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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**PHASE EQUILIBRIA OF SOME CONCENTRATION
PLANES OF THE TI-Ge-Bi-Te SYSTEM AND
THERMODYNAMIC PROPERTIES OF THE
INTERMEDIATE PHASES**

Specialty: 2303.01 – inorganic chemistry

Field of science: chemistry

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GENERAL DESCRIPTION OF WORK

Relevance and degree of investigation of the topic. Binary and complex tellurides of heavy p-elements have long been used as functional materials for various purposes, especially as thermoelectrics with low thermal conductivity. Some ternary compounds ($A^{IV}B_2^VTe_4$, $A^{IV}B_4^VTe_7$, TlB^VTe_2 , $Tl_9B^VTe_6$, $Tl_2A^{IV}Te_3$ et al.) formed in the $A^{IV}-B^V-Te$, $Tl-A^{IV}(B^V)-Te$ ($A^{IV}-Ge, Sn, Pb; B^V-Sb, Bi$) systems exhibit high thermoelectric performance among these materials¹.

Since the end of the first decade of this century, interest in these materials has increased sharply. This is due to the discovery of new unique functional properties in them - the properties of a topological insulator. Soon, the creation of a new generation of electronics is expected - spintronics and topological quantum computers, high-frequency detectors and their application in medicine and security systems, and many other areas of high technology².

Among the $A^{IV}-B^V-Te$ systems, germanium-based systems are more attractive. This is due to the formation in them of compounds belonging to the $A^{IV}Te-mB_2^VTe_3$ and $nGeTe-B_2^VTe_3$ homologous series. The latter are currently materials with a phase transition between crystalline and amorphous states and belong to the most important class of materials used in optical memory devices³.

The creation of scientific basics of directed synthesis of new complex chalcogenide phases requires reliable data on phase equilibria and thermodynamic data of corresponding systems. Analysis of literature data showed that despite the great interest in Van der Waals compounds formed in $Ge-B^V-Te$ systems, data on

¹ Шевельков, А.В. Химические аспекты создания термоэлектрических материалов // Успехи химии, 2008, №77 (1), с. 3-21

² Babanly M.B., E.V.Chulkov, Z.S.Aliev, et al. Phase diagrams in materials science of topological insulators based on metal chalcogenides // Russian Journal of Inorganic Chemistry, 2017, №62 (13), p. 1703-1729

³ Jones R.O. Phase change memory materials: Rationalizing the dominance of Ge/Sb/Te alloys // Physical Review B, 2020, №101 (2), p.024103

phase equilibria are contradictory, and thermodynamic properties of intermediate phases are practically not studied. On the other hand, in the literature, there is no information about thermoelectric materials with anomalously low thermal conductivity formed in Tl-Ge-Bi-Te.

Object and subject of research. The objects of the dissertation research were some concentration planes of the Tl-Ge-Bi-Te system. The subject of the research is the physicochemical study of these systems.

The purpose and objectives of the study. The purpose of the dissertation was to determine the character of the physical-chemical interaction in the GeTe-Bi₂Te₃-Te, Tl₂Te-GeTe-Bi₂Te₃, and Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ systems and the fundamental thermodynamic functions of the intermediate phases identified in them. To achieve this goal, the following **specific tasks** were set and solved:

- ✓ Improvement of synthesis techniques to obtain alloys of the GeTe-Bi₂Te₃-Te and Tl-Ge-Bi-Te systems, as close as possible to the equilibrium state along various concentration planes and study them using methods of physicochemical analysis;

- ✓ construction of a refined T-x phase diagram of the GeTe-Bi₂Te₃ system based on the obtained experimental data, obtaining a reliable scheme of phase equilibria in the GeTe-Bi₂Te₃-Te, Tl₂Te-GeTe-Bi₂Te₃ və Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ systems;

- ✓ Obtaining identified compounds and solid solutions of investigated systems in individual form and their characterization;

- ✓ Study of thermodynamic properties of germanium-bismuth tellurides by EMF method.

Research methods. The studies were done by traditional methods of physico-chemical analysis: differential-thermal analysis (DTA), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and electromotive force (EMF) methods as well as microhardness measurements

DTA was carried on "NETZSCH 404 F1Pegasus system". Powder X-ray diffraction patterns of the alloys were recorded on D8 ADVANCE and D2 Phaser diffractometers and analyzed by the TOPAS V.3 software. For the microstructural analysis, the JEOLJSM-7600F scanning electron microscope was used. The microhardness of

the sample was measured using a ПИМТ-3 device. EMF measurements were carried out using a Keithley 2100 6 1/2 Digit Multimeter high-resistance digital voltmeter, the results were processed using the Microsoft Excel 2010 computer program.

Main defense propositions

1. A new, refined version of the T-x phase diagram of the Ge-Te-Bi₂Te₃ system, thermal properties of the germanium-bismuth tellurides;

2. Pictures of phase equilibria in the GeTe-Bi₂Te₃-Te, Tl₂Te-GeTe-Bi₂Te₃ and Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ systems, including some polythermal and isothermal sections, projections of liquidus and solidus surfaces in the T-x phase diagram;

3. EMF measurements results in some phase regions of the Ge-Te-Bi₂Te₃-Te system, partial molar functions of germanium in alloys, and fundamental thermodynamic functions of germanium-bismuth tellurides.

Scientific novelty.

➤ A new refined version of the phase diagram of the quasi-binary section GeTe-Bi₂Te₃ of the Ge-Bi-Te system was constructed, which differs from that given in the literature, which reflected 6 ternary compounds, and three of them were reflected for the first time. It has been established that all these ternary compounds melt incongruently, including GeBi₆Te₁₀, GeBi₄Te₇, GeBi₂Te₄ and Ge₂Bi₂Te₅ by peritectic reactions, while Ge₃Bi₂Te₆ and Ge₄Bi₂Te₇ decompose by solid-phase reactions.

➤ The projection of the surface of the liquidus of the GeTe-Bi₂Te₃-Te system, some polythermal and isothermal sections of the volume phase diagram were constructed, the fields of primary crystallization and homogeneity, the types and coordinates of non- and monovariant equilibria were determined.

➤ A rare phenomenon in practice was discovered on the phase diagram of the GeTe-Bi₂Te₃-Te system - all the curves coming out of the points of nonvariant equilibrium of one of the boundary systems there is a transition from one type of monovariant equilibrium to another, the transition point is determined and the occurrence of this event is explained.

➤ A mutually consistent picture of phase equilibria was obtained along the $\text{Tl}_2\text{Te-GeTe-Bi}_2\text{Te}_3$ and $\text{Tl}_5\text{Te}_3\text{-Tl}_8\text{GeTe}_5\text{-Tl}_9\text{Bi-Te}_6$ concentration planes of the Tl-Ge-Bi-Te system. In the first plane, a wide area of solid solutions based on binary and ternary compounds, while in the second one, there were continuous solid solutions were found.

➤ Selected alloys of ternary compounds and solid solutions found in the studied systems were synthesized and identified individually. Single crystals of some compounds with a tetradymite-like layered structure were grown by the Bridgman-Stockbarger method and characterized.

➤ By EMF measurements of concentration cells with various reference electrodes for the GeTe compound and six germanium-bismuth tellurides, sets of mutually consistent data on standard thermodynamic functions and standard entropies were obtained.

The theoretical and practical significance of the work. The theoretical significance of the results obtained on the topic of the dissertation lies in determining the nature of the physico-chemical interaction along the $\text{GeTe-Bi}_2\text{Te}_3\text{-Te}$ concentration plane of the Ge-Bi-Te, and $\text{Tl}_2\text{Te-GeTe-Bi}_2\text{Te}_3$ and $\text{Tl}_5\text{Te-Tl}_8\text{GeTe}_5\text{-Tl}_9\text{BiTe}_6$ of the Tl-Ge-Bi-Te systems, identifying in them new telluride phases and determination of crystallographic and fundamental thermodynamic functions. These important new results provide important information for the directed synthesis of the corresponding phases and also make a significant contribution to the materials science of complex compounds exhibiting the properties of a topological insulator, thermoelectric, and other properties.

Testing and application. 15 scientific works, including 8 articles (6 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 following scientific conferences: XV и XVI Всероссийские конференции "Высокочистые вещества и материалы. получение, анализ, применение" (Нижний Новгород, Россия, 2015, 2018); Akademik Toğrul Şahtaxtinskiñin 90 illik yubileyinə həsr olunmuş respublika

elmi konfransı (Bakı, Azərbaycan, 2015); Ümummilli lider Heydər Əliyevin anadan olmasının 92-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların “Kimyanın aktual problemləri” IX Respublika Elmi konfransı (Bakı, Azərbaycan, 2015); XII International Conference "Electronic Processes in Organic and Inorganic Materials" (Kamianets-Podilskyi, Ukraine, 2020); The International Conference on Actual problems of Chemical Engineering, dedicated to the 100th Anniversary of the Azerbaijan State of Oil and Industry University (Baku, Azerbaijan, 2020); XI Международная научная конференция "Кинетика и механизм кристаллизации. Кристаллизация и материалы нового поколения" (Иваново, Россия, 2021).

The results obtained in the dissertation work, including the constructed phase diagrams, thermodynamic functions and crystallographic properties of the detected phases can be used in growing their single crystals, and are also included in the corresponding electronic information databases. According to the "Google Scholar Citations" information system, 18 references were made to the author's 4 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 in the research laboratory "Inorganic Materials Science" of the Department of General and Inorganic Chemistry of Baku State University. Part of the research was carried out within the framework of a DAAD fellowship at the Eberhard Karls University Tübingen, Germany, at the “Solid State Chemistry and Theoretical Inorganic Chemistry” laboratory of the Institute of Inorganic Chemistry.

