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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

INVESTIGATION AND MODELING OF PHASE EQUILIBRIA ON SOME COMPOSİTİON PLANES OF THE Tl-Pb-B^V-Ln-Te (B^V-Sb, Bi; Ln-Sm, Tb) SYSTEMS

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Field of science: Chemistry

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GENERAL DESCRIPTION OF WORK

Relevance and degree of investigation of the topic. In modern technology, there is a continuous search for functional materials with various functions, which stimulates research in this area, and this gives impetus to the development of materials science as a high-tech field of science.

The discovery in the first decade of our century of a topological insulator, which is an unusual quantum state of matter, opened wide opportunities for the creation of materials with unique, even exotic physical properties. This marked the beginning of development in several areas of the electronic industry and high technologies[1].

Research carried out in the first years after the discovery of the topological insulator showed that heavy metal tellurides and phases based on them, which for many years have been widely studied as thermoelectric materials, also exhibit the properties of a topological insulator. Among these phases, thallium tellurides with p^2 and p^3 elements, including compounds of the $TlB^{V}Te_2$, $Tl_9B^{V}Te_6$, $Tl_4A^{IV}Te_3$ (A^{IV}-Sn, Pb; B^{V}-Sb, Bi) occupy a special place. Currently, these compounds are at the center of attention not only as thermoelectric materials[2], but also as promising materials for use in spintronics, quantum computing, optoelectronics, and scanning devices[3]

Due to the specific position in the periodic system of elements, thallium can be in two different oxidation states (+1; +3) in the same compound. Such a situation is also observed in two thallium compounds - TlTe and Tl_5Te_3. In these compounds, thallium atoms are in 1+ and 3+ oxidation states and are in different crystallographic locations. From this point of view, $TlB^{V}Te_2$ can be compared with monotelluride and the $Tl_9B^{V}Te_6$ and $Tl_4A^{IV}Te_3$ compounds can be considered as ternary analogs of the Tl_5Te_3 compound. Interestingly, there are also lanthanoid analogs

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[1] Moore, J.E. The birth of topological insulators // Nature, 2010, v. 464, p.194–198

[2] Шевельков А.В. Химические аспекты создания термоэлектрических материалов // Успехи химии, 2008, т.77 (1), с. 3-21

[3] Babanly M.B., Chulkov E.V., Aliev Z. S., Shevel'kov A.V., and Amiraslanov I. R. Phase diagrams in materials science of topological insulators based on metal chalkogenides // Russ. J. Inorg. Chem., 2017, v. 62(13), p. 1703–1729

of all three mentioned types of ternary compounds: $TlLnTe_2$, Tl_9LnTe_6, and Tl_4LnTe_3 (Ln- rare earth element, REE).

The above-mentioned systems consist of thallium tellurides, which shows the importance of the physicochemical study of these systems. Replacing p^2 and p^3 elements in the crystal structure of these compounds with rare earth elements will not only increase thermoelectric properties but will also provide additional functional properties, for example, magnetic.

The purposeful search and creation of physico-chemical bases of synthesis of new complex phases are largely related to the study of phase equilibria in relevant systems. In addition to showing the presence of new compounds in the system, phase diagrams show the nature of their formation, thermal stability, areas of homogeneity, polymorphic transformations, etc. give full information about In terms of the search for new multicomponent metal tellurides, systems composed of compounds with formula or structural analogs are of particular interest, as one can expect the formation of large solid solution areas in them. This makes it possible to optimize the functional properties of base compounds by changing the composition.

Object and subject of research. Taking into account the above, as object the Tl_2Te-Tl_9TbTe_6-$Tl_9B^VTe_6$ composition planes of the Tl-Tb-B^V-Te (B^V-Sb, Bi) systems and Tl_4PbTe_3-Tl_9LnTe_6-Tl_9BiTe_6 composition planes of the Tl-Pb-Ln-Bi-Te (Ln-Sm, Tb) systems were taken. The *subject* of the research was the investigation and mathematical modeling of phase equilibria in these systems.

The purpose and function of the study. The *purpose* of the dissertation is to study the character of phase equilibria in the Tl_2Te-Tl_9TbTe_6-Tl_9SbTe_6, Tl_2Te-Tl_9TbTe_6-Tl_9BiTe_6, Tl_4PbTe_3-Tl_9SmTe_6-Tl_9BiTe_6 and Tl_4PbTe_3-Tl_9TbTe_6-Tl_9BiTe_6 systems, where the formation of new multicomponent phases with variable composition containing rare earth elements (REE) is expected, as well as the determination, mathematical modeling and thermodynamic analysis of phase diagrams.

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

- ✓ the physical-chemical interactions in the Tl_2Te-TlB^VTe_2-$TlLnTe_2$ compositions region of the Tl-B^V-Tb-Te systems were investigated,

their phase diagrams and various "composition-properties" diagrams were constructed;

- ✓ the experimental study of the phase equilibria in the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9LnTe_6 system in order to construct the volume diagrams, their various poly- and isothermal cross-sections;
- ✓ modeling the liquidus and solidus surfaces of the phases in the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9LnTe_6 system, 3D imaging, and thermodynamic analysis;
- ✓ obtaining individually and characterization of the multinary solid solutions of the investigated systems.

Research methods. Investigations were carried out using a complex of traditional methods of physical and chemical analysis, namely, differential thermal analysis (DTA), X-ray phase analysis (XRD), microstructural analysis (MSA), and scanning electron microscopy (SEM), as well as microhardness measurements. DTA was carried out on a NETZSCH 404 F1Pegasus system" device and a multichannel setup assembled based on "TC-08 Terminal Data Logger" an electronic recorder. Powder diffraction patterns were recorded on a D8 ADVANCE and D2 Phaser device from Bruker and analyzed using computer software for the corresponding diffractometers. C-4EQMM 500T metallographic microscope was used for microstructural analysis. SEM images were obtained using a JEOLJSM-7600F scanning electron microscope. The microhardness of the sample was measured using a ПМТ-3 microhardness tester

Provisions submitted for defense

- New results related to phase equilibria in the Tl_2Te-$TlSb(Bi)Te_2$-$TlTbTe_2$ systems, including solid-phase equilibria diagram and "composition-properties" diagrams of pointed systems;
- T-x-y diagrams of the Tl_4PbTe_3-Tl_9BiTe_6-$Tl_9Sm(Tb)Te_6$ systems, their some polythermal and isothermal sections;
- analytical expressions for the liquidus and solid surfaces of phases in the Tl_4PbTe_3-Tl_9BiTe_6-$Tl_9Sm(Tb)Te_6$ system and corresponding 3D models based on them;
- the information about new variable composition phases revealed in the listed systems, their crystallographic, thermal, thermodynamic,

etc. properties.

Scientific novelty. The following important new scientific results were obtained in the work:

- ✓ the character of the physical-chemical interaction in Tl_2Te-$TlSbTe_2$-$TlTbTe_2$ and Tl_2Te-$TlBiTe_2$-$TlTbTe_2$ systems were determined. The solid-phase equilibria diagrams of both systems were constructed. Based on $TlSbTe_2$, $TlBiTe_2$, and $TlTbTe_2$ compounds, the wide solid solution areas were discovered, and their homogeneous areas were determined;
- ✓ complete pictures of phase equilibria in the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9LnTe_6 five-component systems (Ln-Sm, Tb) were obtained, namely T-x-y phase diagrams, some polythermal and isothermal sections, as well as projections of liquidus and solidus surfaces. The formation of continuous solid solutions with the tetragonal structure of the Tl_5Te_3 in all listed systems is determined;
- ✓ analytical expression for liquidus and solid surfaces of phases in the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9LnTe_6 systems were obtained, Based on them, 3D modeling of volumetric diagrams and thermodynamic analysis were carried out.
- ✓ several samples of the studied multicomponent non-stoichiometric phases were synthesized and characterized individually, and their melting temperature and microhardness, as well as the type and parameters of the crystal lattice, were determined.

