$$

$$\Delta\overline{S}_{Ag}=zF\left(\frac{\partial E}{\partial T}\right)_P=zFb \tag{5}$$

where z is the charge of the active component cation; F – Faraday constant; and a and b are constants of equation (2).

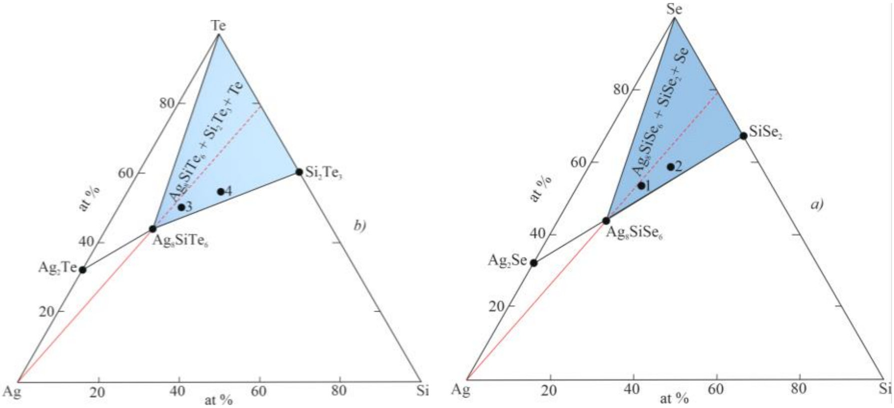

Figure 15. Diagram of solid phase equilibria at 300K for Ag_8SiSe_6-$SiSe_2$-Se composition of Ag-Si-Se system (a). Diagram of solid phase equilibria at 300K for Ag_8SiTe_6+Si_2Te_3+Te composition of Ag-Si-Te system (b) [8]

A graph of temperature dependences of EMF of type (1) solidity circuits is constructed. It was determined that this dependence is linear in the entire temperature range of the measurements for the electrode mixtures belonging to the Ag_8SiTe_6+Si_2Te_3+Te phase field. For samples of the Ag_8SiSe_6+$GeSe_2$+Se phase field, a linear dependence was observed in the temperature range of 360-450K. The reproducibility of EMF values in the temperature range of 300-355 K was very low. This can be explained by the fact that the Ag_8SiSe_6 compound undergoes 2 polymorphic phase transitions in that temperature range, which are at 315 and 354 K, respectively. It is possible that there may be kinetic inhibition in these transitions and the samples may not reach equilibrium during the measurements. At 360 K and higher, the Ag_8SiSe_6 compound is in the high-temperature cubic modification, and the measurements correctly reflect the equilibrium.

As can be seen from the fragments of the solid phase equilibrium diagrams of Ag-Si-Se(Te) systems (Fig. 15), the tie-lines starting from the Ag corner of Gibbs triangle and passing through the stoichiometric compositions of Ag_8SiSe_6 and Ag_8SiTe_6 compounds, respectively and enters Ag_8SiSe_6+$SiSe_2$+Se and Ag_8SiTe_6+Si_2Te_3+Te three-phase fields. That is, the phase diagrams show that under equilibrium conditions (imaginary) Ag removal from the compound Ag_8SiSe_6 would lead to $SiSe_2$ and elemental Se. Similarly, when Ag was removed from Ag_8SiTe_6, a mixture of Si_2Te_3+Te would be obtained. It is seen that according to the solid-phase equilibrium diagram (Fig. 15), the values of the relative partial molar functions are a response to the following virtual-cell reactions:

$$8Ag + SiSe_2 + 4Se = Ag_8SiSe_6 \qquad (6)$$

$$8Ag + 0{,}5Si_2Te_3 + 4{,}5Te = Ag_8SiTe_6 \ (7)$$

Therefore, the integral thermodynamic functions of ternary compounds were calculated from the expressions given below: (Δ Z≡ Δ G, Δ H)

$$\Delta_f Z^o(Ag_8SiSe_6) = 8\Delta\bar{z}_{Ag} + \Delta_f Z^o(SiSe_2) \qquad (8)$$

$$\Delta_f Z^o(Ag_8SiTe_6) = 8\Delta\bar{z}_{Ag} + 0{,}5\Delta_f Z^o(Si_2Te_3) \qquad (9)$$

Absolute entropies can be calculated based on the expressions:

$$S^o(Ag_8SiSe_6)= 8[\overline{\Delta s}_{Ag} + S^o(Ag)] + S^o(SiSe_2) + 4S^o(Se) \qquad (10)$$

$$S^o(Ag_8SiTe_6)= 8[\overline{\Delta s}_{Ag} + S^o(Ag)] + 0{,}5S^o(Si_2Te_3) + 4{,}5S^o(Te) \quad (11)$$

The results of calculations according to equations (8)-(11) are given in Table 5. The errors were calculated by the error accumulation method.

