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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

OBTAINING AND PHYSICO-CHEMICAL STUDY OF THE TOPOLOGICAL INSULATOR PHASES IN THE Bi-Bi$_2$Se$_3$-Bi$_2$Te$_3$ SYSTEM

Specialty: 2303.01 – inorganic chemistry

Field of science: chemistry

Applicantı: **Gunel Samir Zeynalova**

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The work was performed in the "Chemistry" department of Ganja State University.

Scientific supervisor:	D. Sci. Chem., professor **Yusif Amirali Yusibov**
Scientific consultant	Corr.-member of ANAS, professor **Mahammad Baba Babanly**
Official opponents:	D. Sci. Chem., professor **İkhtiyar Bahram Bakhtiyarly**
	D. Sci. Chem., professor **Huseyn Ramazan Gurbanov**
	Ph. D. Chem. **Saba Huseynkhan Mammadova**

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The Chairman of the Dissertation council

Academician
Dilgam Babir Taghiyev

The Scientific secretary of the Dissertation council

Ph. D. Chem.
Ulviyya Akhmed Mammadova

The Chairman of the scientific seminar

D. Sci. Chem., professor
Akif Shikhan Aliyev

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INTRODUCTION

Relevance and degree of investigation of the topic. Bismuth chalcogenides with a tetradymite-like layered structure, in particular Bi_2Se_3 and Bi_2Te_3 compounds, solid solutions, and composite materials based on them, have been the focus of attention of researchers since the middle of the last century as valuable semiconductor and thermoelectric materials. Some of them are used as temperature controllers in portable refrigerators, as well as to generate electricity in space stations.

The discovery in the decade of our century of a topological insulator (TI)- a new quantum state of matter sharply increased interest in this material. It was found that binary and ternary compounds with a tetradymite-like layered structure have the TI property and are promising for use in a number of technologies, ranging from spintronics and quantum computing to medicine and security systems.

Despite the great interest in bismuth selenides and tellurides, reliable scheme pictures of phase equilibria in Bi-Se(Te) systems have not yet been obtained. Different versions of the phase diagrams of both systems known in the literature differ sharply from each other. Even in recent studies of these systems, contradictory data on the composition of the intermediate compounds, their crystal structure, homogeneity ranges, etc. are given.

The analysis of literature data also shows that among the numerous selenides and tellurides of bismuth, the thermodynamic properties have been studied only for compounds Bi_2Se_3 and Bi_2Te_3.

The absence of reliable data on phase equilibria in the binary systems Bi-Se(Te) has a negative impact on research in the field of chemistry and materials science of multicomponent systems based on these systems. For example, analysis shows that known phase diagrams of ternary systems such as Bi-Se-Te, A^{IV}-Bi-Te (A^{IV}-Ge, Sn, Pb) cannot be considered reliable and they need to be clarified.

Object and subject of research. The object of the dissertation research is the Bi-Bi_2Se_3, Bi-Bi_2Te_3, and Bi-Se-Te systems. The subject of research is a complex physico-chemical study of these systems.

The purpose and objectives of the study. Taking into account the foregoing, the main goal of the thesis was to obtain a new mutually consistent set of data on phase equilibria in the Bi-Bi_2Se_3, Bi-Bi_2Te_3, and Bi-Bi_2Se_3-Bi_2Te_3 systems and the thermodynamic properties of intermediate phases. To achieve this goal, the following **specific tasks** were set and solved:

- obtaining samples of Bi-Se(Te) and Bi-Se-Te systems as close to equilibrium as possible and their study by a complex of modern physical methods of analysis by improving the synthesis technique;

- construction of new variants of phase diagrams of the Bi-Bi_2Se_3, Bi-Bi_2Te_3, and Bi-Bi_2Se_3-Bi_2Te_3 systems;

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

- the thermodynamic study of the Bi-Se, Bi-Te, and Bi_2Se_3-Bi_2Te_3-Te-Se using the EMF measurements of the cells relative to the bismuth electrode.

Research Methods. The studies were carried out by traditional methods of physic-chemical analysis: differential-thermal analysis (DTA), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), microstructure analysis, and EMF measurements.

DTA was carried on "NETZSCH 404 F1Pegasus system" and "Termoscan-2" instruments. Powder X-ray diffraction patterns of the alloys were recorded on Bruker D2 Phaser and D8 ADVANCE diffractometers and analyzed by the software of these devices. SEM images were taken with a Field Emission Scanning Electron Microscope JEOLJSM-7600F scanning electron microscope. Alloy microstructures were studied with a BİOBASE. EMF measurements were carried out on a specially assembled electrochemical installation.

Main defense propositions.

- Preparation methods of samples that are maximally close to the equilibrium state for the physical-chemical study of Bi-Se, Bi-Te, and Bi-Se-Te systems;

- information on the new variants of phase diagrams of Bi-Se and Bi-Te systems, melting (decomposition) characteristics, and

temperatures of bismuth selenides and tellurides;

- T-x-y diagram of the Bi-Se-Te system in the Bi-Bi_2Se_3-Bi_2Te_3 compositions area, its iso- and polythermal sections, the variable compositions phases, their homogeneity, and primary crystallization areas;

- the results of EMF measurements in the studied systems, based on them E=a+bT $\pm$t·S_E(T) type linear equations, partial molar functions of bismuth in solids, standard integral thermodynamic functions of bismuth selenide and telluride, as well as $Bi_2Se_{3-x}Te_x$ solid solutions

Scientific novelty. The following **new results** are obtained in the work

- by applying different approaches of the complex physico-chemical study, the new, different from those given in the literature the phase equilibria in Bi-Se, Bi-Te, and Bi-Se-Te systems at ≤40 at% Bi content was obtained;

- 7 selenides and 7 tellurides of bismuth are reflected in the newly constructed T-x phase diagrams of Bi-Se and Bi-Te systems. Except for Bi_2Se_3 and Bi_2Te_3, the peritectic character of melting of these compounds was obtained, the temperatures of those reactions and the composition of the peritectic points were determined;

- in Bi-Se(Te) systems, it was determined that, unlike literature data, there are no large solid solution areas based on selenides and tellurides of bismuth. These compounds, crystallized in a tetradimite-like layered structure and belonging to the nBi_2·$mBi_2Se_3(Te_3)$ homologous series, are compounds with a practically stable composition due to their structural features;

- on a new version of the phase diagram of the Bi-Bi_2Se_3-Bi_2Te_3 system, the fields of primary crystallization and homogeneity of phases are established, the types and coordinates of non- and monovariant equilibria are determined. In the system, continuous fields are formed along the Bi_2Se_3-Bi_2Te_3, Bi_8Se_9-Bi_8Te_9, BiSe-BiTe, and Bi_4Se_3-Bi_4Te_3 sections, while other sections are characterized by the formation of wide areas of solid solutions.

- selective compositions of solid solutions in the Bi-Bi$_2$Se$_3$-Bi$_2$Te$_3$ system were obtained and identified. It has been established that the dependences of the lattice parameters of continuous solid solutions on the composition obey Vegard's rule;

- by EMF measurements of concentration cells relative to the bismuth electrode, the equations for the temperature dependence of the EMF in various phase regions of the Bi-Se, Bi-Te, and Bi$_2$Se$_3$-Bi$_2$Te$_3$-Te-Se systems were obtained and the partial thermodynamic functions of bismuth in these regions were calculated;

- virtual reactions for 14 chemical compounds formed in the studied binary systems were determined, and their standard thermodynamic functions of formation and standard entropies were calculated. The corresponding standard thermodynamic functions of formation and mixing were also determined for various compositions of Bi$_2$Se$_{3-x}$Te$_x$ solid solutions.

The theoretical and practical significance of the work. The theoretical significance of the results obtained in the dissertation lies in the fact that new results on phase equilibria in Bi-Se, Bi-Te, and Bi-Se-Te systems, thermodynamic properties of bismuth selenides and tellurides, as well as solid solutions based on them, are the scientific basis for the development of methods for the directed synthesis of the corresponding phases and the growth of monocrystals and is a contribution to the chemistry and materials science of chalcogenides with a tetradimite-like layered structure.

The practical importance of the obtained results is primarily that the new phases discovered are of great interest as potential topological insulators and thermoelectrics. On the other hand, constructed phase diagrams, thermal, thermodynamic, crystallographic, etc. properties of compounds and solid solutions are fundamental physico-chemical parameters.

Testing and application. 17 scientific works, including 8 articles (including 5 articles in scientific journals indexed in WoS and SCOPUS international databases) were published on the topic of the dissertation.

