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Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 SYSTEM

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Phase equilibria in the quaternary system Tl-Ge-Bi-Te in the composition area Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 were investigated by using differential thermal analysis (DTA) and powder X-ray diffraction (XRD) technique. Some isopleth sections and isothermal sections at 300, 740 and 800 K, as well as projections of liquidus and solidus surfaces were constructed. It found that homogeneity area of solid solutions with Tl_5Te_3 structure (δ-phase) occupied more than 80% of the concentration triangle. A narrow area of solid solutions (α-phase) based on Tl_2Te were detected along boundary system Tl_2Te-Tl_9BiTe_6.

Keywords: *thallium-germanium telluride, thallium-bismuth telluride, phase equilibriums, solid solutions, crystal structure.*

1. INTRODUCTION

Chalcogenides of heavy metals belong to important functional materials with thermoelectric, photoelectric, optical and other properties [1-3]. Some of them exhibit properties of topological insulators and can be used in spintronic devices [4-6]. Moreover, complex thallium chalcogenides constitute a new class of promising thermoelectric materials with anomalously low thermal conductivity [7-10].

Thallium subtelluride, Tl_5Te_3, because of crystal structure features (Sp.gr.I4/mcm, a = 8.930; c = 12.598 Å) [11,12], has a number of ternary cation- and anion analogs such as $Tl_4A^{IV}Te_3$ and $Tl_9B^{V}Te_6$ as well as Tl_5X_2Hal (A^{IV}-Sn, Pb; B^{V}-Sb, Bi; X-Se, Te; Hal-Cl, Br, I) [13-17]. The above-mentioned compounds have a good thermoelectric performance, whereas Tl_9BiTe_6 exhibits the highest ZT value [2, 18-22]. Furthermore, authors [23] found Dirac-like surface states in the $[Tl_4]TlTe_3$ (Tl_5Te_3) and its non-superconducting tin-doped derivative $[Tl_4](Tl_{1-x}Sn_x)Te_3$.

Direct search for new multicomponent compounds based on known ones requires the study of phase equilibria in the corresponding systems. Early we presented the results of phase relations study in the systems including Tl_5Te_3 and its analogs [24-26]. It was shown that the systems are characterized by the formation of continuous areas of solid solutions with Tl_5Te_3-type structure.

In this work, we continue to study similar systems and present a detailed analysis of phase equilibria in the quaternary system Tl-Ge-Bi-Te on the composition area Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5.

Initial compounds of the investigated system are studied in detail. Tl_2Te, Tl_9BiTe_6 and Tl_8GeTe_5 compounds melt congruently at 698 [27], 830 [15] and 753 K [28] respectively. Tl_2Te crystallizes in the monoclinic system (space group C2/c; a = 15.662; b = 8.987; c=31.196Å, β=100.76^0, z=44) [29], while Tl_9BiTe_6 and Tl_8GeTe_5 have tetragonal structure of Tl_5Te_3-type (*I*4/*mcm*) with following parameters: a = 8.855, c = 13.048 Å, z=2; a=8.918, c=13.055 Å, z=2 [22,30]. Boundary Tl_9BiTe_6-Tl_8GeTe_5 and Tl_2Te- Tl_5Te_3-Tl_8GeTe_5 systems are studied in [31, 32] and characterized by the formation of unlimited fields of solid solutions.

2. EXPERIMENTAL

2.1. Materials and syntheses

The following elementary components were used for the investigations: thallium (granules, 99.999 %), bismuth (granules, 99.999 %), germanium (powder, 99.999%), and tellurium (broken ingots 99.999 %).

The components were weighed according to stoichiometric compositions and put into silica tubes, about 20 cm in length and 1 cm in diameter. Then the ampoules were sealed under a vacuum of 10^{-2} Pa. The compounds, 20 gram each, were prepared by melting of the elements in evacuated silica tubes in a single zone electric furnace at a temperature of 30-50^0 above the melting point of the compounds followed by cooling in the switched-off furnace.

The purity of synthesized compounds was checked by differential thermal analysis (DTA) and powder X-ray diffraction (XRD) techniques.

Previously synthesized binary and ternary compounds were used to synthesize the alloys of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system. All the samples were annealed at 650 K after synthesis to achieve complete homogenization.

2.2. Methods

DTA and XRD analyses were used to analyze the samples of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system.

The phase transformation temperatures have been determined using a NETZSCH 404 F1 Pegasus differential scanning calorimeter between a room temperature and ~900 K. The phase identification was performed using a Bruker D8 diffractometer utilizing CuK_α radiation in the 2θ range of 6–70°. The unit cell parameters of starting compounds and intermediate alloys were calculated by indexing powder patterns using Topas V3.0 software.