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), five 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 (251 items). The thesis is presented in 149 pages and contains 60 figures and 21 Tables.

MAIN CONTENT OF WORK

The introduction substantiates the relevance of the dissertation work and provides the purpose, scientific novelty, and practical significance, as well as the main defense propositions.

The first chapter examines modern literature data on the study of binary and more complex tellurides and justifies the choice of research objects.

It also presents literature data on phase equilibria in the GeTe-Bi₂Te₃-Te concentration region of the Ge-Bi-Te system and in the Tl₂Te-GeTe-Bi₂Te₃ and Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ regions of the Tl-Ge-Bi-Te. These data were used in planning experimental studies on the topic of the dissertation and analyzing the results obtained.

The second chapter of the dissertation is devoted to the synthesis and brief description of the methods of physico-chemical analysis used.

The initial binary and ternary compounds of the studied systems were synthesized by melting high-purity elementary components from Alfa Aesar (99.999%) in quartz ampoules under vacuum conditions ($\sim 10^{-2}$ Pa). The synthesized compounds were identified by DTA and XRD methods.

The alloys of the studied systems were obtained from pre-synthesized and identified initial binary and ternary compounds under vacuum conditions in quartz ampoules. After synthesis, depending on the nature of the melting of the alloy, they were annealed for a long time at temperatures 30-50⁰ below the solidus and cooled with the furnace turned off. Specific conditions for the synthesis of compounds and alloys are given in the dissertation

Information about the research methods and devices used is given above (p. 4).

In the **third chapter**, using a new approach to the synthesis of alloys, new results on phase equilibria in the GeTe- Bi₂Te₃-Te system are presented.

Phase equilibria in the GeTe-Bi₂Te₃-Te system. To determine the nature of phase equilibria in this system, the results obtained from some internal sections were processed together with literature data on

boundary quasi-binary systems.

GeTe-Bi₂Te₃ system. In the phase diagram of this section, constructed based on the results of our research, only three ternary compounds are reflected - Ge₃Bi₂Te₆, GeBi₂Te₄ and GeBi₄Te₇. Several sources show that in this section there are compounds of two homologous series (GeTe·mBi₂Te₃ and nGeTe·Bi₂Te₃):

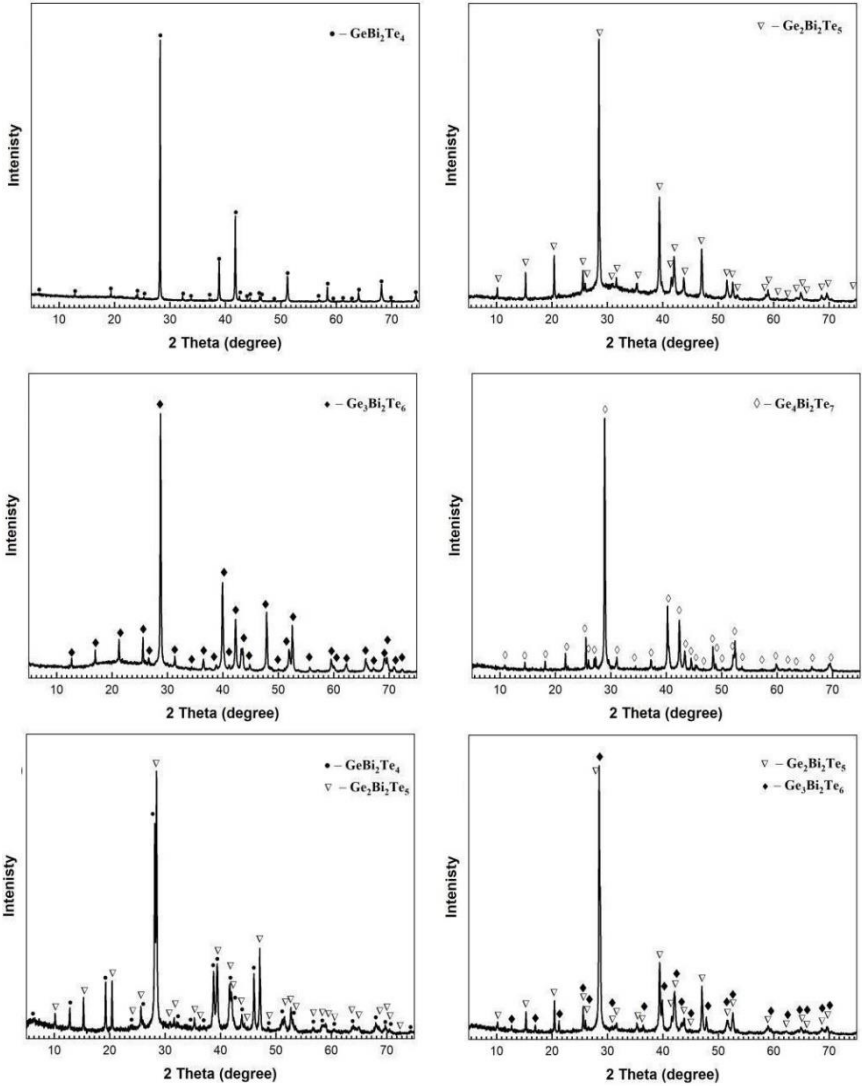
In the literature there are no experimental data on the thermal stability, the nature of melting, and the areas of primary crystallization of most of these compounds.

Taking this into account, in the dissertation using a new approach to the synthesis of alloys, new results on phase equilibria in the GeTe-Bi₂Te₃-Te system were obtained.

The alloys were synthesized in two stages. At the first stage, GeTe and Bi₂Te₃ compounds were synthesized and identified from high-purity elementary components by direct synthesis. At the second stage, these compounds were fused in different ratios along the GeTe-Bi₂Te₃ section. The method for synthesizing alloys at the second stage was developed taking into account the features of crystallization of layered phases.

The specific results presented below were obtained using this method. The samples, obtained by fusion in evacuated ampoules, were quenched from 950-1100 K (from the liquid state) by dropping them into ice water, and then, depending on the composition, were subjected to long-term (1000-1300 hours) annealing at 700-850 K and gradually cooled. Samples with a high GeTe content after heat treatment were quenched from 850 K temperature.

Powder diffraction patterns of some samples of the GeTe-Bi₂Te₃ system, thermally treated at 700 K, are presented in Figure 1. As can be seen, the diffraction patterns of the ternary compounds confirm their homogeneity. Samples corresponding to intermediate compositions are two-phase; their diffraction patterns consist of a set of reflection lines of neighboring compounds. For example, samples containing 30 and 40 mol. % Bi₂Te₃, consist of Ge₂Bi₂Te₅+Ge₃Bi₂Te₆ and GeBi₂Te₄+Ge₂Bi₂Te₅ two-phase mixtures (Fig.1) respectively.



Şəkil 1. Powder diffraction patterns of some ternary compounds and two-phase (30 və 40 mol % Bi₂Te₃) samples of the GeTe- Bi₂Te₃ system

By analyzing powder diffraction patterns of some compounds using the Rietveld method, the types of their crystal lattices were

determined and the lattice parameters were calculated. The results are shown in Table 1.

Table 1
Crystallographic characteristics of some phases
of the GeTe-Bi₂Te₃ system

Composition	Crystal lattice type and parameters, Å	
	700 K	870 K
GeTe	rhombohedr. $R3m$, $a=4.1628(3)$, $c=10.6675(8)$	cubic, $Fm3m$, $a=5.9824(5)$
2 mol% Bi ₂ Te ₃	"-", $a=4.1788(3)$, $c=10.6075(8)$	
4 mol% Bi ₂ Te ₃	"-", $a=4.1965(4)$, $c=10.5582(9)$	"-", $a=5.9904(5)$
6 mol% Bi ₂ Te ₃	"-", $a=4.2107(3)$, $c=10.4815(8)$	
8 mol% Bi ₂ Te ₃	"-", $a=4.2311(4)$, $c=10.4302(9)$	
9 mol% Bi ₂ Te ₃	"-", $a=4.2406(3)$, $c=10.3998(8)$	"-", $a=6.0096(6)$
10 mol% Bi ₂ Te ₃	cubic, $Fm3m$, $a=6.0061(5)$	
15 mol% Bi ₂ Te ₃		"-", $a=6.0238(6)$
Ge ₄ Bi ₂ Te ₇	rhombohedr., $R3m$, $a=4.2638(2)$, $c=73.271(3)$	
Ge ₃ Bi ₂ Te ₆	"-", $a=4.2730(3)$, $c=62.634(4)$	
Ge ₂ Bi ₂ Te ₅	trigonal, $P3m1$, $a=4.2986(2)$, $c=17.335(3)$	
GeBi ₂ Te ₄	rhombohedr., $R3m$, $a=4.3176(3)$, $c=41.259(5)$	
GeBi ₄ Te ₇	trigonal, $P3m1$, $a=4.3556(2)$, $c=23.928(4)$	
GeBi ₆ Te ₁₀	rhombohedr., $R3m$, $a=4.3572(3)$, $c=101.911(2)$	
90 mol% Bi ₂ Te ₃	rhombohedr., $R3m$, $a=4.3693(2)$, $c=30.2132(2)$	

It can be seen from Table 1, that these compounds crystallize in a tetradymite-like layered structure. Their layered structure is confirmed by SEM images (Fig. 2).

Fig. 3 shows powder diffraction patterns of samples containing 0–10 mol. % Bi₂Te₃, annealed at 700 K. As can be seen, all samples within 0-9 mol% Bi₂Te₃ interval are qualitatively similar to each other and are identical to the diffraction pattern of the low-temperature rhombohedral modification of the GeTe compound. This shows that in this composition range, substitutional solid solutions based on the low-temperature modification of GeTe are formed in the GeTe-Bi₂Te₃ system. It is interesting that in solid solutions, as the bismuth

concentration increases, some double diffraction peaks, for example, peaks in the ranges of 25-27°, 42-44°, 69-72°, are located close to each other and at a composition of 10 mol% Bi_2Te_3 they are merged into one peak.