The results of the work were reported and discussed at the follo-

wing scientific conferences: Müasir kimya və biologiyanın aktual problemləri (Gəncə, Azərbaycan, 2017, 2018, 2019, 2021); 5th International Turkic World Conference on Chemical Sciences and Technologies, ITWCCST 2019; 9th Rostocker International Conference "Thermophysical Properties for Technical Thermody- namics" (Rostock, Germany, 2020); XII International conference "Electronic Processes in organic and Inorganic Materials" (Kamia- nets-Podilskyi, Ukraine, 2020); International Conference On Actual Problems Of Chemical Engineering, dedicate to the 100th anniver- sary of the Azerbaijan State Oil and Industry University (Baku, Azerbaijan, 2020); XI Международная научная конференция "Кинетика и механизм кристаллизации. Кристаллизация как форма самоорганизации вещества" (Иваново, Россия, 2021).

The new phases obtained are potential topological insulators and thermoelectric materials and can be used for this purpose. Constructed phase diagrams, physico-chemical parameters of new phases can be included in relevant electronic information bases, as well as textbooks and reference materials, and can be used by researchers working in the materials science field, as well as in teaching special courses in master's programs of higher schools of the republic.

According to the "Google Scholar Citations" information system, 27 references were made to the author's 2 articles published in international scientific journals on the topic of the dissertation.

The name of the organization in which the dissertation work is carried out. The dissertation work was carried out at the Faculty of Chemistry of the Ganja State University.

The total volume of the dissertation with a sign indicating the volume of the structural sections of the dissertation separately. The dissertation consists of an introduction (12.150 symbols), four chapters (Chapter I - 41.703 symbols, II-35.463, III-37.880, IV-27.810), the main results and conclusions (3.167), the list of used literature and published works of the author on the topic of the dissertation (189 items). The thesis is presented in 161 pages and contains 52 figures and 23 tables.

MAIN CONTENT OF WORK

In **the first chapter** of the dissertation, the literature data about phase equilibria, crystal-chemical, thermal, thermodynamic, etc. properties of the intermediate phases in the Bi-Se, Bi-Te, and Bi-Se-Te systems, which are the objects of research are given. Those data were used in the planning of experimental studies and processing of their results.

Here, the modern state of the physico-chemical study of multicomponent chalcogenide systems forming tetradimite-like phases was investigated and the selection of the research objects of the dissertation was justified.

The second chapter is devoted to a brief description of the synthesis and physical-chemical research methods used in the dissertation work.

Reagents with a high degree of purity (99.999%) and elementary components were used for the synthesis of primary binary and ternary compounds of the investigated systems. The synthesis was carried out by melting the mixtures of the corresponding simple substances in a stoichiometric ratio in quartz ampoules under vacuum conditions (10^{-2} Pa). After melting, some of the samples, depending on the composition, were quenched by dropping ampoules into the ice water from 650^0 C and annealed at $250\text{-}500^0$C for 1500 hours.

In **chapter III,** the results of the physico-chemical study of the Bi-Se-Te system in the $Bi\text{-}Bi_2Se_3\text{-}Bi_2Te_3$ composition interval are given.

Since the literature data on the boundary binary Bi-Se and Bi-Te systems, which make up the ternary system, are contradictory,

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first of all, newly clarified schemes of phase equilibria were obtained in them. For this, samples close to the maximum equilibrium state were obtained and studied by various methods.

RFA, DTA, and SEM results showed that the samples obtained by quenching from the liquid state and thermal annealing are closer to the equilibrium state - the degree of their crystallinity is higher, and their phase composition satisfies the Gibbs phase rule. Therefore, we used the results of these samples as a basis for constructing phase diagrams.

Bi-Se system. Comparison of the RFA results of the alloys obtained by "quenching+thermal annealing" with the corresponding literature data showed that, in addition to Bi_2Se_3, the Bi_4Se_3, Bi_8Se_7, BiSe, and Bi_8Se_9 samples are single-phase and have the diffraction patterns given in the literature for the corresponding compounds. It was also determined that in the samples containing Bi_3Se_2 (40 at % Se) and Bi_3Se_4 (57.1 at % Se), although the main phases are Bi_3Se_2 and Bi_3Se_4, they are not homogeneous: in the first case, elemental bismuth and Bi_4Se_3 compound, and in the second one, the diffraction lines of the Bi_8Se_9 and Bi_2Se_3 compounds are also observed. Powder diffractograms of some synthesized bismuth selenides are given in Fig. 1.

Based on powder diffractograms, the crystal lattice types of the synthesized compounds were determined and their parameters were calculated. A comparison of the obtained results (Table 1) with relevant literature data shows a good agreement between them.

Based on the heating thermograms, taking into account the RFA results, a new version of the T-x phase diagram of the Bi-Se system in the $Bi-Bi_{0,4}Se_{0,6}$ compositions interval was constructed (Fig. 2).

It can be seen from the phase diagram that there are 7 phases in the system. Bismuth sesquiselenide melts congruently at 705ºC. The remaining 6 compounds melt with decomposition according to peritectic reactions and form a number of peritectic reactions in the system. The Bi_3Se_2 compound forms a eutectic with elemental Bi.
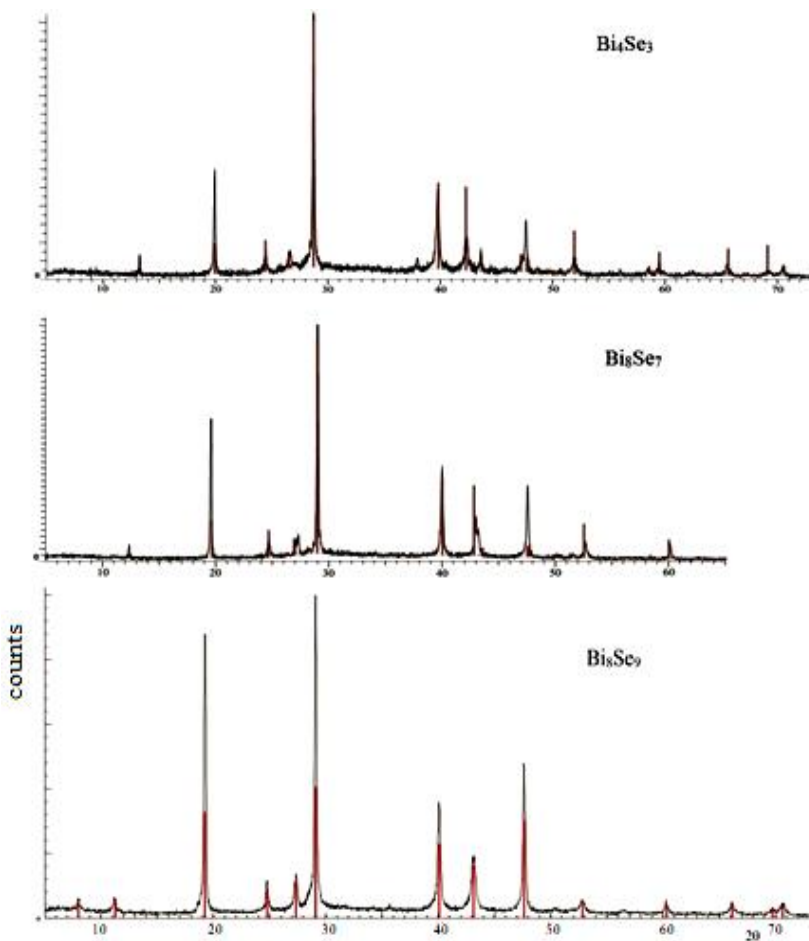
Figure 1. Powder diffractograms of some synthesized bismuth selenides. The red lines - are the literature data.

All nonvariant equilibria observed in the system and the coordinates of the corresponding points are shown in Table 2.

In the dissertation, cooling thermograms and heating thermograms of samples prepared by different methods were investigated and the phase diagram was constructed in the context of comparing different variants of the phase diagram of the Bi-Bi_2Se_3

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system. It was shown that the T-x diagram reflects the equilibrium state more correctly.

<div align="right">Table 1</div>

The crystal lattice types and parameters of the synthesized bismuth selenides and tellurides

| Compound	Syngony, space group, lattice parameters, Å
Bi_2Se_3	*rhombohedral, $R3m$, a = 4.1396(4); c = 28,6360(4)*
Bi_3Se_4	*rhombohedral, $R3m$, a = 4.230; c = 40.400*
Bi_8Se_9	*rhombohedral, $R3m$, a = 4.222; c = 97.10*
BiSe	*trigonal, $P3m1$, a = 4.1790; c = 23.0280*
Bi_8Se_7	*trigonal, $P3m1$, a = 4.220; c = 85.65*
Bi_4Se_3	*rhombohedral, $R3m$, a = 4.332; c = 40.610*
Bi_3Se_2	*trigonal, $P3m1$, a = 4.256; c = 58.720*
Bi_7Te_3	*rhombohedral, $R3m$, a = 4.4726(3); c = 119.04(8)*
Bi_2Te	*trigonal, $P3m1$, a = 4.4683(3); c = 18.068*
Bi_4Te_3	*rhombohedral, $R3m$, a = 4.4472(2); c = 41.886(3)*
BiTe	*trigonal, $P3m1$, a = 4.4328(2); c = 24.014(2)*
Bi_8Te_9	*rhombohedral, $R3m$, a = 4.4245(4); c = 103.91(9)*
Bi_4Te_5	*trigonal, $P3m1$, a = 4.4105(3); c = 54.341(7)*
Bi_2Te_3	*rhombohedral, $R3m$, a = 4.3828(1); c = 30.482(5)*

It should be specially noted that while the BiSe compound has a wide homogeneity area, the literature data has not been confirmed by us. In the 42-55.5 at% Se compositions range, which is indicated as the homogeneity area of this compound, we have demonstrated the presence of 4 chemical compounds (Bi_4Se_3, Bi_8Se_7, BiSe, and Bi_8Se_9) with individual diffraction patterns (Fig. 2). Comparison with T-x compilation diagram presented by Okamoto[1] shows that only 7 of the 15 mentioned compounds have been confirmed by us.