Theoretical and practical significance. The theoretical significance of the results obtained on the topic of the dissertation lies in the fact that experimental results on phase equilibria and mathematical models of the studied systems complement the chemistry and materials science of complex telluride systems. These results provide the scientific basis for obtaining phases of variable composition and single crystals. The practical importance of the results of the work is also that the established phase diagrams, their obtained mathematical models, as well as crystallographic, thermal, thermodynamic, etc. properties are fundamental physico-chemical parameters and can be entered into relevant electronic information systems and databases.

Testing and application. 17 scientific works on the subject of the dissertation, including 11 articles (7 articles in WOS and Scopus in

indexed scientific journals) and 6 scientific theses (5 theses in international conferences) have been printed.

The main results of the dissertation work were presented at the following scientific conferences: *3*rd, and 5th International Turkic World Conference on Chemical Sciences and Technologies, (Baku, Azərbaijan, 10-13 September, 2017; Sakarya, Türkiyə, 25-29 October, 2019); "Высокочистые вещества и материалы. Получение, анализ, применение" XVI всероссийская конференция и IX школа молодых ученых, посвященная 100-летию Г. Г. Девятых (Новгород, Россия, 28-31 май, 2018); II international scientific conference of young researchers dedicated to the 95th anniversary of the national leader of Azerbaijan, H. Aliyev, (Baku, Azərbaijan, 27-28 aprel, 2018); Всероссийская конференция "Химия твердого тела и функциональные материалы" и XII всероссийский симпозиум с международным участием "Термодинамика и материаловедение" (Санкт-Петербург, Россия, 21-28 may, 2018); Ümummilli lider H. Əliyevin anadan olmasının 96-cı ildönümünə həsr olunmuş "Müasir təbiət elmlərinin aktual problemleri" (Gəncə, Azərbaycan, 2-3 may, 2019); 14th International Conference on Theory and Application of Fuzzy Systems and Soft Computing – ICAFS-2020 (Budva, Montenegro, 27-28 avqust, 2020).

The new solid solutions discovered in the work are potential thermoelectric, magnetic, and topological insulator materials, and by conducting relevant physical studies, their functional properties can be optimized and recommendations for application can be made.

Based on the information from the "Google Scholar Citations" information system for 8 published papers in international scientific journals on the topic of the author's dissertation 31 references have been made.

The name of the organization where the dissertation was conducted. The work was performed in the "Thermodynamics of Functional Inorganic Compounds" laboratory of the Inorganic Functional Materials" department of the Institute of Catalysis and Inorganic Chemistry and the Department of Radioecological and Ecochemical Research of the Institute of Ecology of the National Aerospace Agency.

Personal contribution of the author. Experimental research, the processing of the results, and their preparation for publication were carried out mainly by the author. The author's share in the coauthorship of scientific works was decisive.

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 (8878 characters), four chapters (Chapter I - 33663 characters, II-32776, III-60296, IV-34411), main results, 244 scientific literature, and has 156 pages, totaling 173,550 volumes. 60 pictures and 11 tables are included in the dissertation.

In the introductory part (character number 11270), the relevance of the topic of the dissertation is justified, the purpose of the work, the scientific innovation of the obtained results, and the theoretical and practical significance are indicated.

In the first chapter (symbol number 49425) literature data on the topic of the dissertation is given and analyzed.

The second chapter (symbol number 40039) is devoted to a brief description of synthesis and physico-chemical research methods used in the dissertation.

The third chapter (symbol number 31010) gives the results of the study of phase equilibria on the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ and Tl_2Te-$TlTbTe_2$-$TlBiTe_2$ solidity planes of the Tl-Tb-Sb(Bi)-Te four-component systems.

The fourth chapter (symbol number 36546) presents the results of the experimental study of the phase equilibria on the solidity planes of the corresponding five-component systems Tl4PbTe3-Tl_9BiTe_6-Tl_9SmTe_6 and Tl_4PbTe_3-Tl_9BiTe_6-Tl_9TbTe_6, as well as thermodynamic analysis and 3D modeling.

MAIN CONTENT OF THE WORK

In the introduction, the relevance of the topic of the dissertation is substantiated, the purpose of the work, the scientific novelty of the obtained results, and the theoretical and practical significance are indicated.

At the beginning of the **first chapter** (paragraph 1.1), literature information about the functional properties of complex tellurides of thallium is given and the relevance of the work is justified. It has been shown that these compounds are promising functional materials exhibiting thermoelectric, optical, and magnetic properties. The literature data on phase equilibria and physicochemical properties of intermediate phases in the Tl-Te, Sm-Te, Tb-Te boundary binary systems (sections 1.2 and 1.3), as well as on sections Tl_2Te-PbTe, Tl_2Te-$Sb(Bi)_2Te_3$ of the Tl-Pb(Sb, Bi)-Te boundary ternary systems are provided (section 1.4). These data were used in planning experimental studies and analyzing the results.

At the end of the chapter (section 1.5), the modern state of physico-chemical research of multi-component systems based on tellurides of rare earth elements is examined and the choice of research objects for the dissertation work is justified.

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

For the synthesis of the primary binary and ternary compounds of the studied systems, the following highly pure simple substances, products of the German company Alfa Aesar, were used: lead (mass percentage of purity 99.99, registration number 7439-92-1, in the form of ingots); bismuth (99.999, 7440-69-9, ingot); stibium (99.999; 7440-36-0, ingot); thallium (99.99, 13494-80-9, ingot); samarium (99.9, 7440-19-9, small crystals); terbium (99.9, 7440-27-9, small crystals).

At the initial stage of the research, the known binary (Tl_2Te, Tl_5Te_3) and ternary compounds (Tl_4PbTe_3, Tl_9SbTe_6, Tl_9BiTe_6, Tl_9SmTe_6, Tl_9TbTe_6, $TlSbTe_2$, $TlBiTe_2$, $TlTbTe_2$) which are the initial components in those systems were synthesized and identified. In the next stage, using them, intermediate alloys were synthesized.

Taking into account the relatively low melting temperatures of binary (Tl_2Te, Tl_5Te_3) and ternary (Tl_4PbTe_3, Tl_9SbTe_6, Tl_9BiTe_6, and $TlBiTe_2$) thallium tellurides they were synthesized by fusion method under vacuum conditions (~10^{-2} Pa) from stoichiometric quantities of elementary components in vacuumed quartz ampoules.

Taking into account that the $TlSbTe_2$ compound melts at 753 K by decomposition according to the peritectic reaction, the sample was

thermally treated at 700 K for 200 h after fusion.

Considering the high melting temperatures of elemental samarium and terbium (1343 and 1629 K, respectively), as well as their interaction with quartz at high temperatures and some other difficulties, the synthesis of ternary thallium-REE tellurides was carried out by a specially developed method. Therefore, in all syntheses with their participation, the inner walls of the quartz ampoules were graphitized by the thermal decomposition of toluene.

For the synthesis of the Tl_9SmTe_6 and Tl_9TbTe_6 compounds, no elemental components were used, but stoichiometric amounts of Tl_2Te, elemental lanthanide, and tellurium. This was done because thallium lanthanides have high thermodynamic and thermal stability, which prevents the formation of ternary compounds. It has been experimentally established that samples obtained by melting at 1000 K are not in an equilibrium state. On their thermograms and diffractograms, peaks were observed that did not correspond to these compounds. To bring these samples as close to equilibrium as possible, they were ground into powder, mixed, pressed into a cylindrical pellet shape, and heat treated at 700 K for 1000 hours. In some cases, this operation was repeated twice. Only this synthesis technique ensured the production of homogeneous samples. The synthesis of the $TlSmTe_2$ and $TlTbTe_2$ compounds was carried out in the same way. The thermal treatment temperature was 900 K, and the duration was 1500 hours.