During the calculation of integral thermodynamic functions, in addition to the quantities obtained by the EMF method (Table. 4), the standard entropies of the elementary components involved in reactions (6) and (7) taken from the database (Ag-42.55±0.13 J(K) ·mol)), as well as the thermodynamic functions of $SiSe_2$ and Si_2Te_3 compounds were used. Literature data on the thermodynamic properties of both compounds are contradictory.

Table 2.

Equations of the temperature dependence of EMF of type (1) cell in some phase fields of Ag-Si-Se(Te) systems [8]

Phase field	E, mV = a+bt±tS_E(T)
β-Ag_8SiSe_6 + $SiSe_2$ + Se	$249{,}14+0{,}0917T\pm2\left[\frac{2{,}2}{30}+1{,}1\cdot10^{-4}(T-404{,}9)^2\right]^{\frac{1}{2}}$
Ag_8SiTe_6 + Si_2Te_3 + Te	$247{,}58+0{,}0380T\pm2\left[\frac{1{,}9}{30}+3{,}1\cdot10^{-5}(T-374{,}0)^2\right]^{\frac{1}{2}}$

The results of calculations according to equations (8) - (11) are given in table 4. Errors are found by the error detection method.

Table 3.

Partial thermodynamic functions of silver in alloys of Ag-Si-Se(Te) systems (T=298.15K) [8]

Phase field	$-\Delta\bar{G}_{Ag}$	$-\Delta\bar{H}_{Ag}$	$-\Delta\bar{S}_{Ag}$, $J \cdot mol^{-1} \cdot K^{-1}$
	$kJ \cdot mol^{-1}$		
β-Ag_8SiSe_6 + $SiSe_2$ + Se	26,68±0,11	24,04±0,40	8,85±0,98
Ag_8SiTe_6 + Si_2Te_3 + Te	24,98±0,05	23,89±0,20	3,67±0,53

Table 5.

Integral thermodynamic functions of HT-Ag_8SiSe_6 and Ag_8SiTe_6 compounds with some relevant literature data for $SiSe_2$ and Si_2Te_3 compounds[8]

Compound	$-\Delta_f G^o$	$-\Delta_f H^o$	$\Delta_f S^o$	S^o
	$kJ \cdot mol^{-1}$		$kJ \cdot mol^{-1} \cdot K^{-1}$	
$SiSe_2$	175,3±3,5	177,6±3,2[5]	-	95,2±2.0[6]
Si_2Te_3	70,9±10	76,6±10[7]		167,0±3,0[6]
β-Ag_8SiSe_6	388,7±4,4	369,9±6,4	63,1±9,8	675±12
Ag_8SiTe_6	235,3±5,4	229,4±6,6	19,8±9,2	676±11

Study of ionic conductivity of Ag_8GeSe_6 compound. A number of important functional properties of argyrodite family compounds with the general formula $A_8B^{IV}X_6$ (A–Ag, Cu; B^{IV}–Si, Ge, Sn; X–S, Se, Te) were detailed in the dissertation. One of the most interesting of these functional properties is ionic conductivity. The ionic conductivity of binary compounds formed by copper and silver with chalcogenides is detailed in many articles. This type of conductivity, due to the mobility of copper and silver cations, is also expected to exist in argyrodite family compounds. In order to

---

[5] Olin, A. Chemical thermodynamics of selenium / B. Noläng, L. Öhman, E. Rosén [et al.]. – France: -2005. -851p.

[6] Kubaschewski, O. Materials Thermochemistry / C.B. Alcock, P.J. Spenser - Oxford: Pergamon press, -1993. -363s.

[7] Exsteen, G. Thermodynamic study of silicon sesquitelluride using a mass spectrometer, J. Phys. Chem / J. Drowart, A. Vander Auwera-Maheu, R. Callaerts // Journal Physics and Chemistry, -1967. V.71, №.12, -p. 4130-4131.

accurately measure the physical parameters of the Ag_8GeSe_6 compound, it is necessary to have a high degree of purity of this compound. Therefore, the Ag_8GeSe_6 compound was first synthesized, identified by DTA and XRD methods, and then prepared in the form of pellets for physical measurements. The results of these studies were published in [11].