The results of studies to refinement the phase diagram of the Bi-Se system are reflected in [3, 9, 17].

[1] Okamoto, H. The Bi-Se (Bismuth-Selenium) System. // J.Phase Equilibria, 1994, vol.15, 195–201

The Bi-Te system. For this system, as a result of the study of the samples obtained by the "quenching+thermal annealing" method, a new picture of the phase equilibria in the Bi-Bi_2Te_3 composition area was obtained, which is different from what is given in the literature (Fig. 3).
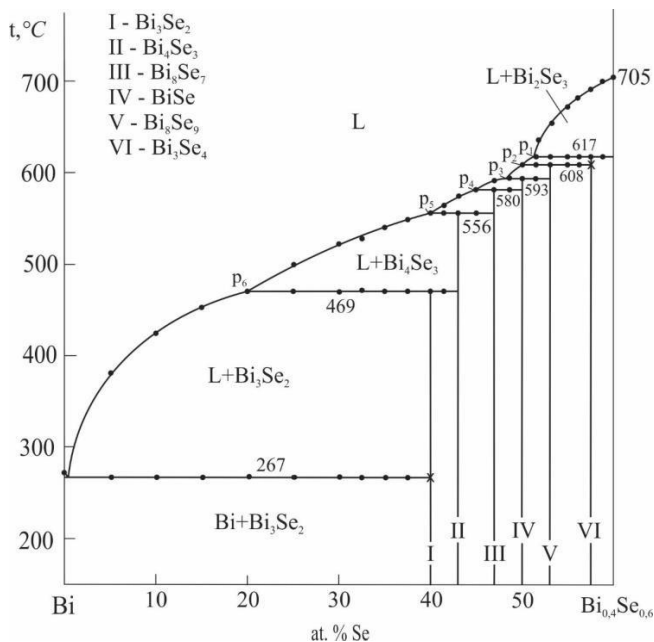
Figure 2. The phase diagram of the Bi-Se system

The nonvariant equilibria in the Bi- Bi_2Se_3 system

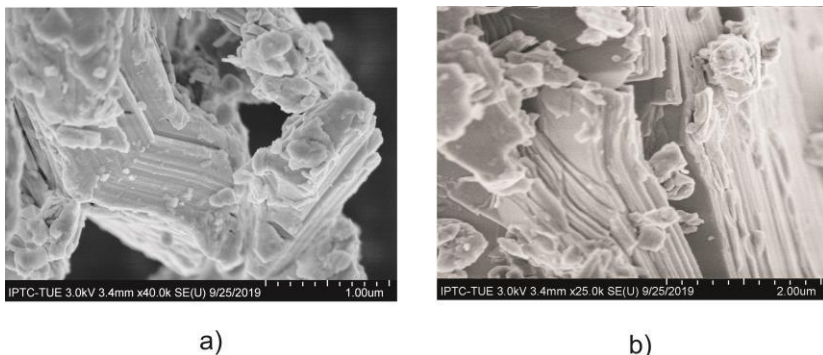| Point in Fig.2	Equilibria	t, ^oC	Composition, mol %	
			Bi	Se
P_1	L+ $Bi_2Se_3 \leftrightarrow Bi_3Se_4$	617	49	51
P_2	L+ $Bi_3Se_4 \leftrightarrow Bi_8Se_9$	608	50	50
P_3	L+ $Bi_8Se_9 \leftrightarrow BiSe$	593	51,5	48,5
P_4	L+ $BiSe \leftrightarrow Bi_8Se_7$	580	56,5	43,5
P_5	L+ $Bi_8Se_7 \leftrightarrow Bi_4Se_3$	556	60	40
P_6	L+ $Bi_4Se_3 \leftrightarrow Bi_3Se_2$	469	80	20
E	L$\leftrightarrow$ Bi+Bi_3Se_2	267	98	2
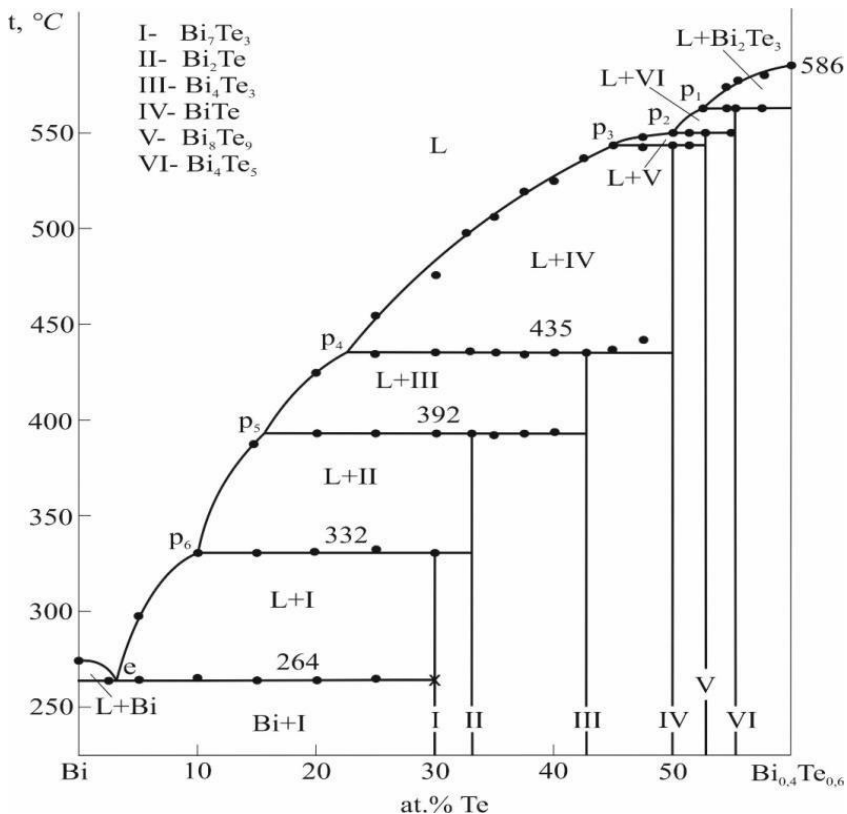
Figure 3. The phase diagram of the Bi-Te system

As in the Bi-Se system, there is a cascade of horizontal lines reflecting 6 peritectic and 1 eutectic equilibria in the T-x diagram of this system. Those nonvariant equilibria and the coordinates of the corresponding points are given in Table 2. Our results show the formation of 7 chemical compounds in the system: Bi_2Te_3, Bi_4Te_5, Bi_8Te_9, BiTe, Bi_4Te_3, Bi_2Te, and Bi_7Te_3. The first congruent melts at 586°C, and the rest melt with decomposition at 562, 550, 541, 435, 392, and 332°C, according to peritectic reactions. The Bi_7Te_3 compound forms a eutectic with ~2.5 at% elemental bismuth and crystallizes at 264°C.

The homogeneity of compounds reflected in the phase diagram

was confirmed by RFA and SEM methods. Fig. 4 shows SEM pictures of the Bi_2Te and Bi_4Te_3 compounds as an example. They indicate the homogeneity and layered structure of both compounds.

a)   b)

Figure 4. The SEM images of the Bi_2Te (a) and Bi_4Te_3 (b) compounds

Point in Fig.3	Equilibria	t, °C	Composition, at %	
			Bi	Te
P1	L+ $Bi_2Te_3 \leftrightarrow Bi_4Te_5$	562	48	52
P2	L+ $Bi_4Te_5 \leftrightarrow Bi_8Se_9$	550	50	50
P3	L+ $Bi_8Te_9 \leftrightarrow BiTe$	541	55	45
P4	L+ $BiTe \leftrightarrow Bi_4Te_3$	435	77	23
P5	L+ $Bi_4Te_3 \leftrightarrow Bi_2Te$	392	84	16
P6	L+ $Bi_2Te \leftrightarrow Bi_7Te_3$	332	90	10
E	L$\leftrightarrow$ Bi+Bi_7Te_3	264	97,5	2,5

Table 1 shows the crystallographic parameters of bismuth tellurides obtained by us. The dissertation provides a comparative analysis of the phase diagram and crystallographic parameters with relevant literature data.