All the synthesized compounds were identified by DTA and XRD methods.

Samples of the studied systems were prepared from previously synthesized and identified initial binary and ternary compounds by melting in quartz ampoules under vacuum conditions. The solidus temperature was determined by taking thermograms of non-homogenized cast samples. The samples were subjected to heat treatment for a long time (800-1000 h) at temperatures $20\text{-}50^0$ below the solidus temperature. In all cases, after to heat treatment intermediate non-homogenized samples were crushed, pressed into tablets, and subjected to long-term (400-500 h) heat treatment at the appropriate temperature in order to achieve an equilibrium state.

The studies were carried out by DTA, XRD, SEM, and MSA methods, as well as by the microhardness measurements. Sample parameters were refined by using the "TopasV3.0 software" computer program.

In the **third chapter**, the results of the study of phase equilibrium in Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ and Tl_2Te-$TlTbTe_2$-$TlBiTe_2$ systems are given.

The results of the study of these systems were reflected in the [5, 9-13, 15] works.

Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ system. As part of the study of the first system, taking into account the discrepancies in the available literature data, the Tl_2Te-Tl_9SbTe_6 boundary system was first investigated.

The ternary compounds Tl_9TbTe_6 and Tl_9SbTe_6, formed in the boundary systems Tl_2Te-Tl_9SbTe_6 and Tl_2Te-$TlTbTe_2$ of the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ system, divide this system into two subordinate subsystems.

There are contradictory data in the literature on the Tl_2Te-Tl_9SbTe_6 system, which is the third side of the investigated subsystem. According to the results of some studies, the Tl_2Te-Tl_9SbTe_6 system is characterized by the formation of unlimited solid solutions between the initial compounds. On the other hand, there are also data on the observation of a morphotropic phase transition in solids solutions near Tl_2Te in this system. Considering that the compounds Tl_2Te (Sp.gr.C2/C) and Tl_9SbTe_6 (Sp.gr.I/4m) have completely different crystal structures, this statement does not seem to be sufficiently substantiated. Taking into account the contradictions in the above-mentioned literature on this system, we again investigated the Tl_2Te-Tl_9SbTe_6 boundary system.

Based on the experimental results obtained (Table 1), it was shown that the Tl_2Te-Tl_9SbTe_6 system (Fig. 1) is a quasi-binary of peritectic type. The coordinates of the liquid phase with $L+\delta\leftrightarrow\alpha$ in peritectic equilibrium are 5 mol.% Tl_9SbTe_6 and 702 K (α- and δ- are solutions based on Tl_2Te and Tl_9SbTe_6, respectively). Homogeneous regions of α- and δ-phases are separated by a two-phase region $\alpha+\delta$.

At peritectic equilibrium temperature the homogeneity area for Tl_2Te is about 7 mol%, and for Tl_9SbTe_6 is 85 mol.%. With the decrease in temperature, these areas become narrower. According to microhardness measurements and XRD results at room temperature, it is ~ 5 and ~ 80 mol.%.

Table 1

DTA, microhardness measurements, and crystal lattice parameters for the alloys of the Tl_2Te-Tl_9SbTe_6 system

Phase	Thermal effects, K	Micro-hardness, MPa	Crystal lattice parameters, Å
Tl_2Te	695	1400	a = 15.662(8); b = 8.987(4); c = 31.196(12), β = 100.760, z = 44
$Tl_{9,95}Sb_{0,05}Te_{5,05}$	702	1515	-
$Tl_{9,9}Sb_{0,1}Te_{5,1}$	702-715	1330; 1520	-
$Tl_{9,8}Sb_{0,2}Te_{5,2}$	708-728	1320	a = 8.9098(4); c = 12.6792(10)
$Tl_{9,6}Sb_{0,4}Te_{5,4}$	727-753	1270	a = 8.8889(5); c = 12.7604(9)
$Tl_{9,5}Sb_{0,5}Te_{5,}$	740-762	-	-
$Tl_{9,4}Sb_{0,6}Te_{5,6}$	750-773	1180	a = 8.8690(4); c = 12.8416(9)
$Tl_{9,2}Sb_{0,8}Te_{5,8}$	775-790	1100	a = 8.8490(3); c = 12.9228(9)
Tl_9SbTe_6	800	1000	a = 8.8301(2); c = 13.0039(10)

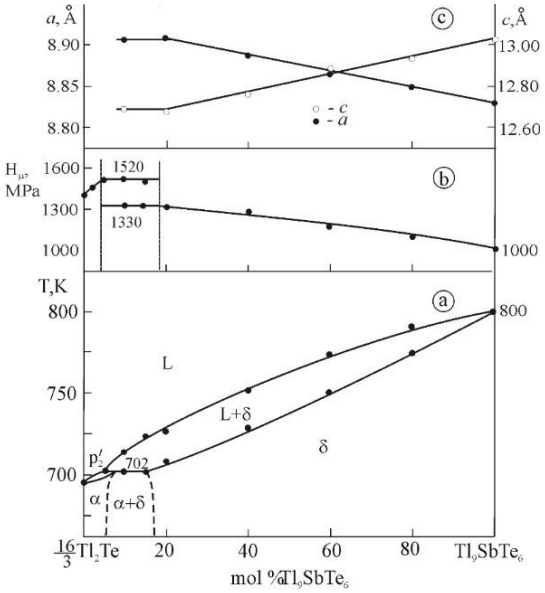

Fig. 1. Phase diagram (a), composition dependences of microhardness (b) and lattice parameters (c) for the alloys of the Tl_2Te-Tl_9SbTe_6 system

The breaking points observed on the composition dependence curves of lattice parameters and microhardness of these solid solutions

indicate saturated compositions of α- and δ-phases.

The solid-phase equilibria diagram (Fig. 2) clearly shows the location of phase fields at room temperature. As you can see, the system consists of two single-phase (α- and δ- phases) separated by a two-phase (α+δ) field. Figure 3 shows the studied internal polythermal sections and alloy compositions. Thus, an isothermal section of the phase diagram at 300 K shows that the region of homogeneity of the δ-phase occupies more than 90% of the area of the concentration triangle.

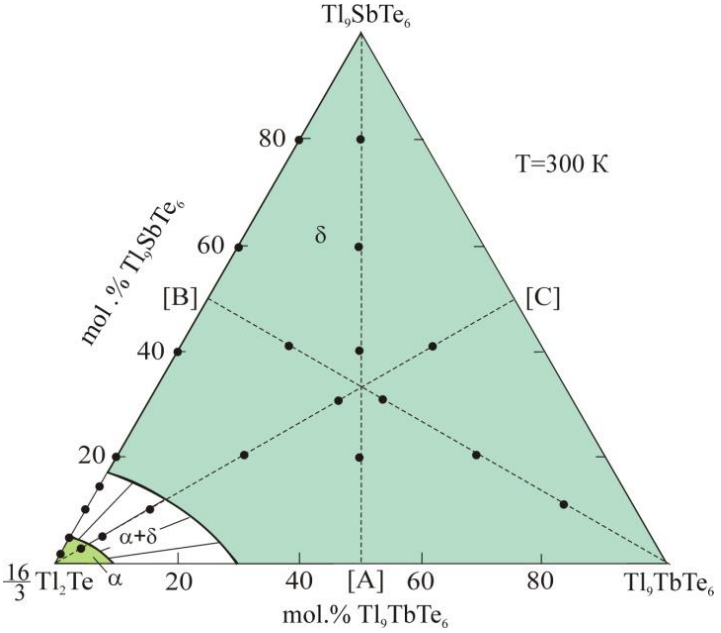

Fig.2. The solid-phase equilibria diagram of the Tl_2Te-Tl_9TbTe_6-Tl_9SbTe_6 system. Broken lines and dots – are studied an internal polythermal sections and alloy compositions.