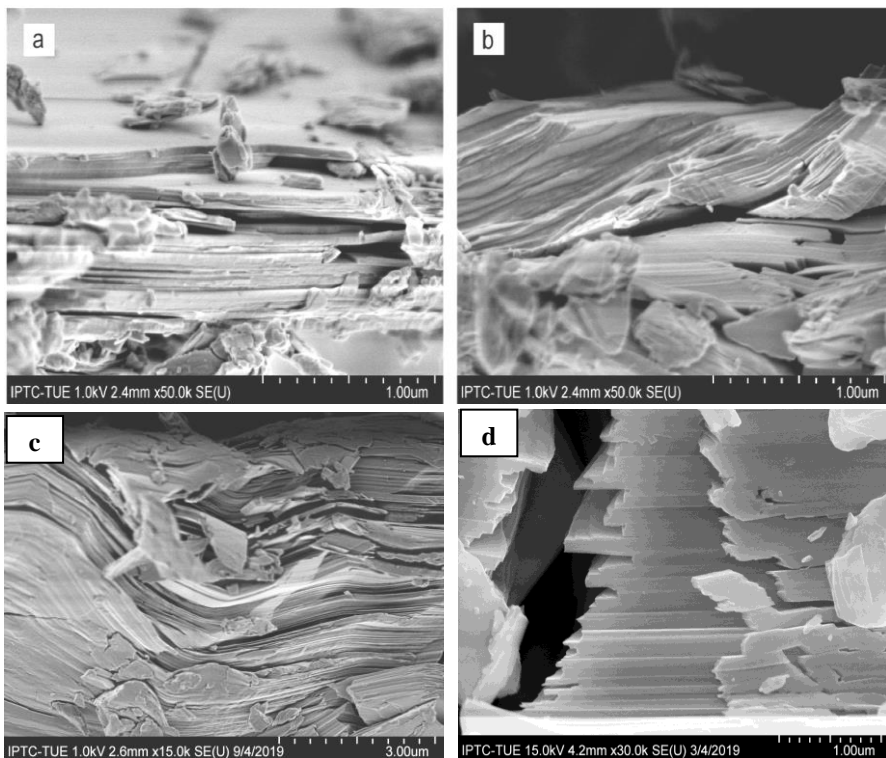


Figure 2. SEM images of the tetradymite-like layered structure compounds. $\text{Ge}_3\text{Bi}_2\text{Te}_6$ (a), $\text{Ge}_4\text{Bi}_2\text{Te}_7$ (b), $\text{Ge}_2\text{Bi}_2\text{Te}_5$ (c) and $\text{GeBi}_6\text{Te}_{10}$ (d).

Analysis of the diffraction pattern of a sample containing 10 mol. % Bi_2Te_3 shows that it is completely indexed in the cubic structure (Table 1).

The interpretation of the results obtained allows us to assert that in the range of 9-10 mol % Bi_2Te_3 a rhombohedral \rightarrow cubic morphotropic phase transition occurs in the system.

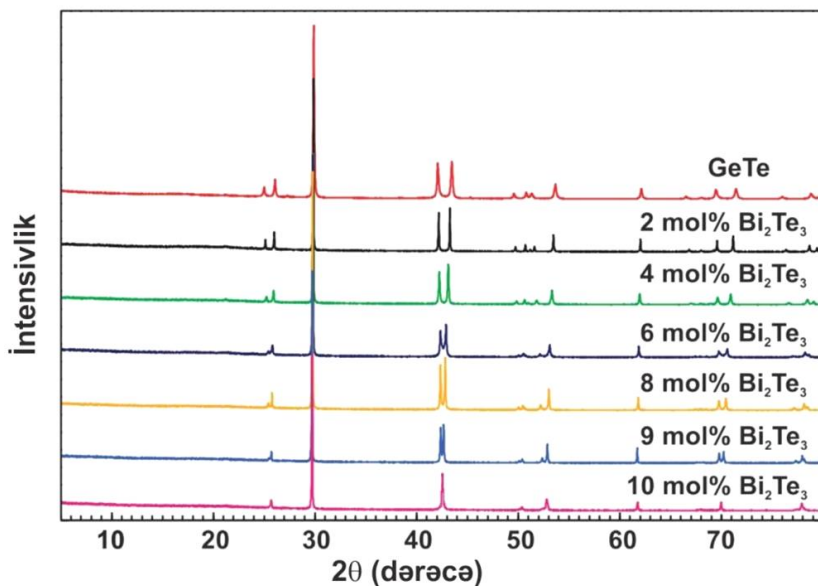


Figure 3. Powder diffraction patterns of samples containing 0–10 mol. % Bi_2Te_3 annealed at 700 K

It should be noted that X-ray diffraction analysis of samples containing 12-20 mol % Bi_2Te_3 shows that they consist of a mixture of cubic and tetradymite-like phases with a layered structure. It can be assumed that the layered phases in equilibrium with the cubic phase belong to the $\text{mGeTe}\cdot\text{Bi}_2\text{Te}_3$ homologous series rich in GeTe, or a mixture of such phases. Unfortunately, we were unable to accurately determine these phases.

To determine the solubility range of the high-temperature cubic modification of GeTe in the $\text{GeTe}\text{-Bi}_2\text{Te}_3$ system, samples of compositions 4, 9, and 15 mol. % Bi_2Te_3 were kept for 10 hours at 850 K and then quenched in cold water. The resulting diffraction pattern was single-phase and had a cubic structure.

Fig. 4 shows graphs constructed based on the results given in Table. 1. It can be seen that in solid solutions with $\text{Ge}\leftrightarrow\text{Bi}$ substitution in both cubic and rhombohedral structures, parameter a increases, and in the latter, parameter c decreases.

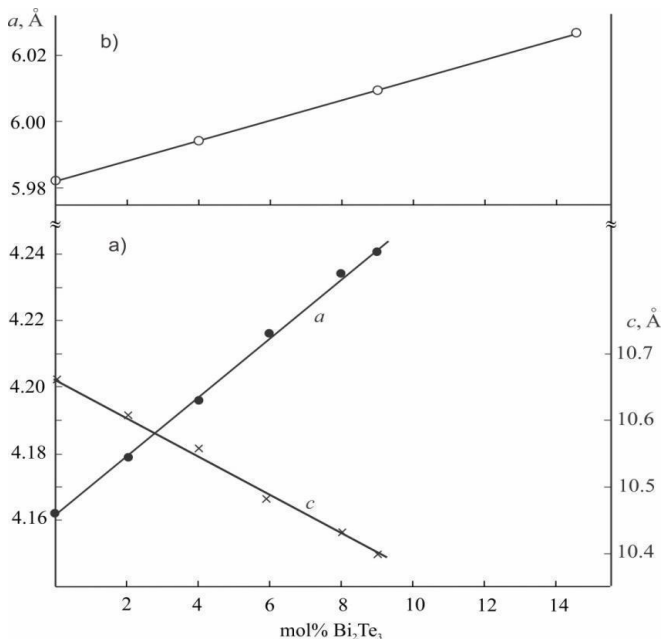


Figure 4. Composition dependences of lattice parameters of solid solutions based on GeTe at 700 K (a) and 870 K (b).

The elemental compositions of the compounds and solid solutions mentioned in Table 1 were confirmed by SEM/EDS method. The EDS spectrum of the $\text{GeBi}_6\text{Te}_{10}$ compound is presented in Figure 5, and Table 2 shows the results obtained for this compound based on the EDS spectrum.

The results of SEM analysis show that both compounds have a single-phase and layered structure. This also confirms their stoichiometric elemental composition.

Based on the above interpretation of the DTA results, a T-x diagram of the GeTe- Bi_2Te_3 system was constructed (Fig. 6). According to this diagram, 6 ternary compounds and wide regions of solid solutions based on both initial binary compounds are formed in the system. Four of the discovered ternary compounds decompose by peritectic reactions.

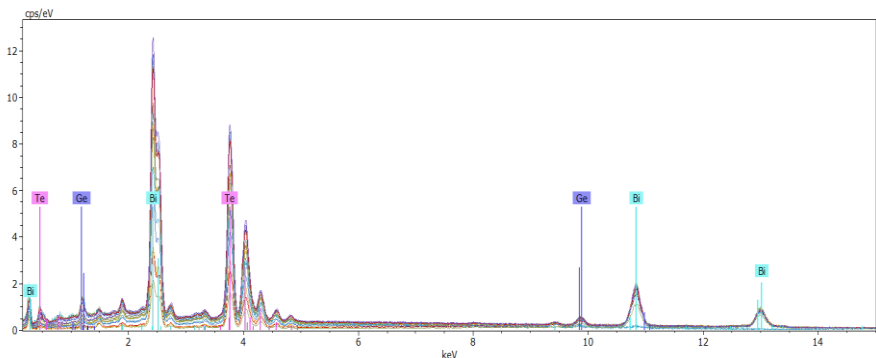


Figure 5. The EDS spectrum of the $\text{GeBi}_6\text{Te}_{10}$ compound

Table 2

The results obtained for the $\text{GeBi}_6\text{Te}_{10}$ compounds based on the EDS spectrum.