Temperature dependence of conductivity of Ag_8GeSe_6 compound. Figure 16 shows the temperature dependencies of the conductivity of the Ag_8GeSe_6 compound at various frequencies. As can be seen from Fig. 16, with an increase in temperature from 250 K to 320 K, the values of electrical conductivity ($\sigma(T)$) change insignificantly. A sharp increase in the values of $\sigma(T)$ is observed at temperatures above 320 K and reaches a maximum at a temperature of 325 K. In this case, the low activation energy (0.09 eV) in the temperature range of 250–320 K indicates the thermal nature of the activation of charge carriers. In the temperature range $T > 320$ K, due to the increase in conductivity, the activation energy takes on higher values (0.14 eV). The maximum value of conductivity is observed at $T = 325$ K, and the frequency of the measuring field is 10^6 Hz. The transition from a low value of the activation energy to its high value is apparently due to a sharp increase in the contribution of ion transport to the total conductivity of the sample. With a further increase in temperature, a decrease in conductivity is observed, which is apparently related to the volume-charge polarization of the crystal interface.

Time dependence of electrical conductivity of Ag_8GeSe_6 crystals. A feature of the charge transfer of ionic conductors is its large contribution to the conductivity of ions in comparison with electronic transfer. The ionic conductivity of high-resistance crystals and semiconductors, under normal conditions, is 6–7 orders of magnitude lower than the contribution of electron transfer to the total conductivity of the sample. To determine the relative contributions of the electronic and ionic components to the total conductivity of the Ag_8GeSe_6 samples at different temperatures, the Wagner polarization method was used. In compounds with a mixed electron-ion character of charge transfer, when measuring the electrical conductivity at direct current, a time dependence of the conductivity is observed. The process is associated with the formation of a double electric layer in the near-surface layer of the sample. When blocking contacts are used as electrodes, mobile ions are delayed at the sample-electrode interface, as a result, under the influence of an electric field, a concentration gradient is created in the sample volume, which in turn leads to the emergence of a diffusion flow of ions directed in the direction opposite to the drift flow (ions). Thus, since the drift and diffusion fluxes of ions are compensated, a current flows through the sample, which is associated with charge transfer only by electrons. Figure 17 shows the time dependence of the conductivity of an electrochemical cell based on Ag_8GeSe_6 crystal.

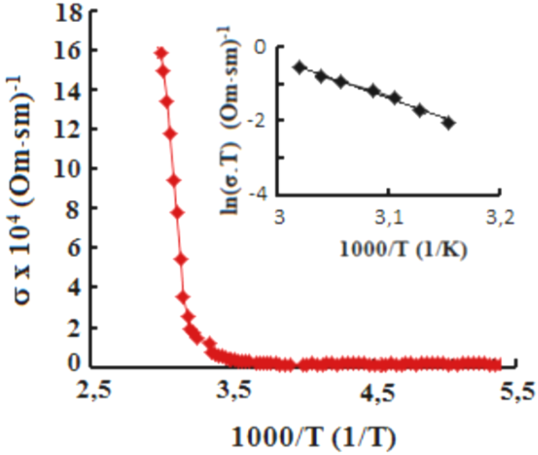

Figure 16. Temperature dependence of the conductivity of the Ag_8GeSe_6 crystal [11]

Silver contacts blocking the ionic contribution to the conductivity are used as electrodes. A constant potential difference is applied to the plates. As can be seen from the figure, in a constant field, the time dependence of the electrical conductivity is nonlinear. As a result, during measurements at the initial moment of time, the total current of ions and electrons flows; in the stationary state, charge transfer is carried out only by electrons. Thus, the result of mutual compensation of the volume charge region near the interface (Ag_8GeSe_6) — silver contact, which has a blocking character, is a decrease in electric current with time in a constant field (Fig. 17, curve 2). In the stationary state at a temperature of 325 K, ~95% ion current flows through the sample.

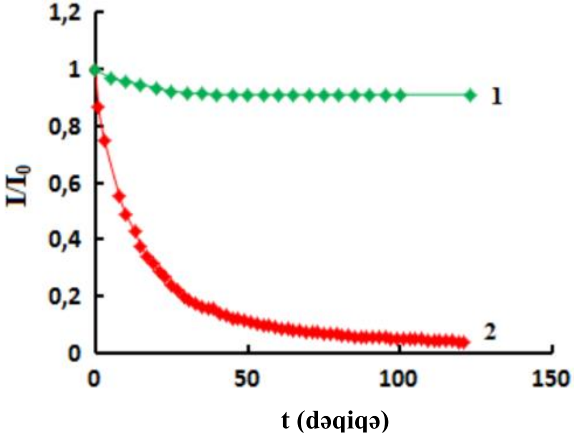

Figure 17. Time dependence of reduced electrical conductivity J(t)/J0 for compound Ag_8GeSe_6. Measurements were made at 300 K (curve 1) and 325 K (curve 2) using silver electrodes [11]