The results of studies to refine the phase diagram of the Bi-Te system are reflected in [4, 8, 1].

T-x-y diagram of the Bi_2-Bi_2Se_3-Bi_2Te_3 system. The Bi_2Se_3-Bi_2Te_3 section of the phase diagram of the Bi-Se-Te system is quasi-binary and is characterized by the complete solubility of the components in each other both in liquid and solid state. This makes it possible to separate and study its Bi-Bi_2Se_3-Bi_2Te_3 concentration area as an independent subsystem. All compounds of this subsystem formed in the Bi-Bi_2Se_3 and Bi-Bi_2Te_3 boundary systems are Van der Waals compounds with a mixed layer structure formed as a result of different alternations of Bi_2 bi- and Bi_2X_3 five layers, it is convenient to express the composition as Bi_2-Bi_2Se_3-Bi_2Te_3.

Solid phase equilibria in the Bi_2-Bi_2Se_3-Bi_2Te_3 system. Based on the RFA results of the samples prepared under the above-pointed conditions, the general picture of the solid phase equilibria in the system was determined (Fig. 5). It was determined that continuous substitution solid solutions are formed on the Bi_4Se_3-Bi_4Te_3, BiSe-Bi-Te, and Bi_8Se_9-Bi_8Te_9 sections. Fig. 6 shows the powder diffractograms of some alloys on the Bi_2Se_3-Bi_4Te_3 section as an example. As can be seen from Fig.6, the diffraction patterns of all mixtures are qualitatively the same with the diffractograms of the primary compounds. As the composition changes from selenide to telluride, the diffraction peaks "shift" in the direction of small angles. This is related to the increase in the density of tellurium in solid solutions and the increase in lattice parameters.

RFA results also show the formation of large (10-20 mol %) solid solution areas based on other binary compounds of the system (Fig. 5).

In Fig. 5, the solid solutions are marked as follows: $Bi_2Se_{3-x}Te_x(\alpha)$, $Bi_8Se_{9-x}Te_x(\gamma)$, $BiSe_{1-x}Te_x(\delta)$, $Bi_4Se_{3-x}Te_x(\varepsilon)$, $Bi_3Se_{4-x}Te_x(\beta_1)$, $Bi_4Te_{5-x}Se_x(\beta_2)$, $Bi_8Se_{7-x}Te_x(\eta_1)$, $Bi_2Te_{1-x}Se_x(\eta_2)$, $Bi_3Se_{2-x}Te_x(\varphi_1)$, $Bi_7Te_{3-x}Se_x(\varphi_2)$. The areas of homogeneity of these phases are in the form of strips with a width of 1-2 mol % directed parallel to the Bi_2Se_3-Bi_2Te_3 system of the concentration triangle. The presence of these homogeneous areas leads to the formation of a number of 2- and 3-phase areas in the system (Fig. 5).
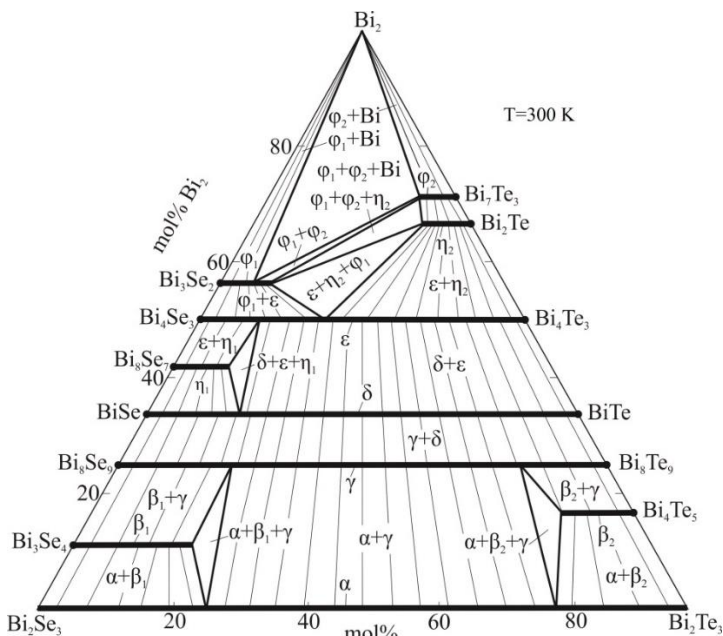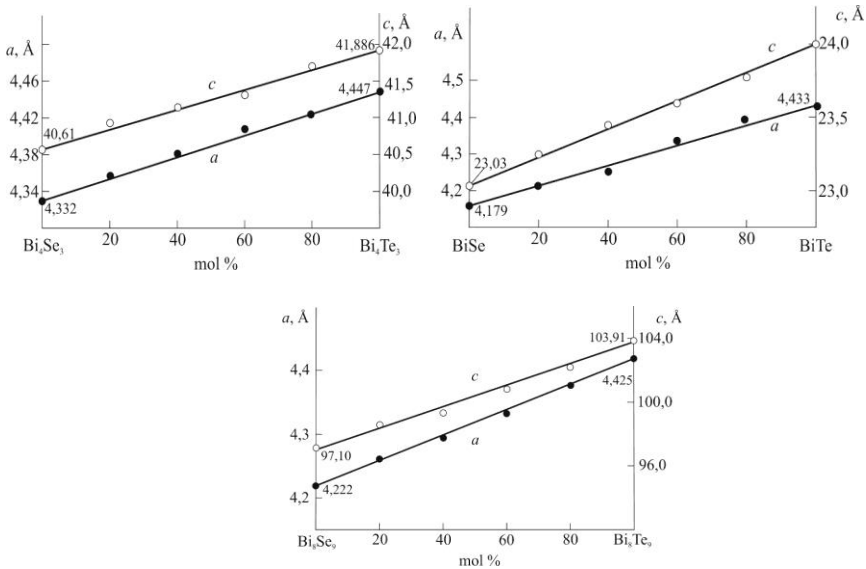
Figure 5. Solid phase equilibria diagram of the Bi_2-Bi_2Se_3-Bi_2Te_3 system at room temperature
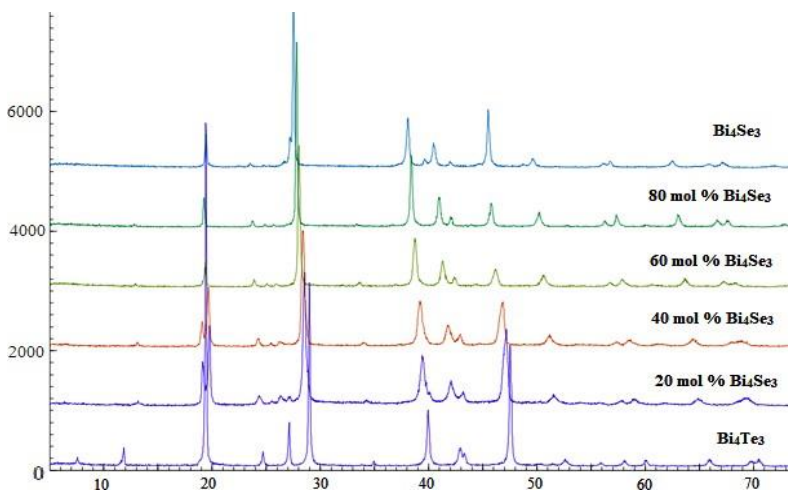
Figure 6. The powder diffractograms of the sone alloys of the Bi_4Se_3-Bi_4Te_3 section

It can be seen from Fig. 7 that the composition dependences of the lattice parameters in solid solutions on the Bi_4Se_3-Bi_4Te_3, BiSe-BiTe və Bi_8Se_9-Bi_8Te_9 sections obey the Vegard rule.

Figure 7. Dependences of crystal lattice parameters on the composition of the Bi_4Se_3-Bi_4Te_3 (a), BiSe-BiTe (b) and Bi_8Se_9-Bi_8Te_9 (c) sections

Liquidus surface of the Bi_2-Bi_2Se_3-Bi_2Te_3 system. The interpretation of the DTA results obtained for the Bi-Bi_2Se_3-Bi_2Te_3 system, taking into account the T-x diagrams of the Bi-Bi_2Se_3 (Fig. 2), Bi- Bi_2Te_3 (Fig. 3) boundary and Bi_2Se_3-Bi_2Te_3 systems and the solid phase equilibria diagram (Fig. 5) allowed to construct the projection of liquidus surface (Fig. 8).