Element	Seriya	Amount, mass %	Amount, at. %	Error mass %
Germanium	K-seriya	2.69	5.65	0.28
Bismut	L- seriya	47.07	34.33	3.33
Tellurium	L- seriya	50.24	60.02	4.10
	Total	100.00	100.00	

According to the phase diagram (Fig. 6), the $\text{Ge}_3\text{Bi}_2\text{Te}_6$ and $\text{Ge}_4\text{Bi}_2\text{Te}_7$ compounds decompose in the solid phase.

In the DTA curves, the thermal effect associated with the decomposition of these compounds in the solid phase is absent. The decomposition temperature at which the effect was detected is shown by dotted lines.

Solid-phase equilibria diagram at 300K (Fig. 7). All ternary compounds of the GeTe - Bi_2Te_3 boundary system, as well as solid solutions α_1 , α_2 , and β - based on binary compounds, form a connod with elemental tellurium.

As can be seen from Fig. 7, solid solutions along the GeTe - Bi_2Te_3 section form $\alpha_1+\text{Te}$, $\alpha_2+\text{Te}$, and $\beta+\text{Te}$ two-phase regions on the phase diagram. Since the homogeneity regions of ternary compounds are small (~ 1 mol.%), the two-phase fields that each of them forms with tellurium are practically degenerate into a line, for example, I + Te, II+Te, etc.

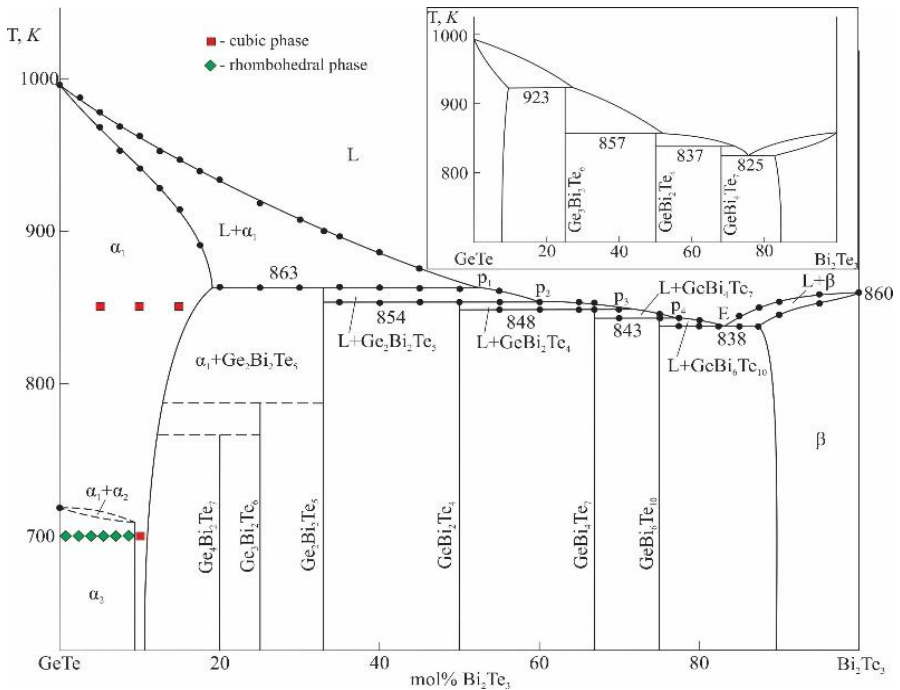


Fig.6. New version of the phase diagram of the GeTe- Bi₂Te₃ system. The previous version of the phase diagram is shown on a reduced scale.

The phase regions shown in Figure 7 were confirmed by RFA and SEM methods. These results are presented and discussed in the dissertation.

Projection of the liquidus surface. The liquidus surface of the GeTe-Bi₂Te₃-Te system consists of 7 fields of primary crystallization of phases. (Fig.8) The largest region 1 belongs to α₁-solid solutions based on the high-temperature of the GeTe compound, and region 2 belongs to β-solid solutions based on Bi₂Te₃. The liquidus surface of the Ge₂Bi₂Te₅, GeBi₂Te₄, GeBi₄Te₇, and GeBi₆Te₁₀ compounds (fields 3-6) in the form of relatively thin stripes between these two wide fields is directed from the GeTe-Bi₂Te₃ boundary system towards the Te corner of the concentration triangle.

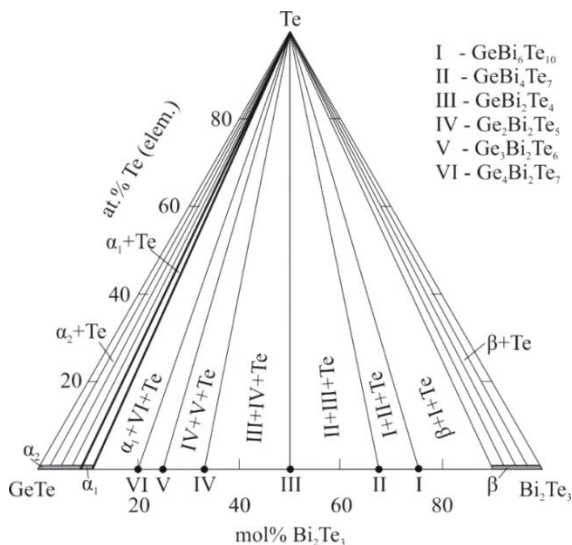


Figure 7. The solid phase equilibria diagram of the GeTe-Bi₂Te₃-Te system at 300 K

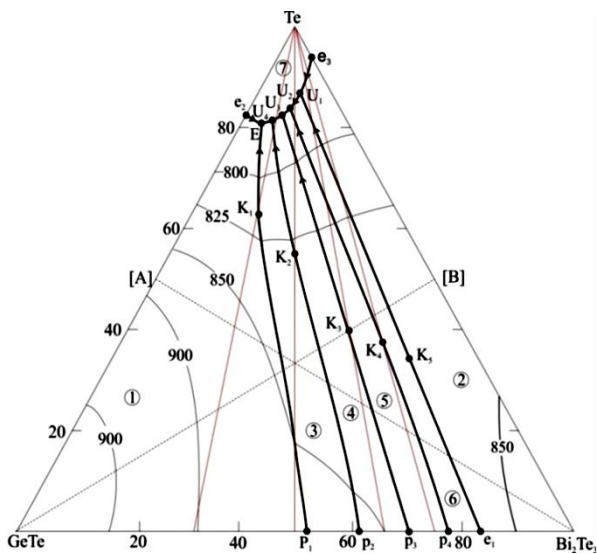


Figure 8. Projection of the liquidus surface of the GeTe-Bi₂Te₃-Te system. Areas of primary crystallization: 1- α ; 2- β ; 3- $\text{Ge}_2\text{Bi}_2\text{Te}_3$; 4- GeBi_2Te_4 ; 5- GeBi_2Te_4 ; 6- $\text{GeBi}_6\text{Te}_{10}$; 7-Te.

The liquidus surfaces of different phases are delimited by some monovariant equilibria curves and nonvariant points. The nonvariant and monovariant equilibria observed in the system are given in Table 3.

Table 3
Non- and monovariant equilibria in the GeTe-Bi₂Te₃-Te system

Poin or curve in Fig.8	Equilibria	T, K
P ₁	$L + \alpha_1 \leftrightarrow \text{Ge}_2\text{Bi}_2\text{Te}_5$	863
P ₂	$L + \text{Ge}_2\text{Bi}_2\text{Te}_5 \leftrightarrow \text{GeBi}_2\text{Te}_4$	854
P ₃	$L + \text{GeBi}_2\text{Te}_4 \leftrightarrow \text{GeBi}_4\text{Te}_7$	848
P ₄	$L + \text{GeBi}_4\text{Te}_7 \leftrightarrow \text{GeBi}_6\text{Te}_{10}$	843
e ₁	$L \leftrightarrow \text{GeBi}_6\text{Te}_{10} + \beta$	838
e ₂	$L \leftrightarrow \alpha_2 + \text{Te}$	653
e ₃	$L \leftrightarrow \beta + \text{Te}$	686
U ₁	$L + \beta \leftrightarrow \text{GeBi}_6\text{Te}_{10} + \text{Te}$	677
U ₂	$L + \text{GeBi}_6\text{Te}_{10} \leftrightarrow \text{GeBi}_4\text{Te}_7 + \text{Te}$	670
U ₃	$L + \text{GeBi}_4\text{Te}_7 \leftrightarrow \text{GeBi}_2\text{Te}_4 + \text{Te}$	662
U ₄	$L + \text{GeBi}_2\text{Te}_4 \leftrightarrow \text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Te}$	653
E	$L \leftrightarrow \alpha_2 + \text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Te}$	645
P ₁ K ₁	$L + \alpha_1 \leftrightarrow \text{Ge}_2\text{Bi}_2\text{Te}_5$	863-815
P ₂ K ₂	$L + \text{Ge}_2\text{Bi}_2\text{Te}_5 \leftrightarrow \text{GeBi}_2\text{Te}_4$	854-827
P ₃ K ₃	$L + \text{GeBi}_2\text{Te}_4 \leftrightarrow \text{GeBi}_4\text{Te}_7$	848-830
P ₄ K ₄	$L + \text{GeBi}_4\text{Te}_7 \leftrightarrow \text{GeBi}_6\text{Te}_{10}$	843-830
e ₁ K ₅	$L \leftrightarrow \text{GeBi}_6\text{Te}_{10} + \beta$	838-830
K ₅ U ₁	$L + \beta \leftrightarrow \text{GeBi}_6\text{Te}_{10}$	830-677
K ₄ U ₂	$L + \text{GeBi}_6\text{Te}_{10} \leftrightarrow \text{GeBi}_4\text{Te}_7$	830-670
K ₃ U ₃	$L + \text{GeBi}_4\text{Te}_7 \leftrightarrow \text{GeBi}_2\text{Te}_4$	830-662
K ₂ U ₄	$L + \text{GeBi}_2\text{Te}_4 \leftrightarrow \text{Ge}_2\text{Bi}_2\text{Te}_5$	827-653
K ₁ E	$L \leftrightarrow \alpha_1 (\alpha_2) + \text{Ge}_2\text{Bi}_2\text{Te}_5$	815-645
e ₃ U ₁	$L \leftrightarrow \beta + \text{Te}$	686-677
U ₁ U ₂	$L \leftrightarrow \text{GeBi}_6\text{Te}_{10} + \text{Te}$	677-670
U ₂ U ₃	$L \leftrightarrow \text{GeBi}_4\text{Te}_7 + \text{Te}$	670-652
U ₃ U ₄	$L \leftrightarrow \text{GeBi}_2\text{Te}_4 + \text{Te}$	662-653
U ₄ E	$L \leftrightarrow \text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Te}$	653-638
e ₂ E	$L \leftrightarrow \alpha_2 + \text{Te}$	653-638

As can be seen from Figure 6 and Table, the monovariant equilibria curves emanating from the peritectic P₁, P₂, P₃, P₄, and

eutectic points e_1 are divided into two parts by transition points K_1 - K_5 . At these points, there is a transition from one type of invariant equilibrium to another. This event was explained in the dissertation.