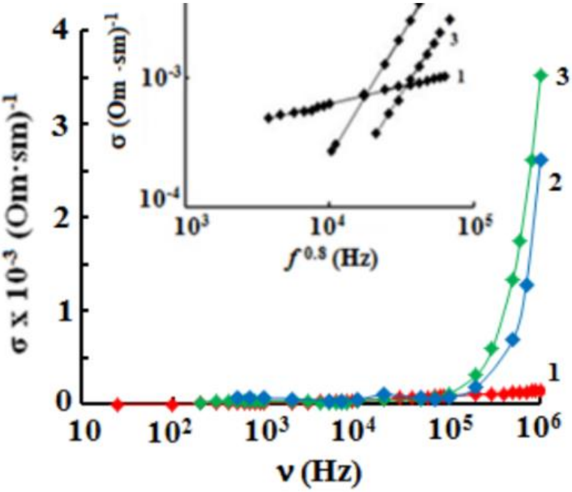

Figure 18. Frequency dependence of the conductivity of Ag_8GeSe_6 compound [11]

RESULTS

1. The character of physico-chemical interaction was determined in Ag_8SiX_6-Ag_8GeX_6 (X-S, Se, Te) systems composed of argyrodite family compounds. It has been shown that the sulfide and selenide systems are quasibinary, and the telluride system is partially quasibinary. In all three systems, limited solid solutions form between high-temperature cubic modifications of the initial compounds. In the sulfide system, the RT-modification of the primary compounds is completely mutually soluble, while in the selenide system, the formation of solid solutions leads to a sharp decrease in the polymorphic transformation temperatures of the ternary compounds and the expansion of the homogeneity area of the high-temperature cubic phase to room temperature and lower temperatures.
2. Complete pictures of phase equilibria in Ag_2X-Ag_8SiX_6-Ag_8GeX_6 systems have been obtained. Projections of the liquidus surfaces of all three systems onto the concentration triangle, as well as some vertical and horizontal sections of the solidity T-x-y phase diagrams were constructed, the primary crystallization and homogeneity areas of the phases, the types and temperatures of the non- and monovariant equilibria formed in the systems were determined. It has been shown that the sulfide and selenide systems are quasi-ternary sections of the corresponding solid tetrahedra, while the telluride system is not quasi-ternary due to the decomposition and melting of Ag_8GeTe_6 compound by peritectic reaction, but it is stable in subsolidus.
3. It was determined that in the diagrams of solid phase equilibria of Ag_2X-Ag_8SiX_6-Ag_8GeX_6 systems, solid solutions based on argyrodite compounds are in the form of thin (1-2 mol % wide) homogeneous strips along the sides of solidity triangles Ag_8SiX_6-Ag_8GeX_6, and form stable connodes with different crystal modifications of Ag_2X compounds.
4. In all three systems, samples of new solid solutions discovered on the basis of argyrodite compounds with different compositions were individually synthesized and identified. Their crystal lattice types

were determined, lattice parameters were calculated, and the latter were shown to be a linear function of composition.

5. Considering the silver electrode, the partial molar functions of silver were calculated in the Ag_8SiSe_6-$SiSe_2$-Se and Ag_8SiTe_6-Si_2Te_3-Te three-phase alloys of the corresponding ternary systems by measuring the density cycles of Ag_4RbJ_5 solid electrolyte in a wide temperature range (300-430 K). Based on the diagrams of solid phase equilibria of the respective systems, equations of virtual cell reactions were determined, sets of mutually adjusted quantities related to standard formation thermodynamic functions and standard entropies of Ag_8SiSe_6 and Ag_8SiTe_6 compounds were obtained.
6. Impedance spectroscopy method showed that above 325 K temperature, Ag_8GeSe_6 compound becomes superionic and Ag+ ions act as charge carriers. At that temperature, the compound has 95% ion and 5% electron conductivity. At the same time, it was determined that the conductivity in localized cases below 300 K temperature occurs by the jump mechanism.