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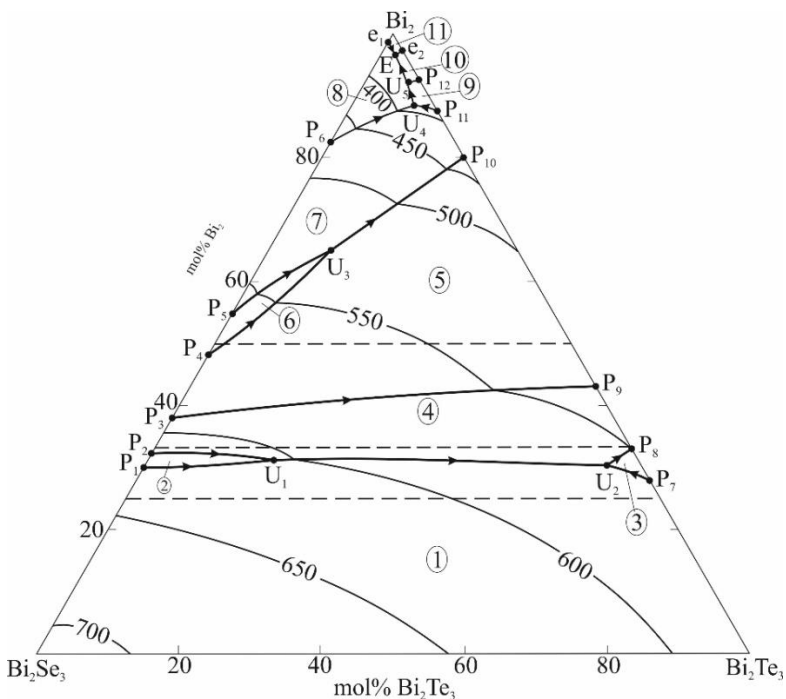
Figure 8. The projection of the liquidus surface of the Bi₂ - Bi₂Se₃ - Bi₂Te₃ system. Primary crystallization fields: 1-α; 2-β₁; 3-β₂; 4-γ; 5-δ; 6- η₁ ;7-ε; 8- φ₁; 9-η₂; 10-φ₂; 11-Bi.

As can be seen, the phase diagram of the system consists of 11 primary crystallization areas. 10 of these areas correspond to the solid solutions based on various binary compounds. The areas of homogeneity of these solid solutions are very wide, and along the three sections they are continuous, which leads to a sharp change in the composition of not only the liquid phase, but also the solid phases depending on the temperature, and the crystallization is very complicatedAnother feature of the system is the absence of quasibinary sections. Only three of the polythermal sections (Bi₄Se₃-Bi₄Te₃, BiSe-BiTe, and Bi₈Se₉-Bi₈Te₉) are quasi-stable. They are given by broken lines in Fig. 8.

Table 4

Non- and monovariant equilibria in the Bi_2-Bi_2Se_3-Bi_2Te_3 system.

Point or curve in Fig.8	Equilibria	t, ⁰C	Composition, mol %		
			Bi_2	Bi_2Se_3	Bi_2Te_3
U_1	L+ $\beta_1 \leftrightarrow \alpha + \gamma$	603	31	8	51
U_2	L+ $\alpha \leftrightarrow \gamma + \beta_2$	557	31	5	64
U_3	L+ $\eta_1 \leftrightarrow \delta + \epsilon$	530	65	26	9
U_4	L+ $\epsilon \leftrightarrow \varphi_1 + \eta_2$	384	88	3	9
U_5	L+ $\eta_2 \leftrightarrow \varphi_1 + \varphi_2$	325	92	2	6
E	L $\leftrightarrow$ Bi+$\varphi_1 + \varphi_2$	262	97	1	2
P_1U_1	L+ $\alpha \leftrightarrow \beta_1$	617-603			
P_2U_1	L+ $\beta_1 \leftrightarrow \gamma$	608-603			
U_1U_2	L+ $\alpha \leftrightarrow \gamma$	603-564			
U_2P_7	L+ $\alpha \leftrightarrow \beta_2$	564-562			
U_2P_8	L+ $\beta_2 \leftrightarrow \gamma$	564-550			
P_3P_9	L+ $\gamma \leftrightarrow \delta$	593-541			
P_4U_3	L+ $\delta \leftrightarrow \eta_1$	580-530			
P_5U_3	L+ $\eta_1 \leftrightarrow \epsilon$	556-530			
U_3P_{10}	L+ $\delta \leftrightarrow \epsilon$	530-435			
P_6U_4	L+ $\epsilon \leftrightarrow \varphi_1$	469-384			
$P_{11}U_4$	L+ $\epsilon \leftrightarrow \eta_2$	392-384			
U_4U_5	L $\leftrightarrow \varphi_1 + \eta_2$	384-325			
$P_{12}U_5$	L+ $\eta_2 \leftrightarrow \varphi_2$	332-325			
u_5E	L $\leftrightarrow \varphi_1 + \varphi_2$	325-262			
e_1E	L $\leftrightarrow \varphi_1 +$ Bi	267-262			
e_2E	L $\leftrightarrow \varphi_2 +$ Bi	264-262			

Note: The nonvariant equilibria of boundary binary systems are given in Tables 2 and 3.

Liquidus surfaces are bounded by a number of monovariant equilibria curves and nonvariant equilibria points (Fig. 8).

The types and temperatures of all non- and monovariant equilibria found in the system are shown in Table 4.

An interesting point is that in three cases, the curves coming

from the adjacent peritectic points (P_1 and P_2; P_4 and P_5; P_7 and P_8) of the same boundary system combine and lead to the creation of nonvariant transition equilibria (U_1, U_2, U_3 points). These transition reactions reflect the limitation of the fields of the β_1-; η_1- and β_2- solid solutions and the formation of the $\alpha+\beta_1+\gamma$, $\delta+\varepsilon+\eta_1$, and $\alpha+\beta_2+\gamma$ three-phase fields, respectively.

In the bismuth-rich part of the concentration triangle, the U_4 and U_5 transitions, as well as the formation of E-four-phase eutectic equilibria, reflect the formation of heterogeneous phase fields involving ε, η_1, η_2, φ_1, φ_2 phases, and elemental bismuth.

Some polythermal sections of the phase diagram of the Bi_2-Bi_2Se_3-Bi_2Te_3 system are given in the thesis and analyzed in detail in the context of the general T-x-y diagram.

New results of phase equilibria in the Bi_2-Bi_2Se_3-Bi_2Te_3 system were published in [1, 2, 13-16].

Chapter IV presents the results of thermodynamic studies conducted by the EHQ method. Information about the basics of the EHQ method, its various modifications used in thermodynamic studies, and the main requirements imposed on them is given in the second chapter of the dissertation. At the beginning of this chapter, the features of applying the EHQ method to multiphase multicomponent systems are explained. Based on these data, the possibility of applying the EHQ method to our research objects is justified. Then, the organization, implementation, and results processing methods of our research using the EHQ method, and the original results we received are presented and discussed.

The results of thermodynamic study of compounds and solid solutions in Bi-Se, Bi-Te and Bi-Se-Te systems are given in papers [5, 7, 8-12, 17].

Thermodynamic properties of bismuth selenides and tellurides. 7 selenides and 7 tellurides of bismuth are reflected in the phase diagram of the Bi-Se and Bi-Te systems constructed by us (Fig. 2 and 3).

To study the thermodynamic properties of these compounds the

$$(-) \text{ Bi (s.) } | \text{ ionic liquid} + Bi^{3+} | \text{ (Bi in alloy) } (+) \qquad (1)$$

type concentration cells were assembled and their EMF were measured in the 300-450 K temperature range. Equilibrium samples were taken from different two-phase areas of the studied systems as the right electrode of the cells. An ionic liquid (morpholine formate) with ~0.2 wt.% $BiCl_3$ (superdry, 99.99% purity) was used as the electrolyte. Morpholine formate was prepared from 99% pure morpholine and 97% pure formic acid. All three reagents were purchased from Alfa Aesar. The morpholine formate was prepared as follows: morpholine is poured into a three-necked flask with a lid. The flask is placed in a bath of ice water. The flask includes a reverse condenser, a dropping funnel and a thermometer for measuring temperature. With vigorous stirring, formic acid was added dropwise to morpholine. Since the reaction in the flask is exothermic, an ice water bath must be used during acid addition to keep the temperature below 25°C. After the addition of formic acid, the excess amine or acid was evaporated, displacing it under low pressure, and the remaining liquid was completely dehydrated to obtain an ionic liquid at 80°C and a pressure of 1-5 mmHg. Dry $BiCl_3$ was added to the obtained ionic liquid in an inert medium (dry nitrogen or argon). The electrolyte prepared in this way was stored in a closed container in an inert gas environment until the assembly of the electrochemical cells.

The most important requirement for electrodes in electrochemical cell is their maximum approximation to the equilibrium state. To do this, samples of both studied systems for a long time (2-3 months) were kept ~50 degrees below the corresponding solidus temperatures. Based on the T-x diagrams of these systems, the optimal temperatures for the heat treatment of samples were determined. After heat treatment, in order to bring the state of alloy electrodes into the temperature range of EMF measurements, they were additionally annealed for 1 week during 380–400 K a temperature interval.