The liquidus surface (Fig. 3) consists of three fields of primary crystallization. In these regions, the α- and δ-phases (regions 1 and 2), as well as the $TlTbTe_2$ compound (region 2), which is located outside the studied concentration plane, primarily crystallize from the liquid. Pri-

mary crystallization of the $TlTbTe_2$ compound from liquid was confirmed by X-ray diffraction.

Some polythermal and isothermal sections of the Tl_2Te-Tl_9SbTe_6-Tl_9TbTe_6 system were plotted. Their detailed description is given in the dissertation.

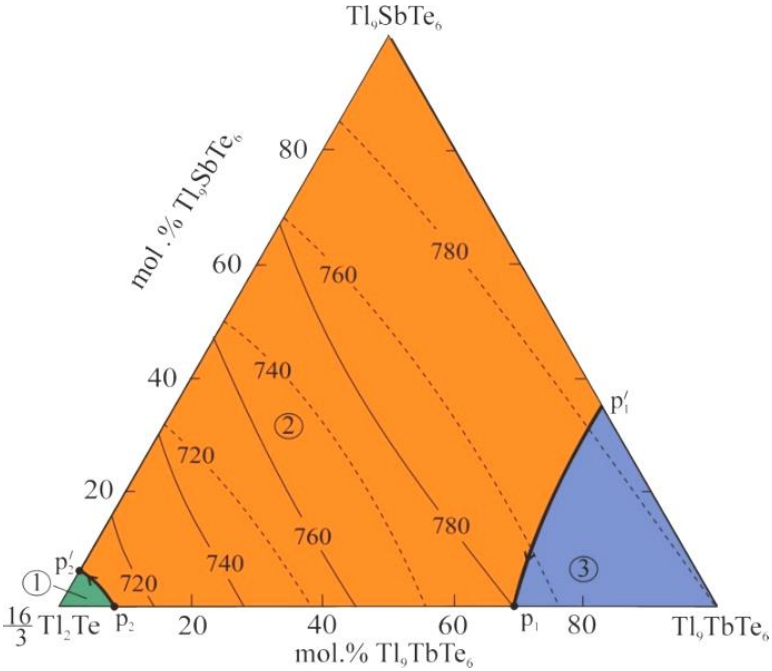

Fig.3. Projection of the liquidus surface of the Tl_2Te-Tl_9TbTe_6-Tl_9SbTe_6 system. Areas of primary crystallization: 1-α; 2-δ; 3- $TlTbTe_2$.

Tl_9TbTe_6-$TlTbTe_2$-$TlSbTe_2$-Tl_9SbTe_6 subsystem. The powder diffraction patterns of the boundary side $TlSbTe_2$-$TlTbTe_2$ of this system are shown in Fig. 4. As can be seen from the picture, the diffraction patterns of alloys containing 70 and 90 mol% $TlSbTe_2$ are qualitatively similar to $TlSbTe_2$. This confirms that they are single-phase. The diffraction patterns of samples containing 20, 40, and 60 mol% $TlSbTe_2$ consist of a totality of reflexes of $TlSbTe_2$ and $TlTbTe_2$ compounds, that is, they are two-phase mixtures formed by mutually saturated solid solutions based on neighboring compounds in the phase diagrams.

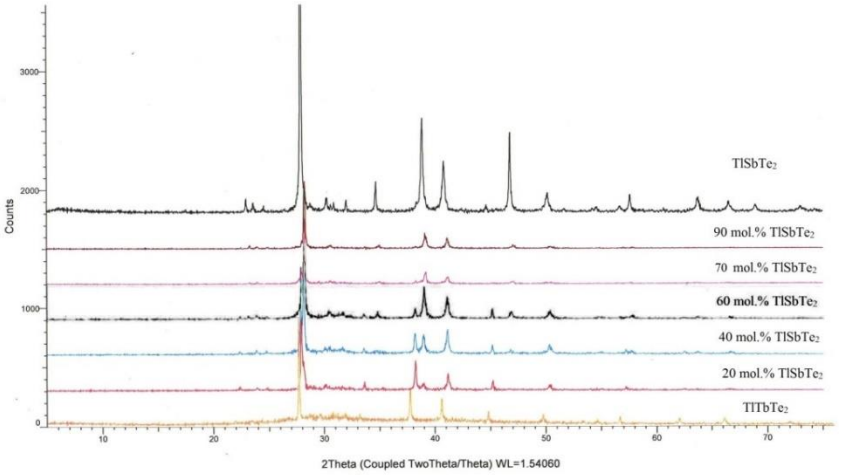

Fig.4. Powder diffraction patterns of some samples of the $TlSbTe_2$-$TlTbTe_2$ system at room temperature.

Based on the powder diffraction parameters, the crystal lattice types of the phases were determined and the lattice parameters were calculated (Table 2). To clarify the region of homogeneity of solid solutions based on primary compounds the graph of the dependence of the parameter on the compositions was plotted (Fig.5). As can be seen from the graph, during the stibium→terbium substitution in solid solutions, the value of "*a"* parameter increases, and the value of "*c*" parameter decreases. The graphs of the dependence of both parameters on composition have break points at compositions of ~30 and 90 mol% $TlTbTe_2$, and at intermediate compositions they remain constant regardless of the concentration. The breakpoints correspond to the mutually saturated compositions of β_2- and β_1-solid solutions based on $TlSbTe_2$ and $TlTbTe_2$, respectively. It should be noted that, regardless of the total composition of the alloys in the two-phase field $\beta_1+\beta_2$, the constancy of the lattice parameters of both phases also reflects the fact that the alloys are in the equilibrium state. The dependence of lattice parameters on composition in the region of homogeneity of the β_2-phase is linear, i.e., it obeys the Vegard rule. Thus, according to the results of X-ray diffraction analysis, the $TlSbTe_2$-$TlTbTe_2$ system is

stable below the solidus and is characterized by limited mutual solubility of the components. The solubility is 30 mol.% $TlSbTe_2$ and 10 mol.% $TlTbTe_2$.

Table 2

Phase composition and parameters of crystal lattices of some samples of the $TlSbTe_2$-$TlTbTe_2$ system

Compositions % $TlSbTe_2$	Phase composition	Rhombic lattice parameters, Å
$TlTbTe_2$	β_1	a = 4.4245(4); c = 23.3025(20)
10	β_1	a = 4.42375 (4); c = 23.3751(21)
20	$\beta_1+\beta_2$	α – *phase:* a = 4.42374 (4); c = 23.3759(21) β – *phase:* a = 4.4180(5); c = 24.0061(20)
40	$\beta_1+\beta_2$	α – *phase:* a = 4.42376 (5); c = 23.3747(21) β – *phase:* a = 4.4183(4); c = 24.0024(20)
60	$\beta_1+\beta_2$	α – *phase:* a = 4.42375 (5); c = 23.3753(21) β – *phase:* a = 4.4184(5); c = 24.0052(20)
70	β_2	a = 4.4180(5); c = 23.9991(20)
80	β_2	a = 4.4173(4); c = 24.1754(20)
90	β_2	a = 4.4165(5); c = 24.2516(21)
100	β_2	a = 4.4155(5); c = 24.2682(21)