3. RESULTS AND DISCUSSION

The combined analysis of experimental and literature data on boundary systems Tl_2Te-Tl_8GeTe_5 [28] and Tl_9BiTe_6-Tl_8GeTe_5 [32] enabled us to construct the self-consistent diagram of phase equilibriums in the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system (Table, Fig.1-4).

Table. Some properties of phases in the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system

Alloy compositions, Fig.1,3		Thermal effects, K	Lattice parameters, Å
Tl_9BiTe_6-[B]	mol % Tl_9BiTe_6		
	100	830	*Tetragomal*, *a*=8.8545(4), *c*=13.0476(9)
	80	800-824	*a*=8.866(4), *c*=13.013(10)
	50	760-800	*a*=8.888(4), *c*=12.961(10)
	20	720-770	*a*=8.891(4), *c*=12.910(9)
	10	700-756	-
	5	698-747	-
	[B]	695-730	*a*=8.915(5); *c*=12.876(12)

Tl_2Te-[A]	mol % Tl_2Te		
	100	698	*monoclinic*, C*2/*c*;* *a* = 15.658 (8); *b* = 8.989 (4); *c* = 31.192Å (12), β = 100.76, z = 44
	90	698	-
	80	696-740	-
	60	715-765	*a*=8.919(5); *c*=12.783(12)
	40	740-782	*a*=8.913(5); *c*=12.875(12)
	20	760-798	*a*=8.908(5); *c*=12.968(12)
	[A]	782-806	*a*=8.903(5); *c*=13.060(13)

Isopleth sections of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system (Fig.1).

Figs.1a,b present the isopleth sections Tl_2Te-[A] and Tl_9BiTe_6-[B] of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system, where A and B are equimolar alloys from the respective boundary system as shown in Fig.3. The liquidus of Tl_2Te-[A] section consists of two curves of primary crystallization of α- and δ-phases. The intersection point of these curves corresponds to the monovariant peritectic reaction L+δ↔α (700-703 K). The L+δ+α area is indicated by a dashed line because it was not fixed experimentally due to a narrow temperatures range. Below the solidus this section passes through α, α+δ and δ phase areas.

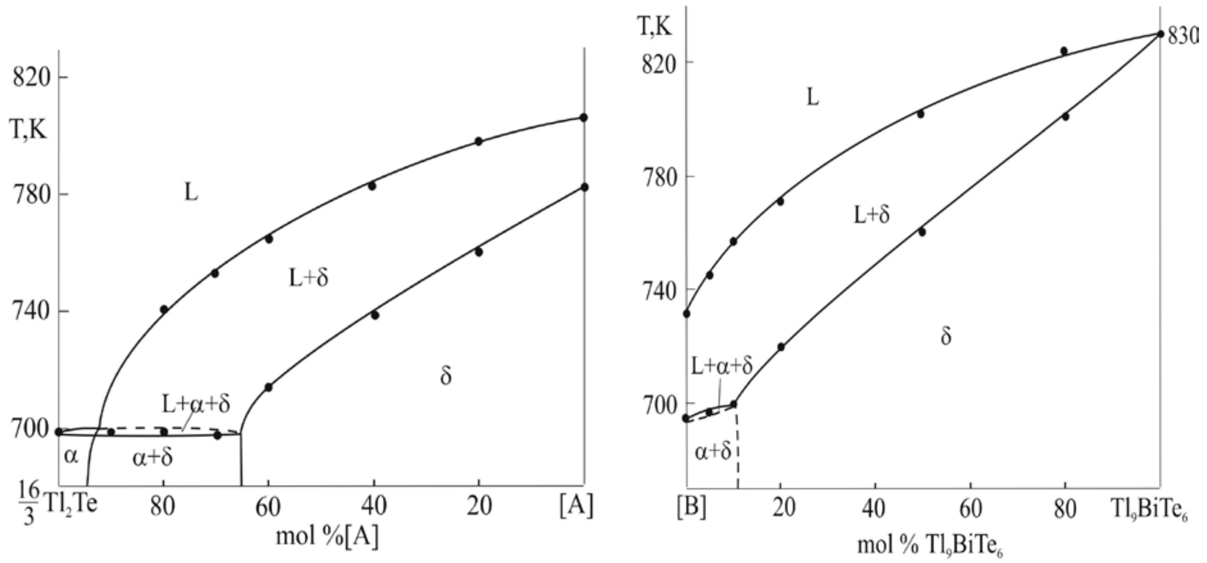


Fig.1. Polythermal sections Tl_2Te-[A] and Tl_9BiTe_6-[B] of the phase diagram of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system where A and B are equimolar alloys from the respective boundary system as shown in Fig.3.