The fourth chapter presents the results of a study of phase equilibria in the Tl-Ge-Bi-Te system along the Tl_2Te - $GeTe$ - Bi_2Te_3 and Tl_2Te - Tl_8GeTe_5 - Tl_9BiTe_6 concentration planes. Both subsystems have been studied for the first time.

Diagram of solid-phase equilibria in the Tl_2Te - $GeTe$ - Bi_2Te_3 system at 300 K (Fig. 9). The system is characterized by the formation of wide fields of solid solutions based on the initial binary ($GeTe$, Bi_2Te_3) (α - and β -phases), and the ternary compound $TlBiTe_2$ (γ -phase), as well as along the quasi-binary section Tl_8GeTe_5 - Tl_9BiTe_6 (δ - phase). Solubility based on other compounds is no more than 1-2 mol.%.

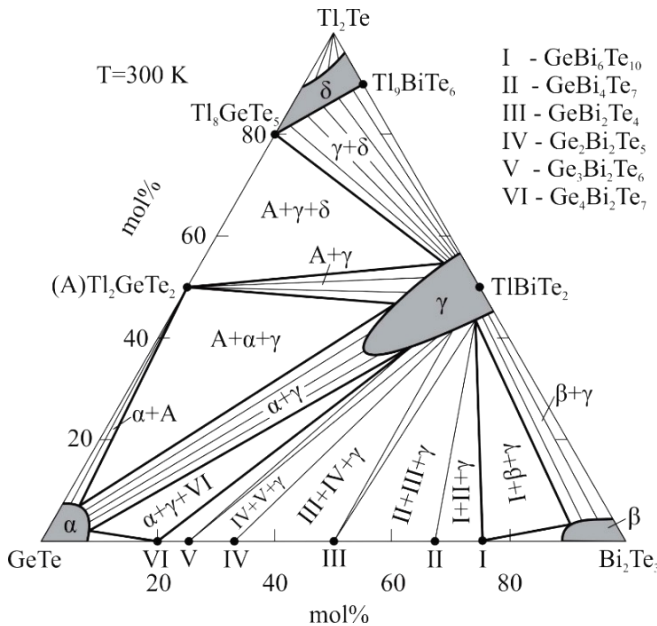


Figure 9. The solid-phase equilibria diagram of the Tl_2Te - $GeTe$ - Bi_2Te_3 system at 300 K

As a result of this interaction, 2- and 3-phase fields are formed on the phase diagram. The decisive role in the formation of these

fields is played mainly by the γ phase based on the TlBiTe_2 . Except for Tl_2Te , all other phases of the system form connodes with α -, β -, δ - solid solutions, the Tl_2GeTe_2 compound, as well as compounds I-VI of the $\text{GeTe}-\text{Bi}_2\text{Te}_3$ system. Some of these connodes form wide geniş $\alpha+\gamma$, $\beta+\gamma$, $\delta+\gamma$, $\text{Tl}_2\text{GeTe}_2-\gamma$, $\alpha+\text{Tl}_2\text{GeTe}_2$ two-phase fields. The remaining two-phase fields occupy relatively small fields or degenerate into connodes.

$\text{Tl}_2\text{Te}-\text{Tl}_8\text{GeTe}_5-\text{Tl}_9\text{BiTe}_6$ subsystem is one of 4 independent subsystems of the quasi-ternary system. Although it occupies a relatively small concentration area (Fig.9), it plays a large role as a thermoelectric material with low thermal conductivity. Since a wide range of solid solutions with a Tl_5Te_3 -type structure is formed in this subsystem, it is studied in more detail and described in the dissertation.

Liquidus surface projection of the $\text{Tl}_2\text{Te}-\text{GeTe}-\text{TlBiTe}_2$ system (Fig. 10). In the figure, the dotted lines show quasi-binary and stable (quasi-stable) sections below the solidus. The surface of the liquidus of the $\text{Tl}_2\text{Te}-\text{GeTe}-\text{TlBiTe}_2$ system consists of 5 areas of primary crystallization of phases. Three of them (regions 1, 2, and 3) cover very wide composition ranges and reflect the primary crystallization of δ -, α - and γ -solid solutions. Non- and monovariant equilibria delimiting the liquidus surfaces of the phases are given in Table 4.

$\text{Tl}_8\text{GeTe}_5-\text{Tl}_9\text{BiTe}_6-\text{TlBiTe}_2$ subsystem (Fig. 10) belongs to the monovariant eutectic type. The liquidus surface consists of two sections corresponding to the primary crystallization of the γ - and δ -phases. These fields are delimited by the monovariant equilibrium $L \leftrightarrow \gamma + \delta$, corresponding to the eutectic curve e_5e_6 . Below the solidus, the phase diagram consists of homogeneous fields of the γ - and δ -phases separated by a two-phase field.

$\text{GeTe}-\text{Tl}_8\text{GeTe}_5-\text{TlBiTe}_2$ subsystem has a more complex scheme of phase equilibria (Fig. 10). Two boundary components of this subsystem - $\text{GeTe}-\text{TlBiTe}_2$ and $\text{Tl}_8\text{GeTe}_5-\text{TlBiTe}_2$ belong to the eutectic type, the third is characterized by peritectic and eutectic equilibria. Monovariant equilibria emanating from the indicated nonvariant points (e_1 , e_2 , e_6 , P), interact with each other, which leads to the formation of transition (U) and eutectic (E) equilibria (Table 4).

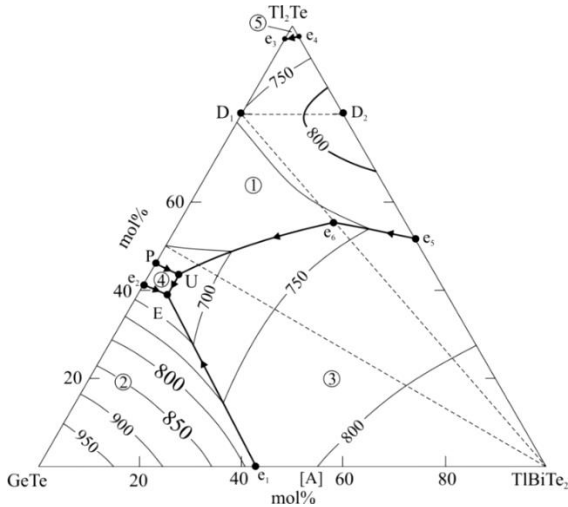


Figure 10. Liquidus surface projection of the Tl_2Te - $GeTe$ - $TlBiTe_2$ system. Areas of primary crystallization of phases: 1- δ ; 2- α ; 3- β ; 4- Tl_2GeTe_2 , 5- Tl_2Te . Dashed lines are quasi-binary and stable below solidus sections.

**Table 4
Non- and monovariant equilibria in the Tl_2Te - $GeTe$ - $TlBiTe_2$ system**

Point or curve in Fig.10	Equilibria	T, K
D_1	$L \leftrightarrow Tl_8GeTe_5 (\delta)$	753
D_2	$L \leftrightarrow Tl_9BiTe_6 (\delta)$	830
P	$L + \delta \leftrightarrow Tl_2GeTe_2$	690
e_1	$L \leftrightarrow \alpha' + \gamma'$	785
e_2	$L \leftrightarrow \alpha' + Tl_2GeTe_2$	683
e_3	$L \leftrightarrow Tl_2Te + \delta (Tl_8GeTe_5)$	695
e_4	$L \leftrightarrow Tl_2Te + \delta (Tl_9BiTe_6)$	697
e_5	$L \leftrightarrow \gamma + \delta (Tl_9BiTe_6)$	763
e_6	$L \leftrightarrow \gamma + \delta (Tl_8GeTe_5)$	740
U	$L + \delta \leftrightarrow Tl_2GeTe_2 + \gamma$	683
E	$L \leftrightarrow \alpha + \gamma + Tl_2GeTe_2$	675
e_1E	$L \leftrightarrow \alpha'(\alpha) + \gamma'(\gamma)$	785-675
e_2E	$L \leftrightarrow \alpha'(\alpha) + Tl_2GeTe_2$	683-675
e_4e_3	$L \leftrightarrow Tl_2Te + \delta$	697-695
e_5e_6	$L \leftrightarrow \gamma + \delta$	763-740
e_6U	$L \leftrightarrow \gamma + \delta (Tl_8GeTe_5)$	740-683
PU	$L + \delta \leftrightarrow Tl_2GeTe_2$	690-683
UE	$L \leftrightarrow Tl_2GeTe_2 + \gamma$	683-675

Crystallization is completed by the transition reaction U (Table 4) due to a lack of liquid phase (L) with the formation of a three-phase field $Tl_2Te+\delta+\gamma$, and with a lack of δ -phase, a two-phase field $Tl_2GeTe_2+\gamma$ is formed.