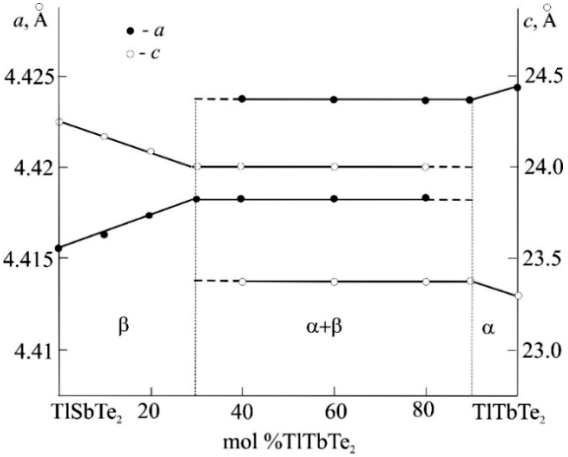

Fig.5. Dependences of the parameter on the compositions for the alloys of the $TlSbTe_2$-$TlTbTe_2$ system

To determine the nature of solid phase equilibria in the $TlTbTe_2$-

Tl_9TbTe_6-Tl_9SbTe_6-$TlSbTe_2$ subsystem, several annealed alloys were investigated by the XRD method. It has been established that unlimited solid solutions (δ-phases) formed in the Tl_9SbTe_6-Tl_9TbTe_6 system interact with solid solutions based on the $TlTbTe_2$ (β_1-phase) and $TlSbTe_2$ (β_2-phase). This leads to the formation of β_1+δ and β_2+δ two-phase fields delimited by a $\beta_1+\beta_2+\delta$ three-phase field.

Based on the results obtained, a solid-phase equilibria diagram of the Tl_2Te-$TlTbTe_2$-$TlSbTe_2$ system was constructed (Fig.6). As can be seen, the homogeneity region of continuous δ-solid solutions formed along the Tl_9TbTe_6-Tl_9SbTe_6 section penetrates the thallium-rich region and occupies most of the Tl_2Te- Tl_9TbTe_6-Tl_9SbTe_6 concentration triangle.

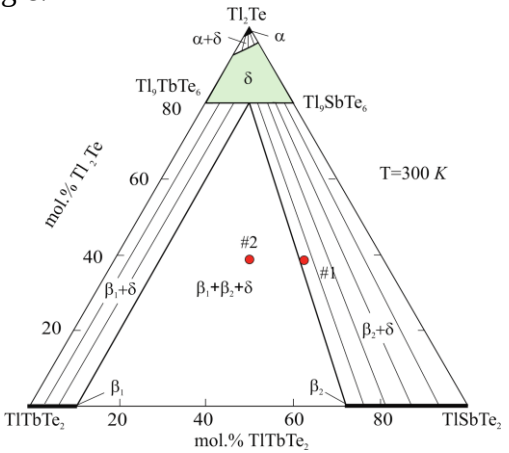

Fig.6. Solid-phase equilibria diagram of the $TlTbTe_2$-Tl_9TbTe_6-Tl_9SbTe_6-$TlSbTe_2$ subsystem

In the Tl_9SbTe_6-Tl_9TbTe_6-$TlTbTe_2$-$TlSbTe_2$ concentration region, the region of homogeneity of the δ-phase practically does not extend beyond the Tl_9SbTe_6-Tl_9TbTe_6 cross-section. The regions of homogeneity of solid solutions β_1- and β_2-, formed on the basis of primary compounds in the $TlTbTe_2$-$TlSbTe_2$ boundary system, slightly (about 1-2 mol%) penetrate into the concentration triangle. In this region, the δ-phase forms stable tie-lines with β_1- and β_2- solid solutions and β_1+δ and β_2+δ two-phase regions. These regions are limited by a

wide three-phase region $\beta_1+\beta_2+\delta$.

The bismuth analog of the Tl_2Te-Tl_9TbTe_6-Tl_9SbTe_6 system has a qualitatively similar picture of phase equilibria. The dissertation presents and describes in detail a diagram of solid-phase equilibria, as well as projections of the liquidus and solidus surfaces of the system, some polythermal and isothermal sections.

In the **fourth chapter**, the results of investigations of the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9SmTe_6 and Tl_4PbTe_3 -Tl_9BiTe_6-Tl_9TbTe_6 five-component systems (pages 4.1 and 4.2), as well as thermodynamic analysis and modeling (paragraph 4.3) are given.

The results of the study of these systems were reflected in the works of [1-4, 6-8, 14, 16, 17].

Tl_4PbTe_3-Tl_9BiTe_6-Tl_9SmTe_6 system. Samples of this system were synthesized from pre-synthesized and identified ternary compounds in vacuumized graphitized quartz ampoules. The intermediate alloys of the investigated systems were subjected to heat treatment at 700 K for 800 h. After melting, samples containing more than 60 mole % Tl_9SmTe_6 were ground into powder, pressed into pellets, and again annealed under the indicated conditions. Alloys on two boundary systems (Tl_4PbTe_3-Tl_9SmTe_6 və Tl_9BiTe_6-Tl_9SmTe_6) and some alloys on internal sections were prepared. The analysis of experimental results and literature data made it possible to determine the nature of the phase relations in the Tl_4PbTe_3-Tl_9SmTe_6-Tl_9BiTe_6 system.

Tl_4PbTe_3-Tl_9SmTe_6 and Tl_9BiTe_6-Tl_9SmTe_6 systems.

The results of DTA, microhardness, and crystal lattice parameters of the synthesized and annealed samples are shown in Table 3. Phase diagrams and corresponding "composition-properties" diagrams based on them were constructed (Fig.7).

Tl_4PbTe_3-Tl_9SmTe_6 and Tl_9BiTe_6-Tl_9SmTe_6 systems (Fig.7) are characterized by the formation of unlimited solid solutions (δ-phase) of the Tl_5Te_3- type. However, due to the incongruent nature of Tl_9SmTe_6 melting, they are represented by non-quasi-binary sections of the quaternary systems Tl-Pb-Sm-Te and Tl-Bi-Sm-Te and are stable below solidus. In the composition range of 0-60 mol.%, δ-solid solutions are crystallized from the melt, and in the region that is richer in Tl_9SmTe_6, the $TlSmTe_2$ phase is primarily crystallized. This leads to

the formation of two-phase L+$TlSmTe_2$ and three-phase L+$TlSmTe_2$+δ regions in a wide range of compositions (60-100 mol % Tl_9SmTe_6). However, due to a very small temperature interval, the three-phase field L+$TlSmTe_2$+δ was not detected experimentally and is shown by dashed lines (Fig. 7).

Тд$SmTe_2$ is first crystallized from a liquid rich in Tl_9SmTe_6. This is confirmed by the methods of X-ray structural analysis and SEM. For this, the sample from this area after the DTA method, was ground into powder and subjected to long-term heat treatment. Then they took a diffractogram and an SEM image. It is established that in addition to $TlSmTe_2$, there are reflections of other phases on the diffraction diagram. This proves the primary crystallization of the compound $TlSmTe_2$ from the liquid.