The right electrodes of the electrochemical cells were prepared from preliminarily synthesized and annealed in the above temperature rejimes samples, ground into powder and pressed in the form of tablets with a diameter of 5–6 mm. and 2-3 mm thick on a molybdenum wire, which plays the role of a current conductor. The left

electrode was made in the same way from elemental bismuth.

Special protective coatings were applied to the prepared electrode samples. This is important to protect them from damage during the assembly of the electrochemical cell and to avoid possible contacts between the electrodes during the experiments.

Then the surface of the conductive wires is cleaned by passing them through a natural gas flame and covered with special capillary glass tubes to prevent short circuits between the conductors of different electrodes in the cell during EMF measurements.

Various types of electrochemical cells are used in EMF studies with liquid electrolyte. To do this, we assembled the device described in the monograph[3]. The assembled device allows to simultaneously study up to eight alloy electrodes. The electrochemical cell and all the glass elements inside it are made of Pyrex glass. The cell body is made of a pipe with a diameter of 50-60 mm. After preparing the electrochemical cell by this method and filling half of its volume with electrolyte, dry and pure gaseous nitrogen or argon (300–400 mm.s.s.) was introduced into the cell through the protrusion.

EMF measurements were carried out using B7-34A and Keithley Model 193 digital high-resistance voltmeters. In addition to the electrochemical cell, an electric furnace, a thermocouple and measuring instruments were used in the EMF measurements. The temperature gradient in the furnace did not exceed 3-4 degrees at a height of 100 mm. If we take into account that the electrodes inside the cell are located at the same height with an accuracy of ±10 mm, then the temperature gradient between them is equal to zero. From above, the furnace is covered with a thick asbestos sheet. During the experiments, the temperature was measured with an accuracy of ±0.5 ^{0}C using a pre-calibrated mercury thermometer and a chromel-alumel thermocouple.

After assembly, the electrochemical device was kept at a temperature of ~380 K for ~3-4 days without measurements. It is im-

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[3] Babanly M.B., Yusibov Yu.A. Electrochemical methods in thermodynamics of inorganic systems, Baku, ELM, 2011

portant not to apply electric current to the system until equilibrium has been established, otherwise even slight change reactions may occur between the electrolyte and the electrodes in the galvanic cell.

Our measurements showed that the first repeating EMF values of (1)-type cells were measured after 1-2 days, and subsequent values were measured 3-5 hours after a certain stable temperature was obtained. If the values obtained as a result of repeated measurements at the same temperature did not differ by more than 0.2 mV, these values were considered to be in equilibrium.

Before and after electrochemical experiments, the masses of selective electrodes were determined. It has been established that the loss of their mass does not exceed ~0.01%. This indicates that the electrodes do not interact with the electrolyte and through it, which confirms the reversibility of electrochemical cells.

EMF measurements were carried out both during heating and during furnace cooling. It has been established that the results obtained do not depend on the rate of temperature change, which proves the reversibility of the used electrochemical cell.

Based on the EMF measurements, it was determined that the EMF values for each electrode are repeated with an accuracy of $\pm2mV$ at the given temperature, and the EMF dependences on temperature are linear.

Fig. 9 shows the EMF dependencies on temperature for some phase fields of the Bi-Se system. As can be seen, EMF is a linear function of composition.

The results of EMF measurements were processed by the least-squares method and are presented in the form of linear equations of type (2)

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

In (2), n is the number of pairs of E and T values, S_E and S_b are the dispersions of the individual EMF measurements and coefficient b, $\overline{T}$ is the average temperature, and t is the Student criterion. At a confidence level of 95% and the number of experimental points $n=$

20, the Student criterion is $t \leq 2$.
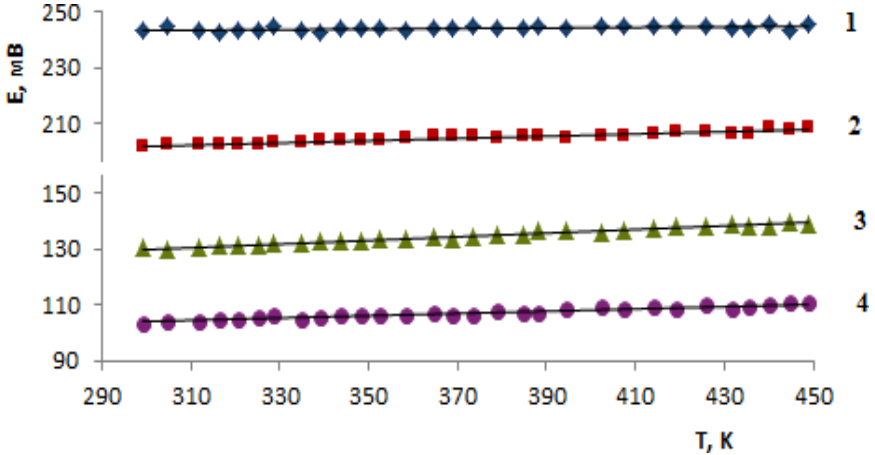
Figure 9. Temperature dependences of EHQ for Bi_2Se_3+Se (1), $Bi_3Se_4+Bi_2Se_3$ (2), $Bi_8Se_9+Bi_3Se_4$ (3), $BiSe+Bi_8Se_9$ (4) two-phase fields of the Bi-Se system

Those equations for the Bi-Se system are given in Table 5. From these equations by using the thermodynamic relations

$$\overline{\Delta G}_{Bi} = -zFE \qquad (3)$$

$$\overline{\Delta S}_{Bi} = zF\left(\frac{\partial E}{\partial T}\right)_P = zFb \qquad (4)$$

$$\overline{\Delta H}_{Bi} = -zF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right] = -zFa \qquad (5)$$

the partial molar functions of bismuth were calculated (Table 6). In the relations (3)-(5), the z - is the charge of the potential-forming component; F - Faraday constant; a and b are constants of equation (2).

Table 5

Temperature dependences of EHQ in Bi-Se system (T=300-450 K)

Phase area	$E, mV = a + bT \pm t \cdot S_E(T)$
Bi_2Se_3+Se	$241.08 + 0.0082T \pm 2\left[\dfrac{0.33}{30} + 5.4 \cdot 10^{-6}(T - 374.53)\right]^{1/2}$
$Bi_3Se_4+Bi_2Se_3$	$190.31 + 0.0391T \pm 2\left[\dfrac{0.18}{30} + 2.9 \cdot 10^{-6}(T - 374.53)\right]^{1/2}$
$Bi_8Se_9+Bi_3Se_4$	$11.08 + 0.0633T \pm 2\left[\dfrac{0.17}{30} + 2.8 \cdot 10^{-6}(T - 374.53)\right]^{1/2}$
$BiSe+Bi_8Se_9$	$90.19 + 0.0452T \pm 2\left[\dfrac{0.24}{30} + 4.2 \cdot 10^{-6}(T - 374.92)\right]^{1/2}$
Bi_8Se_7+BiSe	$67.59 + 0.0685T \pm 2\left[\dfrac{0.28}{30} + 4.9 \cdot 10^{-6}(T - 374.92)\right]^{1/2}$
$Bi_4Se_3+Bi_8Se_7$	$60.04 + 0.0548T \pm 2\left[\dfrac{0.16}{30} + 2.8 \cdot 10^{-6}(T - 374.92)\right]^{1/2}$
$Bi_3Se_2+Bi_4Se_3$	$29.07 + 0.0884T \pm 2\left[\dfrac{0.24}{30} + 4.1 \cdot 10^{-6}(T - 374.92)\right]^{1/2}$
Bi_2Te_3+Te	$136.73 - 0.0133T \pm 2\left[\dfrac{0.21}{30} + 3.4 \cdot 10^{-6}(T - 376.17)^2\right]^{1/2}$
$Bi_4Te_5+Bi_2Te_3$	$89.16 + 0.0428T \pm 2\left[\dfrac{0.23}{30} + 3.7 \cdot 10^{-6}(T - 376.17)^2\right]^{1/2}$
$Bi_8Te_9+Bi_4Te_5$	$78.93 + 0.0268T \pm 2\left[\dfrac{0.23}{30} + 3.9 \cdot 10^{-6}(T - 376.17)^2\right]^{1/2}$
$BiTe +Bi_8Te_9$	$65.54 + 0.00238T \pm 2\left[\dfrac{0.23}{30} + 3.7 \cdot 10^{-6}(T - 376.38)^2\right]^{1/2}$
Bi_4Te_3-BiTe	$43.41 + 0.0290T \pm 2\left[\dfrac{0.27}{30} + 4.5 \cdot 10^{-6}(T - 376.38)^2\right]^{1/2}$
$Bi_2Te-Bi_4Te_3$	$30.39 + 0.0358T \pm 2\left[\dfrac{0.22}{30} + 3.7 \cdot 10^{-6}(T - 376.38)^2\right]^{1/2}$
$Bi_7Te_3-Bi_2Te$	$10.71 + 0.0627T \pm 2\left[\dfrac{0.21}{30} + 3.4 \cdot 10^{-6}(T - 376.38)^2\right]^{1/2}$