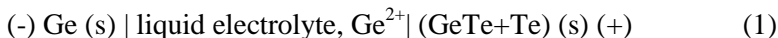
When crystallization is completed by the invariant eutectic (E) reaction, a three-phase field $\alpha+\gamma+Tl_2GeTe_2$ is formed in the subsolidus.

In the third and fourth chapters of the dissertation, some polythermal sections of the phase diagrams of both systems are presented and explained in detail.

The fifth chapter is devoted to the study of the thermodynamic properties of the GeTe compound and the three-component phases of the Ge-Bi-Te system using the electromotive force (EMF) method.

At the beginning of the chapter, the essence of the EMF method, its advantages and disadvantages are discussed, the use of the EMF method with solid and liquid electrolytes in thermodynamic studies of multicomponent heterogeneous systems is explained, and the planning of experimental studies is also given. Then the conduct of research using the EMF method and the method of mathematical processing of the results are described. In the last two paragraphs, the results of a thermodynamic study of the intermediate phases of the Ge-Te and Ge-Bi-Te systems are discussed.

For the thermodynamic study of the Ge-Te system, cells of type (1) were used, and for the study of the Ge-Bi-Te system, cells of type (2) were used.



In both cells, a glycerol solution of potassium chloride was used as the electrolyte. The measurements were carried out in the 300-450 K temperature range. It was determined that the EMF values are repeatable and vary linearly depending on temperature. This shows the reversibility of the cells used and the independence of the composition of the equilibrium phases from temperature. This provides the basis for thermodynamic calculations.

EMF measurements were carried out using a high-resistance digital voltmeter Keithley 2100 6 1/2 Digit Multimeter, the results were processed using the Microsoft Excel 2010 computer program.

The experimental technique is explained in detail in the dissertation.

The results of EMF measurements were processed by the least-squares method and are presented in the form of linear equations of type (3)

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

In (3), 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 , \bar{T} is the average temperature.

The resulting linear equation for the GeTe+Te field has the form

$$E, \text{ mV} = 256.50 + 0.0586 T \pm 2 \left[\frac{1.64}{30} + 2.6 \cdot 10^{-5} (T - 376.5)^2 \right]^{1/2}$$

From this equation and

$$\Delta \bar{G}_{\text{Ge}} = -zFE \quad (4)$$

$$\Delta \bar{S}_{\text{Ge}} = zF \left(\frac{\partial E}{\partial T} \right)_P = zFb \quad (5)$$

$$\Delta \bar{H}_{\text{Ge}} = -zF \left[E - T \left(\frac{\partial E}{\partial T} \right)_P \right] = -zFa \quad (6)$$

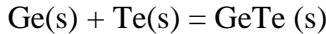
thermodynamic relations, the relative partial thermodynamic functions of germanium in the GeTe+Te two-phase region at 298.15 K were calculated.

$$\Delta \bar{G}_{\text{Ge}} = -52.87 \pm 0.09 \text{ kJ/mol}$$

$$\Delta \bar{H}_{\text{Ge}} = -49.50 \pm 0.38 \text{ kJ/mol}$$

$$\Delta \bar{S}_{\text{Ge}} = 11.30 \pm 1.00 \text{ J/(K} \cdot \text{mol)}$$

In expressions (4)-(6), z is the charge of the cation of the mobile component (Ge^{2+}), F is the Faraday number, a and b are constants in equation (3). According to the phase diagram of the Ge-Te system, these quantities are thermodynamic functions of the following potential-forming reaction in cells of type (1):



That is, they are the standard formation thermodynamic functions of the GeTe compound.

Yəni onlar GeTe birləşməsinin standart əmələgəlmə termodinamik funksiyalarıdır. Using data for the standard entropies of elemental Ge ($S_{\text{Ge}}^0 = 31.13 \pm 0.3 \text{ C} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) and Te ($S_{\text{Te}}^0 = 49.50 \pm 0.21 \text{ C} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) by relation

$$S_{\text{GeTe}}^0 = S_{\text{Ge}}^0 + S_{\text{Te}}^0 + \Delta_f S_{\text{GeTe}}^0$$

the standard entropy of the GeTe compound was calculated: $S^0_{\text{GeTe}} = 91.1 \text{ C}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

The dissertation provides a comparative analysis of the obtained standard thermodynamic functions of the GeTe compound with literature data.

Linear equations obtained based on EMF measurements in cells of type (2) in various phase regions of the Ge-Bi-Te system are given in Table 5.

The relative partial molar Gibbs free energy, enthalpy, and entropy of GeTe in the alloys were calculated using the resulting equations and thermodynamic expressions like (4)-(6) (Table 6). These quantities represent the difference between the corresponding partial mole functions of germanium for the left and right electrodes of cells of type (2):

$$\Delta\bar{G}_{\text{GeTe}}(\text{ in alloy}) = \Delta\bar{G}_{\text{Ge}}(\text{ in alloy}) - \Delta\bar{G}_{\text{Ge}}(\text{ in GeTe})$$

Thus

$$\Delta\bar{G}_{\text{Ge}}(\text{ in alloy}) = \Delta\bar{G}_{\text{GeTe}}(\text{ in alloy}) + \Delta\bar{G}_{\text{Ge}}(\text{ in GeTe})$$

Table 5
Temperature dependence of EMF of the cells of type (2) in some
phase areas of the Ge-Bi-Te system in the 300-450 K
temperature range

Phase area	$E = a + bT \pm 2S_E(T)$
$\beta(5 \text{ mol \% GeTe}) + \text{Te}$	$157.89 + 0.0752 T \pm 2 \left[\frac{1.5}{30} + 2.4 \cdot 10^{-5} (T - 376.5)^2 \right]^{1/2}$
$\beta(10 \text{ mol \% GeTe}) + \text{Te}$	$135.47 + 0.0641 T \pm 2 \left[\frac{1.1}{30} + 1.7 \cdot 10^{-5} (T - 376.5)^2 \right]^{1/2}$
$\beta + \text{GeBi}_6\text{Te}_{10} + \text{Te}$	$128.28 + 0.0520 T \pm 2 \left[\frac{1.4}{30} + 2.2 \cdot 10^{-5} (T - 376.1)^2 \right]^{1/2}$
$\text{GeBi}_6\text{Te}_{10} + \text{GeBi}_4\text{Te}_7 + \text{Te}$	$103.20 + 0.0511 T \pm 2 \left[\frac{1.3}{30} + 2.0 \cdot 10^{-5} (T - 376.4)^2 \right]^{1/2}$
$\text{GeBi}_4\text{Te}_7 + \text{GeBi}_2\text{Te}_4 + \text{Te}$	$95.79 + 0.0281 T \pm 2 \left[\frac{1.0}{30} + 1.7 \cdot 10^{-5} (T - 376.7)^2 \right]^{1/2}$
$\text{GeBi}_2\text{Te}_4 + \text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Te}$	$57.81 + 0.0385 T \pm 2 \left[\frac{1.2}{30} + 2.0 \cdot 10^{-5} (T - 376.7)^2 \right]^{1/2}$
$\text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Ge}_3\text{Bi}_2\text{Te}_6 + \text{Te}$	$35.81 + 0.0430 T \pm 2 \left[\frac{1.5}{30} + 2.5 \cdot 10^{-5} (T - 376.7)^2 \right]^{1/2}$
$\text{Ge}_3\text{Bi}_2\text{Te}_6 + \text{Ge}_4\text{Bi}_2\text{Te}_7 + \text{Te}$	$20.78 + 0.0478 T \pm 2 \left[\frac{2.1}{30} + 2.1 \cdot 10^{-5} (T - 377.4)^2 \right]^{1/2}$

Therefore, the calculation of the partial thermodynamic functions of germanium in alloys can be carried out by summing the corresponding partial molar functions of Ge in GeTe with the data in Table 6. The results obtained are given in Table 7

Table 6
**The relative partial molar functions of GeTe in alloys
of the Ge-Bi-Te system (T=298 K)**

Phase area	$-\Delta\bar{G}_{GeTe}$	$\Delta\bar{H}_{GeTe}$	$\Delta\bar{S}_{GeTe}$
	kJ/mol		J/mol·K
$\beta(5 \text{ mol \% GeTe}) + \text{Te}$	34.79 ± 0.09	30.47 ± 0.36	14.49 ± 0.95
$\beta(10 \text{ mol \% GeTe}) + \text{Te}$	29.83 ± 0.07	26.14 ± 0.30	12.38 ± 0.80
$\beta + \text{GeBi}_6\text{Te}_{10} + \text{Te}$	27.74 ± 0.08	24.75 ± 0.34	10.03 ± 0.91
$\text{GeBi}_6\text{Te}_{10} + \text{GeBi}_4\text{Te}_7 + \text{Te}$	22.85 ± 0.08	19.91 ± 0.32	9.86 ± 0.85
$\text{GeBi}_4\text{Te}_7 + \text{GeBi}_2\text{Te}_4 + \text{Te}$	20.10 ± 0.07	18.48 ± 0.30	5.43 ± 0.78
$\text{GeBi}_2\text{Te}_4 + \text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Te}$	13.37 ± 0.08	13.37 ± 0.08	7.41 ± 0.86
$\text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Ge}_3\text{Bi}_2\text{Te}_6 + \text{Te}$	9.39 ± 0.09	6.91 ± 0.37	8.32 ± 0.97
$\text{Ge}_3\text{Bi}_2\text{Te}_6 + \text{Ge}_4\text{Bi}_2\text{Te}_7 + \text{Te}$	6.76 ± 0.08	4.01 ± 0.34	9.22 ± 0.89

The calculation of standard thermodynamic functions of β -solid solutions was carried out by graphically integration of the Gibbs-Duhem equation along the GeTe- Bi_2Te_3 section.