Table 3

Results of DTA, microhardness, and crystal lattice parameters of the alloys of the Tl_4PbTe_3 -Tl_9BiTe_6-Tl_9SmTe_6 system

Composition	Thermal effects of heating, K	Microhardness, MPa	Tetraqonal lattice parametrs, Å	
			a	*c*
Tl_4PbTe_3	893	1120	8.8409(5)	13.0556(6)
$Tl_{8.2}Pb_{1.6}Sm_{0.2}Te_6$	845-875	1160	8.8504(4)	13.0482(9)
$Tl_{8.4}Pb_{1.2}Sm_{0.4}Te_6$	820-850	1180	8.8602(5)	13.0387(8)
$Tl_{8.5}Pb_{1.0}Sm_{0.5}Te_6$	817-845	-	8.8645(6)	13.0343(9)
$Tl_{8.6}Pb_{0.8}Sm_{0.6}Te_6$	790-830	1150	8.8702(6)	13.0298(9)
$Tl_{8.8}Pb_{0.4}Sm_{0.8}Te_6$	775-800; 1190	1140	8.8788(5)	13.0280(9)
$Tl_{8.9}Pb_{0.2}Sm_{0.9}Te_6$	760-775; 1155	-	-	-
Tl_9SmTe_6	755; 1180	1080	8.8882(5)	13.0132(7)
$Tl_9Bi_{0,1}Sm_{0,9}Te_6$	760; 1150	-	-	-
$Tl_9Bi_{0,2}Sm_{0,8}Te_6$	765-775; 1095	1120	8.8810(4)	13.0201(7)
$Tl_9Bi_{0,4}Sm_{0,6}Te_6$	770-790	1140	8.8741(5)	13.0279(8)
$Tl_9Bi_{0,5}Sm_{05}Te_6$	780-800	-	8.8710(5)	13.0301(8)
$Tl_9Bi_{0,6}Sm_{0,4}Te_6$	785-810	1110	8.8673(5)	13.0340(9)
$Tl_9Bi_{0,8}Sm_{0,2}Te_6$	810-820	1070	8.8614(5)	13.0410(8)
Tl_9BiTe_6	830	980	8.8545(4)	13.0476(7)

For both Tl_4PbTe_3-Tl_9SmTe_6 and Tl_9BiTe_6-Tl_9SmTe_6 systems, the dependence of the microhardness on the composition was determined. The graph is a curve passing through the maximum (Figure 7). Such a

picture is typical for systems that form continuous solid solutions. The increase in the value of microhardness due to the formation of solid solutions based on compounds of stoichiometric composition is explained by the fact that during substitutions (in our case, Pb↔Sm and Bi↔Sm substitutions) deformation occurs in the crystal lattice due to the difference in the ionic radii of the atoms, and it increases with the increase in hardness. This leads to an increase in microhardness.

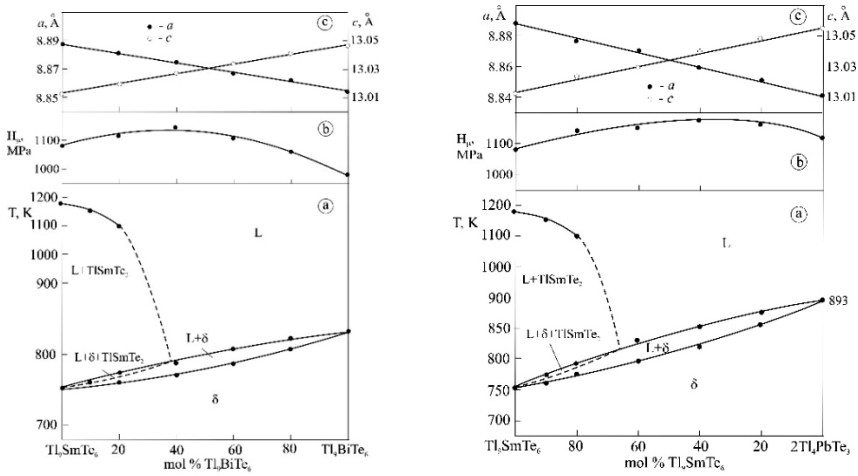

Fig. 7. Phase diagram (a), the dependence of microhardness (b) and parameters of the tetragonal lattice (в) on the composition of alloys of the Tl_9SmTe_6-Tl_9BiTe_6 and Tl_9SmTe_6-Tl_9PbTe_6 systems

Intermediate compositions have qualitatively similar patterns to the initial compounds. They crystallize in a tetragonal structure of the Tl_5Te type with a slight displacement relative to initial compounds. Powder diffractograms are indexed in the Tl_5Te_3-type tetragonal structure. The dependence of lattice parameters on the composition obeys Vegard's rule.

The liquidus and solidus surfaces. The liquidus projection of the T-x-y diagram of the system consists of two areas corresponding to the initial crystallization of δ- solid solutions and $TlSmTe_2$ compound delimited by the L+$TlSmTe_2$↔δ peritectic equilibrium. The solidus projection of the system consists of a surface, corresponding to the

completion of crystallization of the δ- phase (Fig.8).

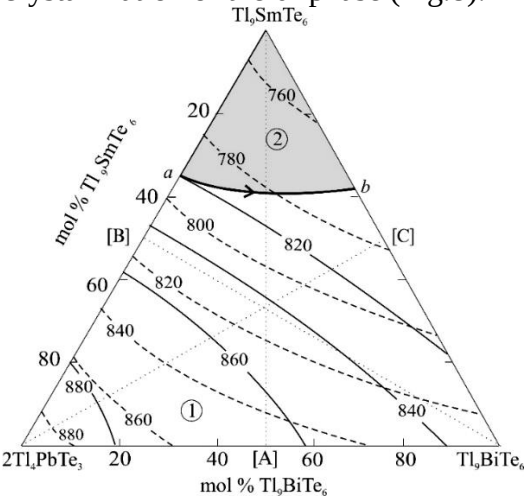

Fig. 8. Projection of the liquid surface of the Tl_4PbTe_3-Tl_9SmTe_6-Tl_9BiTe_6 system. Areas of primary crystallization 1-δ; 2-$TlSmTe_2$. A, B, and C are the equimolar composition of the corresponding boundary system. Dashed lines are solid curves, dashed lines are polythermal cross-sections.

The experimental results obtained show that the Tl_4PbTe_3 -Tl_9BiTe_6-Tl_9TbTe_6 system is characterized by a similar pattern of phase equilibria. The dissertation presents and describes in detail a diagram of solid-phase equilibria, as well as projections of the liquidus and solidus surfaces of the system, some polythermal and isothermal sections.

3D modeling of the phase diagram of the Tl_4PbTe_3-Tl_9SmTe_6-Tl_9BiTe_6 system.

In application to real semiconductor systems, solving the inverse problem of phase equilibria theory (calculating thermodynamic functions from phase diagrams) is of greater practical interest, since experimental research into thermodynamic properties lags significantly behind the study of phase equilibria.

For a thermodynamically correct solution of this problem, in addition to phase diagrams, certain information about the properties of the phases is necessary. G.F. Voronin investigated possible variants of

correct solutions for the required minimum sets of initial data[4]. For most real systems, there are no minimum data necessary for the implementation of thermodynamically correct solution methods. Therefore, more approximate methods are used to obtain thermodynamic information collected in phase diagrams. The most frequently used methods are based on various model assumptions that allow calculations to be carried out with very limited initial data. The main drawback of this approach is that it is impossible to determine the degree of conformity of the model adopted within the framework of thermodynamics. Therefore, such estimates always have an unknown error due to the inadequacy of the phase model, i.e. they are thermodynamically incorrect. However, this approach can be used if you make sure that the selected model is close to reality.

To modeling the volumetric T-x-y diagram of a ternary or quasi-ternary system, it is important to obtain their three-dimensional (3D) images. The basic principle of construction of a three-dimensional (3D) computer model of a phase diagram is the construction of three-dimensional images of its phase equilibrium surfaces and phase fields. The use of 3D computer models of T-x-y diagrams allows one to take into account various options for the geometric structure of the systems being studied. 3D modeling allows us to determine the number and type of surfaces (linear or nonlinear surfaces, flat, domed, etc.), the number of phase regions, which solid phases have a constant or variable composition in three-phase regions, convert tabular data into three-dimensional ones and, finally, allows to build a geometric model of the T-x-y diagram.