Table 6
Partial thermodynamic functions of the bismuth in the Bi-Se and Bi-Te systems at 298 K

Phase area	$-\overline{\Delta G}_{Bi}$	$-\overline{\Delta H}_{Bi}$	$\overline{\Delta S}_{Bi}$
	$kC \cdot mol^{-1}$		$C \cdot mol^{-1} \cdot K^{-1}$
Bi_2Se_3+Se	70.50 ± 0.08	69.78 ± 0.33	2.41 ± 0.87
$Bi_3Se_4+Bi_2Se_3$	58.46 ± 0.06	55.09 ± 0.25	11.32 ± 0.66
$Bi_8Se_9+Bi_3Se_4$	37.61 ± 0.06	32.15 ± 0.24	18.32 ± 0.65
$BiSe+Bi_8Se_9$	30.01 ± 0.07	26.11 ± 0.30	13.08 ± 0.79
Bi_8Se_7+BiSe	25.48 ± 0.08	19.57 ± 0.32	19.84 ± 0.85
$Bi_4Se_3+Bi_8Se_7$	22.11 ± 0.06	17.38 ± 0.25	15.85 ± 0.65
$Bi_3Se_2+Bi_4Se_3$	16.04 ± 0.07	8.42 ± 0.30	25.58 ± 0.78
Bi_2Te_3+Te	38.43 ± 0.06	39.58 ± 0.27	-3.85 ± 0.71
$Bi_4Te_5+Bi_2Te_3$	29.50 ± 0.07	25.81 ± 0.28	12.38 ± 0.74
$Bi_8Te_9+Bi_4Te_5$	25.16 ± 0.07	22.85 ± 0.29	7.76 ± 0.76
$BiTe+Bi_8Te_9$	21.024 ± 0.07	18.97 ± 0.28	6.89 ± 0.74
Bi_4Te_3+BiTe	15.07 ± 0.07	12.56 ± 0.31	8.40 ± 0.82
$Bi_2Te+Bi_4Te_3$	11.89 ± 0.07	8.80 ± 0.28	10.37 ± 0.74
$Bi_7Te_3+Bi_2Te$	8.52 ± 0.07	3.10 ± 0.27	18.16 ± 0.72

Based on the phase diagrams of Bi-Se and Bi-Te systems, the potential-forming reactions corresponding to this partial molar quantity were made, and the standard integral thermodynamic functions of the compounds were calculated (Table 7).

As an example, let's look at the calculations steps for the Bi_2Se_3 and Bi_3Se_4 compounds. Potential-forming reactions for those compounds according to the phase diagram is in the following form of equations

$$Bi+1.5Se=0.5Bi_2Se_3 \qquad (6)$$
$$Bi+4Bi_2Se_3=3Bi_3Se_4 \qquad (7)$$

According to equations (6), (7), the standard thermodynamic functions of the formation for Bi_2Se_3 and Bi_3Se_4 can be calculated from the relations

$$\Delta_f Z^0(Bi_2Se_3) = 2\overline{\Delta Z_{Bi}} \qquad (8)$$

$$\Delta_f Z^0(\mathrm{Bi_3Se_4}) = \frac{1}{3}\overline{\Delta Z_{Bi}} + \frac{4}{3}\Delta_f Z^0(\mathrm{Bi_2Se_3}) \qquad (9)$$

here $Z \equiv G$, H, while standard entropy – by using the relations

$$S^0(\mathrm{Bi_2Se_3}) = 2\Delta\overline{S}_{Bi} + 2S^0(\mathrm{Bi}) + 3S^0(\mathrm{Te}) \qquad (10)$$

$$S^0(\mathrm{Bi_3Se_4}) = \frac{1}{3}\Delta\overline{S}_{Bi} + \frac{1}{3}S^0(\mathrm{Bi}) + \frac{4}{3}S^0(\mathrm{Bi_2Se_3}) \qquad (11)$$

Standard integral thermodynamic functions of other compounds were calculated similarly. In the calculations, the values of standard entropies of bismuth, selenium, and tellurium given in the literature (Bi - 56.7 ± 0.5 J·mol^{-1}·K^{-1}, Se - 42.1 ± 0.2 J·mol^{-1}·K^{-1}, Te - 49.5 ± 0.21 J·mol^{-1}·K^{-1}) was used. Errors were found by the method of uncertainty propagation.

Table 7

Standard integral thermodynamic functions of the bismuth selenides and tellurides

Compound	$-\Delta_f G^0(298K)$	$-\Delta_f H^0(298K)$	S°(298 K)
	kC·mol^{-1}		C·mol^{-1}·K^{-1}
$\mathrm{Bi_2Se_3}$	141.0 ± 0.2	139.6 ± 0.7	245.1 ± 4.3
$\mathrm{Bi_3Se_4}$	207.5 ± 0.3	204.5 ± 1.1	349.5 ± 6.1
$\mathrm{Bi_8Se_9}$	513.9 ± 0.8	500.3 ± 2.9	880.2 ± 15.3
BiSe	60.4 ± 0.1	58.5 ± 0.4	105.6 ± 1.8
$\mathrm{Bi_8Se_7}$	448.3 ± 0.8	429.1 ± 3.9	815.0 ± 14.0
$\mathrm{Bi_4Se_3}$	$204.8. \pm 0.4$	193.8 ± 1.9	391.0 ± 6.8
$\mathrm{Bi_3Se_2}$	141.9 ± 0.3	132.0 ± 1.5	288.1 ± 5.0
$\mathrm{Bi_2Te_3}$	76.9 ± 0.2	79.2 ± 0.5	254.2 ± 3.0
$\mathrm{Bi_4Te_5}$	147.8 ± 0.8	149.2 ± 1.1	375.2 ± 5.1
$\mathrm{Bi_8Te_9}$	268.2 ± 1.5	286.8 ± 2.3	897.0 ± 12.0
BiTe	34.2 ± 0.2	34.0 ± 0.3	106.7 ± 1.3
$\mathrm{Bi_4Te_3}$	$117.7 \pm 0,7$	114.6 ± 1.2	385.2 ± 5.3
$\mathrm{Bi_2Te}$	47.2 ± 0.2	44.1 ± 0.6	173.1 ± 2.8
$\mathrm{Bi_7Te_3}$	150.1 ± 0.7	135.4 ± 2.1	594.2 ± 9.6

In the dissertation, the thermodynamic data obtained by us for $\mathrm{Bi_2Se_3}$, $\mathrm{Bi_2Te_3}$, BiTe və $\mathrm{Bi_2Te}$ compounds are compared with litera-

ture data. The thermodynamic functions of other compounds were determined by us for the first time.

Thermodynamic properties of $Bi_2Se_{3-x}Te_3$ solid solutions. EMF measurements showed that the EMF values of the concentration cell of type (1) are a monotonic function of the composition. This is due to the formation of continuous substitutional solid solutions in the system

Based on EMF measurements, the partial thermodynamic functions of bismuth in solid solutions were calculated and graphs of their composition dependence were constructed (Fig. 9). It can be seen from the Figure that all partial molar quantities are continuous functions of composition. This confirms the formation of continuous solid solutions in the system.

Fig. 10 shows the solid phase equilibria diagram of the Bi_2Se_3-Bi_2Te_3-Te-Se subsystem. It can be seen that the conode lines in the $\alpha+\beta$ two-phase field are cross-sectional. Therefore, the potential-forming reaction can be in the following form:

$$Bi + 1.5Se_{1-y}Te_y = 0.5Bi_2Se_{3-x}Te_x \qquad (12)$$
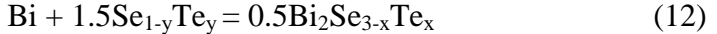
For studied (y = 0.2, 0.4, 0.6, 0.67, 0.8) compositions, the potential forming reaction for specific compounds can easily comply. For example, when x=0.6, y=0.2, the potentiating reaction is as follows:

$$Bi+1.5Se_{0.8}Te_{0.2} = 0.5Bi_2Se_{2.4}Te_{0.6} \qquad (13)$$

For this reaction, the standard Gibbs formation free energy, enthalpy, and entropy for the β-phase with $Bi_2Se_{2.4}Te_{0.6}$ composition can be calculated using the following relations

$$\Delta_f Z^0 = 2\Delta\bar{Z}_{Bi} + 3\Delta Z_{mix}(Se_{0.8}Te_{0.2}) \qquad (14)$$

$$\Delta_f S^0 = 2\Delta\bar{S}_{Bi} + 2S^0_{Bi} + 3\Delta S_{mix}(Se_{0.8}Te_{0.2}) \qquad (15)$$

$$S^0 = 2\Delta\bar{S}_{Bi} + 2S^0_{Bi} + 3\Delta S_{mix}(Se_{0.8}Te_{0.2}) + 2.4S^0(Se) + 0.6S^0(Te) \qquad (16)$$