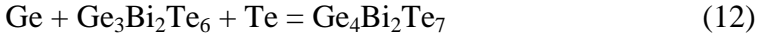
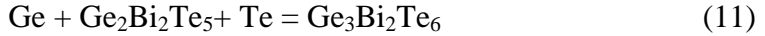
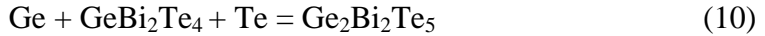
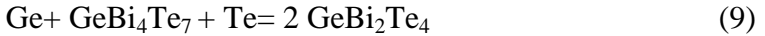
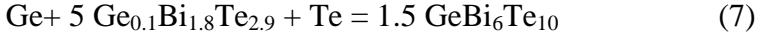
$$\Delta_f Z^0(\beta) = (1-x) \int_0^x \frac{\Delta\bar{Z}_{GeTe}}{(1-x)^2} dx + (1-x)\Delta_f Z^0(\text{Bi}_2\text{Te}_3) + x\Delta_f Z^0(\text{GeTe})$$

Table 7
**Relative partial molar functions of germanium in alloys
of the Ge-Bi-Te system (T=298 K)**

Phase area	$-\Delta\bar{G}_{Ge}$	$-\Delta\bar{H}_{Ge}$	$\Delta\bar{S}_{Ge}$
	kJ/mol		J/mol·K
$\beta(5 \text{ mol \% GeTe}) + \text{Te}$	87.66 ± 0.18	79.97 ± 0.76	25.8 ± 1.96
$\beta(10 \text{ mol \% GeTe}) + \text{Te}$	82.70 ± 0.16	75.64 ± 0.70	23.7 ± 1.90
$\beta + \text{GeBi}_6\text{Te}_{10} + \text{Te}$	80.61 ± 0.17	74.25 ± 0.74	21.3 ± 1.94
$\text{GeBi}_6\text{Te}_{10} + \text{GeBi}_4\text{Te}_7 + \text{Te}$	75.72 ± 0.17	69.41 ± 0.72	21.2 ± 1.92
$\text{GeBi}_4\text{Te}_7 + \text{GeBi}_2\text{Te}_4 + \text{Te}$	72.97 ± 0.16	67.98 ± 0.70	16.7 ± 1.90
$\text{GeBi}_2\text{Te}_4 + \text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Te}$	66.24 ± 0.17	60.66 ± 0.73	18.7 ± 1.93
$\text{Ge}_2\text{Bi}_2\text{Te}_5 + \text{Ge}_3\text{Bi}_2\text{Te}_6 + \text{Te}$	62.26 ± 0.18	56.41 ± 0.77	19.6 ± 1.97
$\text{Ge}_3\text{Bi}_2\text{Te}_6 + \text{Ge}_4\text{Bi}_2\text{Te}_7 + \text{Te}$	59.63 ± 0.17	53.51 ± 0.74	20.5 ± 1.94

In this equation, x is the mole fraction of GeTe, $\Delta\bar{Z}_{GeTe}$ - are the partial molar functions of GeTe in the β -phase (Table 6), and $\Delta_f Z^0(\text{Bi}_2\text{Te}_3)$ - are the standard thermodynamic functions of the Bi_2Te_3 compound formation.

Taking into account the constancy of the phase composition of phases in equilibrium in the indicated three-phase fields, standard integral thermodynamic functions of ternary compounds were calculated by the potential-forming reaction method. According to the solid-phase equilibria diagram (Fig. 7), the partial molar functions of germanium in the corresponding phase regions are functions of the following potential-forming reactions (all substances are in crystalline state)



Based on these equations, the standard thermodynamic functions of the formation ($Z \equiv G, H$) of the $\text{GeBi}_6\text{Te}_{10}$, GeBi_4Te_7 , GeBi_2Te_4 , $\text{Ge}_2\text{Bi}_2\text{Te}_5$, $\text{Ge}_3\text{Bi}_2\text{Te}_6$ and $\text{Ge}_4\text{Bi}_2\text{Te}_7$ compounds were calculated by following relations:

$$\Delta_f Z^0(\text{GeBi}_6\text{Te}_{10}) = \frac{2}{3} \overline{\Delta Z}_{\text{Ge}} + \frac{2}{5} \Delta_f Z^0(\text{Ge}_{0.1}\text{Bi}_{1.8}\text{Te}_{2.9}) \quad (13)$$

$$\Delta_f Z^0(\text{GeBi}_4\text{Te}_7) = \frac{1}{3} \overline{\Delta Z}_{\text{Ge}} + \frac{2}{3} \Delta_f Z^0(\text{GeBi}_6\text{Te}_{10}) \quad (14)$$

$$\Delta_f Z^0(\text{GeBi}_2\text{Te}_4) = 0.5 \overline{\Delta Z}_{\text{Ge}} + 0.5 \Delta_f Z^0(\text{GeBi}_4\text{Te}_7) \quad (15)$$

$$\Delta_f Z^0(\text{Ge}_2\text{Bi}_2\text{Te}_5) = \overline{\Delta Z}_{\text{Ge}} + \Delta_f Z^0(\text{GeBi}_2\text{Te}_4) \quad (16)$$

$$\Delta_f Z^0(\text{Ge}_3\text{Bi}_2\text{Te}_6) = \overline{\Delta Z}_{\text{Ge}} + \Delta_f Z^0(\text{Ge}_2\text{Bi}_2\text{Te}_5) \quad (17)$$

$$\Delta_f Z^0(\text{Ge}_4\text{Bi}_2\text{Te}_7) = \overline{\Delta Z}_{\text{Ge}} + \Delta_f Z^0(\text{Ge}_3\text{Bi}_2\text{Te}_6) \quad (18)$$

$$S^0(\text{GeBi}_6\text{Te}_{10}) = \frac{2}{3} \overline{\Delta S}_{\text{Ge}} + \frac{2}{3} S^0(\text{Ge}) + \frac{2}{3} S^0(\text{Te}) + \frac{2}{5} S^0(\text{Ge}_{0.1}\text{Bi}_{1.8}\text{Te}_{2.9}) \quad (19)$$

$$S^0(\text{GeBi}_4\text{Te}_7) = \frac{1}{3}\overline{\Delta S}_{\text{Ge}} + \frac{1}{3}S^0(\text{Ge}) + \frac{1}{3}S^0(\text{Te}) + \frac{2}{3}S^0(\text{GeBi}_6\text{Te}_{10}) \quad (20)$$

$$S^0(\text{GeBi}_2\text{Te}_4) = 0.5\overline{\Delta S}_{\text{Ge}} + 0.5S^0(\text{Ge}) + 0.5S^0(\text{Te}) + 0.5S^0(\text{GeBi}_4\text{Te}_7) \quad (21)$$

$$S^0(\text{Ge}_2\text{Bi}_2\text{Te}_5) = \Delta\overline{S}_{\text{Ge}} + S^0(\text{Ge}) + S^0(\text{Te}) + S^0(\text{GeBi}_2\text{Te}_4) \quad (22)$$

$$S^0(\text{Ge}_3\text{Bi}_2\text{Te}_6) = \Delta\overline{S}_{\text{Ge}} + S^0(\text{Ge}) + S^0(\text{Te}) + S^0(\text{Ge}_2\text{Bi}_2\text{Te}_5) \quad (23)$$

$$S^0(\text{Ge}_4\text{Bi}_2\text{Te}_7) = \Delta\overline{S}_{\text{Ge}} + S^0(\text{Ge}) + S^0(\text{Te}) + S^0(\text{Ge}_3\text{Bi}_2\text{Te}_6) \quad (24)$$

In the calculations, in addition to the partial molar data given in Table 7, standard entropies of Ge ($31.13 \pm 0.30 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), Te ($49.50 \pm 0.21 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, as well as standard integral thermodynamic functions of the Bi_2Te_3 compound) were also used (Table 8).

Table 8

Standard integral thermodynamic functions of the binary and ternary phases of the Ge-Bi-Te system

Phase	$-\Delta_f G^\circ(298 \text{ K})$	$-\Delta_f H^\circ(298 \text{ K})$	$S^\circ(298 \text{ K})$
	kJ/mol		J/mol·K
GeTe	52.9 ± 0.1	49.5 ± 0.4	91.1 ± 1.4
Bi_2Te_3 (əðəbiyyat)	76.9 ± 0.2	79.2 ± 0.5	254.2 ± 3.0
$\beta(\text{Ge}_{0.05}\text{Bi}_{1.9}\text{Te}_{2.9})$	77.5 ± 0.2	79.2 ± 0.6	246.8 ± 3.0
$\beta(\text{Ge}_{0.1}\text{Bi}_{1.8}\text{Te}_{2.8})$	77.9 ± 0.2	79.0 ± 0.6	239.3 ± 3.0
$\text{GeBi}_6\text{Te}_{10}$	313.4 ± 0.8	312.8 ± 2.5	865.6 ± 11.7
GeBi_4Te_7	234.2 ± 0.6	231.7 ± 1.9	611.0 ± 8.7
	-	191 ± 14^4	-
GeBi_2Te_4	153.6 ± 0.4	149.8 ± 1.3	354.2 ± 5.6
	-	114 ± 8^4	-
$\text{Ge}_2\text{Bi}_2\text{Te}_5$	219.8 ± 0.6	210 ± 2.0	453.5 ± 8.1
$\text{Ge}_3\text{Bi}_2\text{Te}_6$	282.1 ± 0.8	266.9 ± 2.8	553.7 ± 10.6
$\text{Ge}_4\text{Bi}_2\text{Te}_7$	341.7 ± 1.0	320.4 ± 3.6	654.8 ± 13.1

Errors were found by the method of uncertainty propagation.