In order to visualize the three-dimensional liquidus surfaces of the $2Tl_4PbTe_3$-Tl_9BiTe_6-Tl_9SmTe_6 and $2Tl_4PbTe_3$-Tl_9BiTe_6-Tl_9TbTe_6 systems, the analytical version of the OriginLab program was used.

For the 3D modeling of the phase diagram of the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9SmTe_6 system, first for its Tl_9SmTe_6(1)-$2Tl_4PbTe_3$(2),

[4] Voronin G.F., Gerasimov Ya.I. Using data on the thermodynamic properties of metals and alloys to calculate phase diagrams. - In the book: Phase diagrams of metal systems. - Moscow: Nauka. - 1981. pp. 41-48

Tl_9SmTe_6(1)-Tl_9BiTe_6(3) və $2Tl_4PbTe_3$(2)-Tl_9BiTe_6(3) boundary systems the analytical expressions of the liquidus and solidus obtained.

For this, fuzzy positions were used for the composition of phases in equilibrium in heterogeneous fields[5].

Due to the monotonic dependence of the liquidus and solidus temperatures of systems 1-2 and 1-3 on the composition, the following equations were used for them:

$$T(\text{liquidus}) = a+bx+(c\pm\Delta)x(1-x)$$

$$T(\text{solidus}) = a+bx+(d\pm\Delta)x(1-x)$$

Taking into account the complex dependence of the liquidus and solidus temperatures on the composition in the 2-3 system

$$T(\text{likvidus}) = a+bx+(c_0+c_1x+c_2x^2)x(1-x)$$

$$T(\text{solidus}) = a+bx+(d_0+d_1x+d_2x^2+d_3x^3)x(1-x)$$

equations were used. Here, coefficients *a* and *b* are determined based on the melting temperatures of Tl_9SmTe_6, Tl_4PbTe_3, and Tl_9BiTe_6 compounds, coefficients *c* and *d* are related to experimental errors. The following equations were used for the liquidus and solidus surfaces of the Tl_9SmTe_6(1)-$2Tl_4PbTe_3$(2)-Tl_9BiTe_6(3) ternary system:

$$T(\text{likvidus}) = yT_{liq}(1\text{-}2)+(1\text{-}y)T_{liq}(1\text{-}3)+T_{liq}(2\text{-}3)y(1\text{-}y)(1\text{-}x)$$

$$T(\text{solidus}) = yT_{sol}(1\text{-}2)+(1\text{-}y)T_{sol}(1\text{-}3)+T_{sol}(2\text{-}3)+by(1\text{-}y)(1\text{-}x)^2$$

In the above expressions, *x*- is the mole fraction of Tl_9SmTe_6 compound; ; $y = x_2 / (1\text{-}x)$; $(1\text{-}y) = x_3 / (1\text{-}x)$; x_2, x_3- are mole fractions of Tl_4PbTe_3 and Tl_9BiTe_6 compounds, respectively.

An asymmetric version of the associated regular solution model was used to calculate the free energy of the formation of solid solutions formed in boundary systems:

$$\Delta G_T^0 = (a+bT)x^m(1-x)^n + RT[p\,x\ln x + q(1-x)\ln(1-x)]$$

Here, the first term represents the enthalpy of the mixing of solid solutions in the asymmetric version of the regular solutions model. The mixing parameter for unlimited solid solutions $a<0$, $b>0$; the second limit

[5] Mammadov, A.N., Aliev, Z.S., Babanly, M.B. Study of the Uncertainty Heterogeneous Phase Equilibria Areas in the Binary YbTe-SnTe Alloy System. // 13th International Conference on Theory and Application of Fuzzy Systems and Soft Computing (ICAFS 2018). Advances in Intelligent Systems and Computing, - Springer, Cham, - 2019, - vol. 896, - p. 815-822

is the configurational entropy of mixing of solid solutions according to the model of non-molecular compounds; p and q indicate the number of different atoms in compounds; R= 8.314 $J \cdot mol^{-1} \cdot K^{-1}$.

The optimization of the liquidus and solidus curves was carried out using a multi-objective genetic algorithm (MGA) according to the following scheme[6]: first, for the GMA the search range for each parameter was determined based on the DTA results. Then, by varying the values of the variables, the liquidus and solidus formalized by them provided the best match to the experiment. A fuzzy logic evaluation scheme looks at all possible values of a given term and converts them to a value between 0 and 1. The cost is zero in the worst approach and one in the best. Using a fuzzy logic scheme, the optimization is carried out until a fitness level of 1 or closer is reached for all members. When this state is reached, the final set obtained is used to determine the uncertainty bounds on the model parameters.

The following analytical dependences were obtained for the liquidus and solidus curves of the two boundary systems:

For $2Tl_4PbTe_3$- Tl_9SmTe_6 system

1)T(liq)=893-138*x+70*x*(1-x); 2)T(liq)= 893-138*x+56*x*(1-x);
3)T(liq)=893-138*x+44*x*(1-x); 4)T(sol)= 893-138*x-52*x*(1-x);
5)T(sol)= 893-138*x-62*x*(1-x); 6)T(sol)= 893-138*x-70*x*(1-x) .

For Tl_9BiTe_6 –Tl_9SmTe_6 system

1) T(liq)=830-75*x+52*x*(1-x); 2)T(liq)=830-75*x+45*x*(1-x)
3) T(liq)=830-75*x+39*x*(1-x); 4)T(sol)=830-75*x-43*x*(1-x);
5) T(sol)=830-75*x-50*x*(1-x); 6)T(sol)=830-75*x-57*x*(1-x).

For Tl_9BiTe_6 -$2Tl_4PbTe_3$ system

1) T(liq)=830+63*x+x*(1-x)*(46.7-100.7*x+80.4*x^2);
2) T(liq)=830+63*x+x*(1-x)*(46.7120.7*x+98.4*x^2);
3) T(liq)=830+63*x+x*(1-x)*(42.7-130*x+98.4*x^2),
4)T(sol)=830+63*x+x*(1-x)*(-45+68*x-184*x^2+125*x^3) ;
5)T(sol)=830+63*x+x*(1-x)*(-55+68*x-184*x^2+125*x^3);
6)T(sol)=830+63*x+x*(1-x)*(-65+68*x-184*x^2+125*x^3).

[6] Mamedov, A.N. Thermodynamics of systems with non-molecular compounds / A.N.Mamedov. - LAP Germany, - 2015. - 124 p

Based on these equations, liquidus and solidus curves were constructed for these systems (Fig. 9). As can be seen, the calculated liquidus and solidus curves are in good agreement with the experimental results.

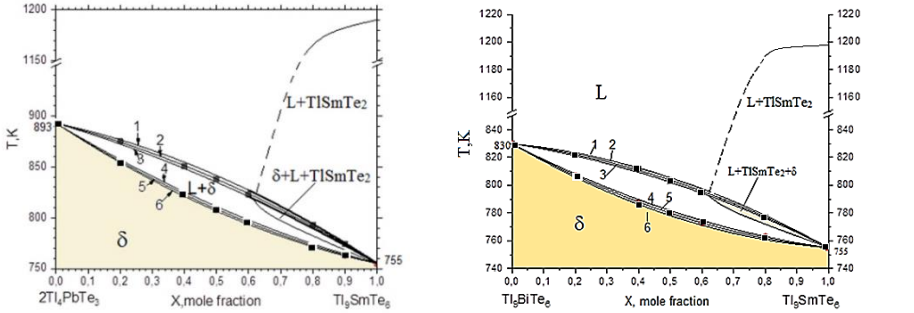

Fig. 9. Phase diagram of the $2Tl_4PbTe_3$- Tl_9SmTe_6 and Tl_9BiTe_6 – Tl_9SmTe_6 systems. The lines – calculation, squares – experience.