In calculations based on these equations, the entropy of mixing of $Se_{1-y}Te_y$ solid solutions (ΔS_{mix}) and the Gibbs free energy of mixing was calculated in the ideal solution approach, because according

to the literature data, the mixing ratio of these solutions is practically zero.
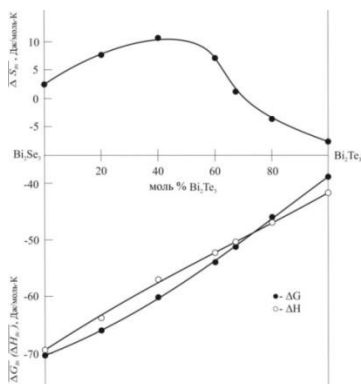
Figure 10. Composition dependence curves of partial molar functions of bismuth at 298 K in the Bi_2Se_3-Bi_2Te_3 system
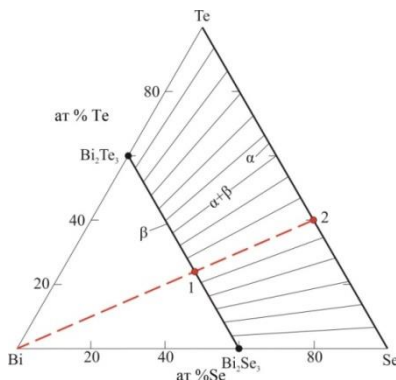
Figure 11. Solid phase equilibria diagram of the Bi_2Se_3-Bi_2Te_3-Te-Se omposition area of the Bi-Se-Te system

Calculations results are given in Table 8.

The Gibbs free energy and enthalpy of the formation of solid solutions of the Bi_2Se_3-Bi_2Te_3 system from binary compounds were calculated by combining the standard thermodynamic functions of the formation of solid solutions with the corresponding functions of primary binary compounds.

Fig. 12 shows the isotherms of these functions at 298 K. It can be seen from the Figure that the absolute value of the mixing enthalpy does not exceed 1 kC·mol^{-1}, and its sign changes from positive to negative at approximately 50-60 mol% Bi_2Te_3. Comparison with Figure 10 shows that the sign of the partial entropy of bismuth in solid solutions also changes in those compositions. On the other hand, the deepest negative values of the Gibbs free energy of mixing correspond to 60-70 mol% Bi_2Te_3 compositions. The above is in good agreement with the literature data about the occurrence of structure ordering in solid solutions in 60-70 mol% Bi_2Te_3 content.

Standard integral thermodynamic functions of phases in the Bi$_2$Se$_3$-Bi$_2$Te$_3$ system

Phase	$-\Delta_f G^0$ (298K)	$-\Delta_f H^0$ (298K)	S^0 (298K)
	kC/mol		C/(mol·K)
Bi$_2$Se$_3$	141.0 ± 0,2	139.6 ± 0,7	245.1 ± 4.3
Bi$_2$Se$_{2.4}$Te$_{0.6}$	135.8±0.2	127.5±0.6	272.0±3.0
Bi$_2$Se$_{1.8}$Te$_{1.2}$	124.5±0.2	112.9±0.6	287.6±3.3
Bi$_2$Se$_{1.2}$Te$_{1.8}$	113.7±0.2	104.3±0.6	284.6±3.2
Bi$_2$SeTe$_2$	106.0±0.2	101.6±0.6	269.0±3.0
Bi$_2$Se$_{0.6}$Te$_{2.4}$	95.7±0.2	94.0±0.6	263.2±3.1
Bi$_2$Te$_3$	76.9±0.2	79.2±0.6	254.2±3.0

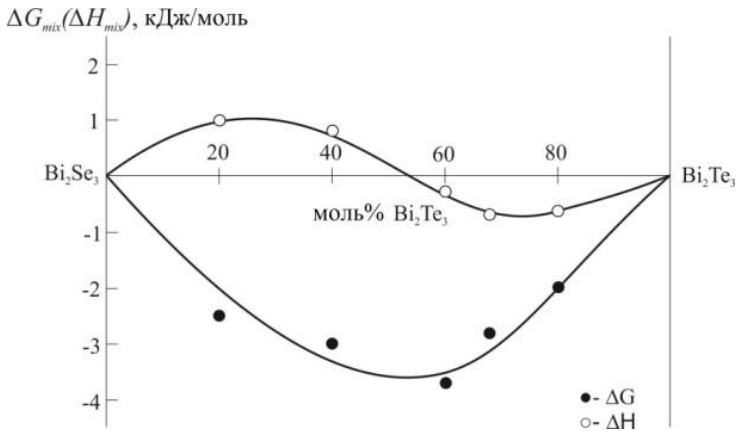**Figure 12. Composition dependences of the thermodynamic functions of the Bi$_2$Se$_{3-x}$Te$_x$ solid solutions formed from Bi$_2$Se$_3$ and Bi$_2$Te$_3$ compounds (T=298 K)**

Results

1. Samples close to thermodynamic equilibrium were obtained using various approaches. As a result of their study by a complex of experimental methods of physicochemical analysis, new schemes of phase equilibria in binary Bi-Se, Bi-Te, and ternary Bi-Se-Te system in a Bi-Bi$_2$Se$_3$, Bi-Bi$_2$Te$_3$ və Bi$_2$Se$_3$-Bi$_2$Te$_3$ compositions range different from those known in the literature, were obtained.

2. In the presented new versions of the phase diagrams of Bi-Bi_2Se_3 and Bi-Bi_2Te_3 systems, the 7 selenides of bismuth (Bi_3Se_2, Bi_4Se_3, Bi_8Se_7, BiSe, Bi_8Se_9, Bi_3Se_4 and Bi_2Se_3) and 7 tellurides (Bi_7Te_3, Bi_2Te, Bi_4Te_3, BiTe, Bi_8Te_9, Bi_4Te_5 and Bi_2Te_3) is reflected. Except for the congruent melting Bi_2Se_3 and Bi_2Te_3, the incongruent melting of all these compounds was determined through a series of peritectic reactions, and the coordinates of the corresponding nonvariant equilibrium points were determined.

3. All bismuth selenides and tellurides present in the T-x phase diagram of both binary systems crystallize in a tetradimite-like layered structure and, contrary to the information given in the literature, have practically stable composition rather than large areas of homogeneity. In particular, in the regions of homogeneity of compounds BiSe and BiTe, indicated in the previous versions of the phase diagrams, several individual compounds were found and the presence of corresponding two-phase regions between them were obtained.

4. The projection of the liquidus surface of the Bi-Bi_2Se_3-Bi_2Te_3 system, the isothermal section of the phase diagram at 300 K, and a series of polythermal sections were constructed. It was established that the liquidus surface projection consists of primary crystallization areas of eleven phases, limited by different monovariant equilibrium curves and points of nonvariant equilibrium. The types and coordinates of all these equilibria were determined;

5. It is determined that in the Bi-Bi_2Se_3-Bi_2Te_3 subsystem along the boundary quasi-binary system Bi_2Se_3-Bi_2Te_3, as well as in the internal sections of Bi_8Se_9-Bi_8Te_9, BiSe-BiTe and Bi_4Se_3-Bi_4Te_3, the continuous series of solid solutions are formed, while based on other bismuth selenides and tellurides are formed wide regions of homogeneity. Samples of these solid solutions of the selected composition were synthesized individually, the types and parameters of their crystal lattices were determined, and it was shown that the dependence of the lattice parameters on the composition in continuous substitutional solid solutions obeys Vegard's rule.

6. For the first time, solid-phase equilibria and thermodynamic proper-

ties of intermediate phases in Bi-Se and Bi-Te systems were studied by the EMF method. A new version of the phase diagram of both systems was confirmed by EMF measurements of the concentration cells using an ionic liquid as an electrolyte in the temperature range of 300-450 K. The equations for the temperature dependence of the EMF in various phase regions were compiled, and the partial thermodynamic functions of bismuth were calculated. Based on the phase diagrams, the potential-forming reactions responsible for these partial molar functions are composed, and the standard thermodynamic formation functions and standard entropies of all compounds are determined.

7. The Bi-Se-Te system was studied by the EMF method in the Bi_2Se_3-Bi_2Te_3-Te-Se compositions range, the solid-phase equilibria character in this region was determined, the partial molar functions of bismuth in $Bi_2Se_{3-x}Te_x$ solid solutions, as well as the standard thermodynamic functions of the formation of solid solutions and thermodynamic mixing functions of initial binary compounds.

The results of the dissertation were published in the following scientific works:

1. Zeynalova G.S., Yusibov Y.Ə., Şevelkov A.V., Babanlı M.B. BiSe-BiTe sisteminin fiziki-kimyəvi tədqiqi / Ümummilli lider H.Əliyevin anadan olmasmm 94-cü ildönümünə həsr olunmuş "Müasir təbiət elmlərinin aktual problemleri", Gəncə, 2017, s.6-8

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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.

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