The obtained thermodynamic results are a complex of mutually regulated quantities and are the fundamental physico-chemical indicators of the relevant substances.

⁴ Skoropanov A.S., Valevsky B.L., Skums V.F. et al. Physico-chemical study of Ge(Pb)Te-Bi₂(Sb₂)Te₃ system ternary compounds // Thermochimia Acta, 1985, №90, p. 331-334

RESULTS

1. Using the methods of DTA, XRD, SEM, and microstructural analysis, as well as measurements of microhardness and EMF of various types of cells, the physicochemical nature of the interaction in the Tl-Ge-Bi-Te system along the GeTe-Bi₂Te₃-Te, Tl₂Te-GeTe-Bi₂Te₃ v̄ Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ concentration planes was determined
2. A new phase diagram of the GeTe-Bi₂Te₃ quasi-binary system was constructed, which differs from that given in the literature. This diagram shows the formation of the (three of them for the first time) Ge₄Bi₂Te₇, Ge₃Bi₂Te₆, Ge₂Bi₂Te₅, GeBi₂Te₄, GeBi₄Te₇ v̄ GeBi₆Te₁₀ compounds. It is shown that the first two decompose according to a solid-phase reaction, while the rest melt incongruently. Wide fields of solid solutions were discovered in the system, including those based on both crystalline modifications of GeTe, and the occurrence of a morphotropic phase transition between them was shown.
3. A projection of the GeTe-Bi₂Te₃-Te system onto the concentration triangle and a number of vertical and isothermal sections of the phase diagram were constructed. Areas of primary crystallization of seven phases were discovered in the system, and types and coordinates of non- and monovariant equilibria were determined.
4. A transition from one type of equilibrium to another was discovered at all monovariant equilibria emanating from the peritectic and eutectic points of the GeTe-Bi₂Te₃ quasibinary section of the T-x-y phase diagram of the GeTe-Bi₂Te₃-Te system and an explanation for this transition was given.
5. For the first time, the scheme of phase equilibria in the Tl-Ge-Bi-Te system along the Tl₂Te-GeTe-Bi₂Te₃ v̄ Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ concentration planes has been determined. For the first system, a phase diagram was constructed for the Tl₂Te-GeTe-TlBiTe₂ compositions region, and for the second, a complete T-x-y diagram, various iso- and polythermal sections were constructed, non-, mono- and two-dimensional equilibria were determined. It has been shown that the Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ system is characterized by the formation of continuous, and the Tl₂Te-Ge

Te-Bi₂Te₃ system is characterized by wide ranges of solid solutions based on GeTe, Bi₂Te₃, TlBiTe₂ compounds.

6. Selected alloys of ternary compounds formed in the GeTe-Bi₂Te₃ system, as well as solid solutions, were synthesized and identified. It was shown that the synthesized bismuth-germanium tellurides crystallize in a tetradymite-like layered structure, and the parameters of their crystal lattices were refined by the Rietveld method. Single crystals of some ternary compounds were expressed using the Bridgman-Stockbarger method and their layering was confirmed by X-ray diffraction.
7. It has been established that solid solutions with a tetragonal structure of the Tl₅Te₃, formed in the quasi-binary system Tl₈GeTe₅-Tl₉BiTe₆, penetrating deep into the Tl₅Te₃-Tl₈GeTe₅-Tl₉BiTe₆ and Tl₂Te-Tl₈GeTe₅-Tl₉BiTe₆ concentration planes form unlimited solid solutions in the first system, while in the second - wide areas of homogeneity. This opens up the possibility of controlling their functional properties by changing their compositions.
8. By EMF measurements of the cells relative to Ge and GeTe reference electrodes, the homogeneity fields in the Ge-Te and GeTe-Bi₂Te₃-Te systems were determined, and the partial molar free Gibbs energy, enthalpy and entropy of the quasi-component GeTe were calculated. Based on the solid-phase equilibria diagram, the potential-forming reactions responsible for these partial functions were determined, and mutually consistent complexes of standard thermodynamic formation functions and standard entropies of the GeTe, GeBi₆Te₁₀, GeBi₄Te₇, GeBi₂Te₄, Ge₂Bi₂Te₅, Ge₃Bi₂Te₆ and Ge₄Bi₂Te₇ compounds were obtained.

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

1. Алекперова Т.М., Амирасланов И.Р., Бабанлы М.Б. Фазовые равновесия в системе Tl₈GeTe₅-Tl₉BiTe₆ и некоторые свойства твердых растворов // Кимья Problemləri - 2015. №4, - s. 376-381.
2. Алекперова Т.М., Гусейнов Ф.Н., Юсифова И.М., Имамалиева С.З. Получение и термоэлектрические свойства твердых растворов со структурой Tl₅Te₃ в системе Tl-Ge-Bi-Te / Тезисы

- докладов XV конференции и VIII школы молодых ученых. Нижний Новгород, - 2015, - с.105.
3. Алекперова Т.М., Гусейнов Ф.Н., Юсифова И.М. Т-х-у диаграмма системы $Tl_2Te-Tl_8GeTe_5-Tl_9BiTe_6$ / Akademik Toğrul Şahtaxtinskiyin 90 illik yubileyinə həsr olunmuş respublika elmi konfransı. Bakı, - 2015. - s.130.
 4. Ələkbərova T.M., Yusifova İ.M. $Tl_8GeTe_5-Tl_9BiTe_6$ sistemində bərk məhlulların sintezi və tədqiqi / Ümummilli Lider Heydər Əliyevin anadan olmasının 92-ci ildönümünə həsr olunmuş doktorant, magistr və gənc tədqiqatçıların “Kimyanın aktual problemləri” IX Respublika Elmi konfransının materialları. Bakı, - 2015. - s.69.
 5. Алекберова Т.М., Гусейнов Ф.Н., Бабанлы М.Б. Фазовые равновесия в системе $Tl_2Te-Tl_5Te_3-Tl_8GeTe_6$ // Международный журнал прикладных и фундаментальных исследований, -2016. № (11), - с. 946-950.
 6. Alakbarova T.M., Jafarov Y.I., Mustafayeva A.L., Babanly M.B. $Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5$ system // Kimya problemləri, - 2017. №4, - p. 355-363.
 7. Алекперова Т.М., Мирзоева Р.Дж., Султанова С.Г., Бабанлы М.Б. Исследование фазовых равновесий в системе $Tl_2Te-Tl_8GeTe_5-Tl_9BiTe_6$ / XVI Всероссийская конференция и IX Школа молодых ученых, посвященные 100-летию академика Г.Г.Девярых. Нижний Новгород, - 2018. - с. 148.
 8. Alakbarova T.M., Orujlu E.N., Imamaliyeva S.Z., Babanly M.B. Solid phase equilibria in the $GeTe-Bi_2Te_3$ system and crystal structures of the intermediate phases / XII International Conference "Electronic Processes in Organic and Inorganic Materials" (ICEPOM-12). Kamianets-Podilskyi, Ukraine, - 2020. - p.268.
 9. Alakbarova T.M., Orujlu E.N., Sultanova S.G., Bulanova M.V., Babanly M.B. Phase equilibrium in the $GeTe-Bi_2Te_3$ system and some properties of intermediate phases / The International Conference on Actual problems of Chemical Engineering, dedicated to the 100th Anniversary of the Azerbaijan State of Oil and Industry University (APCE 2020). Baku, - 2020. - p.140.
 10. Alakbarova T.M., H.-J.Meyer, E.N.Orujlu, Amiraslanov İ.R., Babanly M.B. Phase equilibria of the $GeTe-Bi_2Te_3$ quasi-binary

- system in the range 0-50 mol % Bi_2Te_3 // Phase transitions, - 2021. №94 (5), - p. 366-375.
11. Alakbarova T.M. Thermodynamic properties of germanium telluride // New Materials, Compounds and Applications, - 2021. №5 (1), - p. 59-65.
 12. Alakbarova T.M., Meyer H.-J., Babanly M.B. Phase diagram of the $\text{GeBi}_2\text{Te}_4\text{-Bi}_2\text{Te}_3$ system and thermodynamic properties of the germanium-bismuth tellurides / XI Международная научная конференция "Кинетика и механизм кристаллизации. Кристаллизация и материалы нового поколения", Иваново, - 2021, - p. 232-233.
 13. Alakbarova T.M., Orujlu E.N., Babanly D.M., İmaməliyeva S.Z., Babanly M.B. Solid-phase equilibria in the $\text{GeBi}_2\text{Te}_4\text{-Bi}_2\text{Te}_3\text{-Te}$ system and thermodynamic properties of compounds of the $\text{GeTe}\cdot m\text{Bi}_2\text{Te}_3$ homologous series // Physics and Chemistry of Solid State, - 2022. №23 (1), - p. 25-33.
 14. Alakbarova T.M., Meyer H.-J., Orujlu E.N., Babanly M.B. A refined phase diagram of the $\text{GeTe-Bi}_2\text{Te}_3$ system // Condensed Matter and Interphases, - 2022. №24 (1), - p. 11-18.
 15. Alakbarova T.M. Physicochemical interactions in $\text{TlBiTe}_2\text{-Tl}_8\text{GeTe}_5$ (Tl_2GeTe_2) systems // New Materials, Compounds and Applications, - 2022. №6 (2), - p. 162-168.



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