THE MAIN RESULTS OF THE DISSERTATION WERE PUBLISHED IN THE FOLLOWING SCIENTIFIC WORKS:

1. Ashirov, G.M. Crystallization and phase transitions of solid solutions in the Ag_8SiS_6-$Ag_8Ge(Sn)S_6$ systems / S.R.Aslanlı, L.F.Mashadiyeva, I.C.Alverdıyev [et al.] // 9th Rostocker International Conference: “Thermophysical Properties for Technical Thermodynamics”, - Rostock, Germany, -2020, -p. 68.
2. Ashirov, G.M. Phase equılıbrıa and solıd solutıons ın the Ag_2Se-Ag_8SiSe_6-Ag_8GeSe_6 system / G.M.Shukurova, Y.İ.Jafarov, L.F.Mashadiyeva // XI Международная научная конференция "Кинетика и механизм кристаллизации, Кристаллизация и материалы нового поколения" кластер конференций, -Иваново, -Россия, -2021, -р.207.
3. Ashirov, G.M. Phase equilibria and solid solutions in the Ag_2Te-Ag_8SiTe_6-Ag_8GeTe_6 system / K.N.Babanly, L.F.Mashadiyeva, Y.A.Yusibov, M.B. Babanly//10th Rostocker International Confe-

rence: "Thermophysical Properties for Technical Thermodynamics", - Rostock, -Germany, -2021, -p.83.

4. Ashirov, G.M. Ag_8SiS_6-Ag_8GeS_6 sistemində bərk məhlulların alınması və rentgenoqrafik tədqiqi / L.F.Mashadiyeva, Y.A.Yusibov, M.B.Babanly // "Müasir təbiət və iqtisad elmlərinin aktual problemləri" beynəlxalq elmi konfrans, - Gəncə, -2021, -p.5-8.
5. Əşirov, G.M. Ag_8SiS_6–Ag_8GeS_6 sistemində faza tarazlıqları // "Gənc Tədqiqatçı" Jurnalı, -Bakı, -2022, -№1, -s. 50-56.
6. Ashirov, G.M. Phase equilibria in the Ag_8SiTe_6-Ag_8GeTe_6 system // Azerbaijan Chemical Journal, -2022, -№1, -p. 89-93.
7. Ashirov, G.M. Ag_8SiSe_6-Ag_8GeSe_6 sistemində bərk məhlulların alınması və rentgenoqrafik tədqiqi / L.F.Mashadiyeva, Y.A.Yusibov, M.B.Babanly [et al.] // Müasir təbiət və iqtisad elmlərinin aktual problemləri" beynəlxalq elmi konfrans, -Gəncə, -2022, -s.18-20.
8. Ashirov, G.M. Thermodynamic study of silver-silicon selenides (tellurides) by the emf method with Ag_4RbI_5 solid electrolyte / K.N.Babanly, L.F.Mashadiyeva // Gənc Tədqiqatçı" Jurnalı, - Bakı, - 2023, - №3, - s.45-56.
9. Ashirov, G.M. Phase equilibra in the Ag_2Se–Ag_8GeSe_6–Ag_8SiSe_6 system and characterization of the $Ag_8Si_{1-x}Ge_xSe_6$ solid solutiion / K.N.Babanly, L.F.Mashadiyeva, Y.A.Yusibov, M.B.Babanly // Chemical Problems, -Baku, -2023, -№3, -p. 229-241.
10. Ashirov, G.M. Phase equilibra in the Ag_2S–Ag_8GeS_6–Ag_8SiS_6 system and some properties of solid solutions / K.N.Babanly, L.F.Mashadiyeva, Y.A.Yusibov, M.B.Babanly // Condensed Matter and Interphases, -2023, -№2, -p. 292-301 .
11. Ashirov, G.M. Ionic conductivity of the Ag_8GeSe_6 compound / R.M.Sardarly, L.F.Mashadiyeva, N.A.Aliyeva [et al.] // Modern Physics Letters B, -2023, -v.36, -№32n33, -p. 2250171.

The defense will be held on 30 may 2024 at 10^{00} at the meeting of the Dissertation council ED1.15 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Catalysis and Inorganic Chemistry named after acad. M. Naghiyev of the Ministry of Science and Education of the Republic of Azerbaijan

Address: H.Javid, 113, AZ-1143, Baku, Azerbaijan
E-mail: kqki@kqki.science.az

The dissertation is available in the library of the Institute of Catalysis and Inorganic Chemistry named after acad. M.Naghiyev of the Ministry of Science and Education of the Republic of Azerbaijan.

Electronic versions of dissertation and its abstract are available on the official website of the at acad.M.Naghiyev Institute of Catalysis and Inorganic Chemistry of the Ministry of Science and Education of the Republic of Azerbaijan www.kqkiamea.az

Abstract was sent to the required addresses on 29 april 2024

Signed for print: 25.04.2024

Paper format: 60x84$^{1/16}$

Volume: 36 331 characters

Number of hard copies: 20