As a result of 3D modeling of the liquidus and solidus surfaces of the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9SmTe_6 system (Fig. 10), the following formulas were obtained:

T (for $TlSmTe_2$ liquidus**)**=(-1248+4673*x-2300*x^2)*y+
(-1248+4673*x- 2300*x^2)*(1-y),

T (solid solutions liquidus)= y*T_{liq}(1-2)+(1-y)*T_{liq}(1-3)+*a*y*(1-y)*(1-x_1)=(893-138*x+56*x*(1-x))*y+(830-75*x+
45*x*(1-x))*(1-y)+ 40*y*(1-y)*(1-x) ,

T (solidus)= y*T_{sol}(1-2)+(1-y)*T_{sol}(1-3)+*b*y*(1-y)*(1-x)^2 =
(893-138*x-62*x*(1-x))*y+(830-75*x-50*x*(1-x))*(1-y)+
44*y*(1-y)*(1-x)^2 .

Calculations showed that in the temperature range T = 300-900 K, the second-order derivative of the Gibbs mixing free energy is greater than zero. Consequently, the stability of the function (Ψ>0) in the entire range of compositions is also greater than that of the furnace, and this indicates the thermodynamic stability of solid solutions.

The 3D thermodynamic modeling of the Tl_8PbTe_3-Tl_9BiTe_6-

Tl_9TbTe_6 system was carried out in the same way.

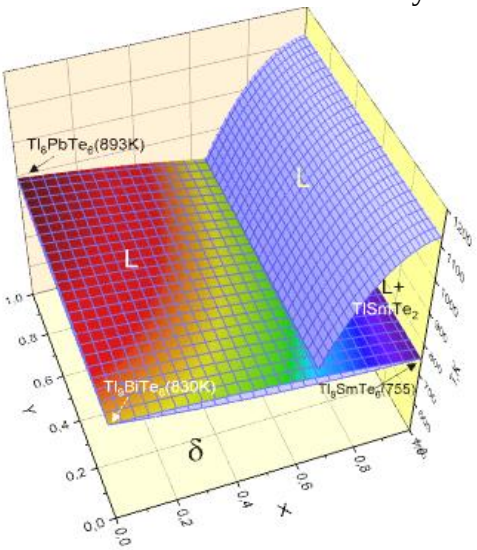

Fig.10. 3D visualized model of the Tl_8PbTe_3 -Tl_9BiTe_6- Tl_9SmTe_6 system

Thus, a 3D model of the phase diagram of both considered quasiternary systems has been constructed, which is in good agreement with the experimental results of thermodynamic analysis and shows that in a complex system consisting of ternary compounds that are structural analogs of the Tl_5Te_3 compound thermodynamically stable continuous solid solutions are formed and these solid solutions can be considered as regular.

RESULTS

1. The nature of interactions in Tl-B^V-Tb-Te (B^V-Sb, Bi) systems in the Tl_2Te-TlB^VTe_2-$TlTbTe_2$ compositions regions was determined by methods of DTA, XRD, SEM, and microhardness measurements. Solid-phase equilibria diagrams and a number of "composition-properties" diagrams were constructed. It was shown that even though both systems are non-quasi-ternary, they are stable in subsolidus. The Tl_9TbTe_6-$Tl_9B^VTe_6$ sections, which form continuous solid solutions, divide the system into two independent subsystems:

Tl_2Te-$Tl_9B^VTe_6$-Tl_9TbTe_6 və TlB^VTe_2-$Tl_9B^VTe_6$-Tl_9TbTe_6-$TlTbTe_2$.

2. Complete pictures of phase equilibria in T-x-y coordinates for Tl_2Te-$Tl_9B^VTe_6$-Tl_9TbTe_6 subsystems were obtained. Projections of liquidus and solidus for systems, some polythermal and isothermal sections were constructed. It was determined that the liquidus surfaces consist of three fields corresponding to solid solutions formed in the $Tl_9B^VTe_6$-Tl_9TbTe_6 systems (δ-phase), as well as primary crystallization of Tl_2Te and $TlTbTe_2$ phases. Solidus consists of 2 surfaces belonging to the first two phases. The homogeneous region of the δ-phase sharply penetrates the concentration triangle, occupying up to 90% of its area.
3. In the TlB^VTe_2-$Tl_9B^VTe_6$-Tl_9TbTe_6-$TlTbTe_2$ subsystems, solid solutions formed along the $Tl_9B^VTe_6$-Tl_9TbTe_6 boundary systems (δ-phase) interact with solid solutions (β_1 and β_2) based on $TlTbTe_2$ and TlB^VTe_2 compounds and form $\beta_1+\delta$, $\beta_2+\delta$ and $\beta_1+\beta_2+\delta$ heterogeneous fields. Fields of homogeneity of β_1- and β_2-phases, as well as their boundaries, were determined by various physico-chemical methods.
4. A complex of new mutually agreed results on phase equilibria in the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9SmTe_6 and Tl_4PbTe_3-Tl_9BiTe_6-Tl_9TbTe_6 concentration planes of corresponding five-component systems were obtained. A series of vertical and horizontal sections of T-x diagrams of both subsystems, as well as projection surfaces of liquidus and solidus, were constructed. It was established that the surface of the liquidus consists of the δ-phase and $TlLnTe_2$ compounds (Ln-Sm, Tb), while the solidus corresponds to the surface of the δ-phase. Due to the incongruent melting character of the Tl_9SmTe_6 and Tl_9TbTe_6, both subsystems are not quasi-ternary, but are stable in the subsolidus and are characterized by the formation of continuous solid solutions that crystallize in a tetragonal lattice of the Tl_5Te_3 type.
5. Based on the approximation of regular solutions, the analytical equations of the liquidus and solidus in the Tl_4PbTe_3-Tl_9BiTe_6-Tl_9SmTe_6 and Tl_4PbTe_3-Tl_9BiTe_6-Tl_9TbTe_6 were obtained, and their 3D models were constructed and visualized. Based on these

models, a thermodynamic analysis of phase diagrams was carried out, and the correspondence of liquid and solid solutions to the model of regular solutions was shown.

6. Based on the obtained results on phase equilibria in the studied four- and five-component systems, some samples of the detected phases of variable composition with a given composition were synthesized and characterized. The nature and temperature intervals of the crystallization of these samples from the liquid are determined, and their crystallographic parameters are also determined. The discovered new solid solutions have adjustable composition and functional properties, and are of interest as magnetic topological insulators and thermoelectric materials.

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

1. Alakbarzade, G.I. Tl_4PbTe_3-Tl_9SmTe_6 system / G.I.Alakbarzade, D.M.Babanly, S.Z.Imamaliyeva // Condensed Matter and Interphases, - 2017. 19 (4), - c. 474-478.
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3. Imamaliyeva, S.Z. Phase equilibria in the Tl_4PbTe_3-Tl_9SmTe_6-Tl_9BiTe_6 section of the Tl-Pb-Bi-Sm-Te system / S.Z.Imamaliyeva, G.I.Alakbarzade, M.A.Mahmudova [et al.] // Acta Chimica Slovenica, - 2018. vol.65, - p. 365–371.
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Tl_9LnTe_6-Tl_9BiTe_6 (Ln-Sm, Gd, Tb) // "Высокочистые вещества и материалы. Получение, анализ, применение" XVI всероссийская конф. и IX школа молодых ученых, посв. 100-летию Г.Г.Девятых, - Новгород, - 2018, - с. 22.

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