Along the Tl_9BiTe_6-[B] section, the δ-phase primary crystallizes over the entire compositions range. Then a monovariant peritectic process L+δ↔α takes place (Fig.3a). The L+δ+α phase is shown by a dashed line because not fixed experimentally due to a narrow interval of temperatures. A narrow (10 mol%) two-phase region α+δ is found below 700 K.

X-ray analysis of the selected powdered samples testifies to the phase diagrams of the above-mentioned systems. For example, the XRD patterns for different compositions of the Tl_2Te-[A] section are presented (Fig.2). The alloys with compositions ≤60 mol% Tl_2Te are monophasic with Tl_5Te_3-type diffraction patterns (Fig.2, diffraction patterns 1-3), while alloy with 80mol% Tl_2Te composition is biphasic and besides the δ-phase reflections contains weak reflections of α-phase based on Tl_2Te (Fig.2, diffraction pattern 4).

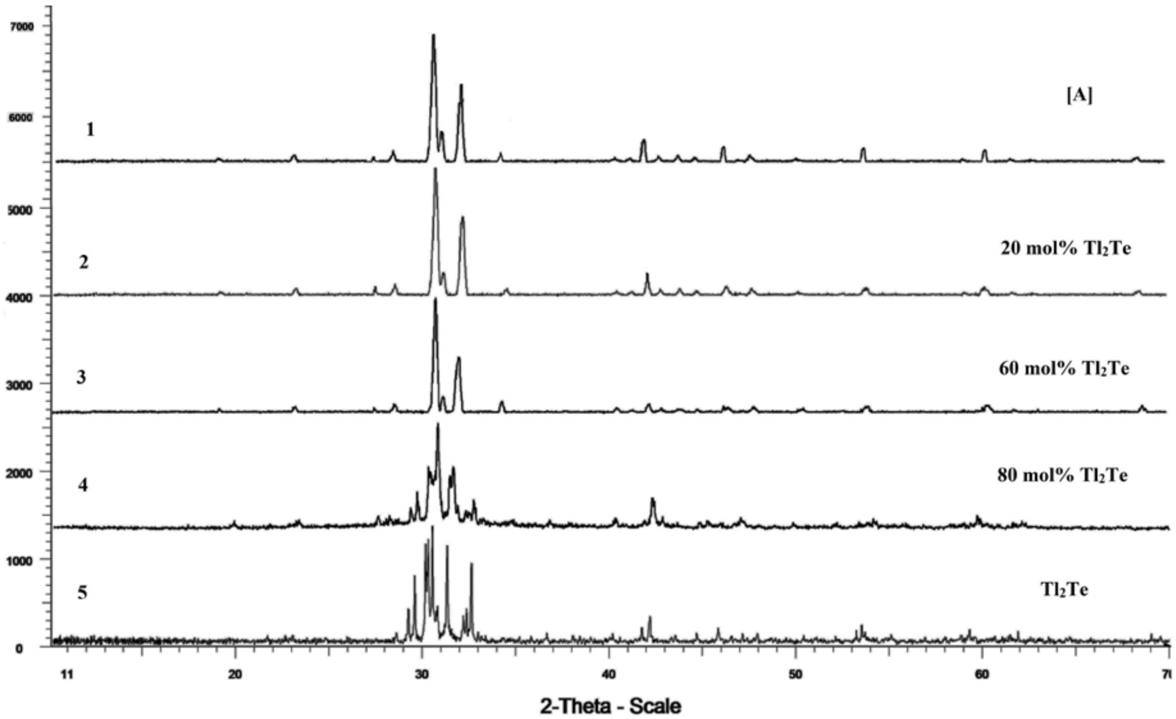


Fig.2. XRD patterns for different compositions in the Tl_2Te-[A] section. [A] are equimolar alloy from the boundary system Tl_9BiTe_6-Tl_8GeTe_5 as shown on Fig.3.

The liquidus surface projection (Fig. 3).

The liquidus of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system consists of two fields of the primary crystallization of α- and δ-phases. These fields are separated by pe line which corresponds to the monovariant peritectic equilibrium L+δ↔α. Near the eutectic point (e) the peritectic equilibrium L+δ↔α must be transformed into L↔α+δ eutectic equilibrium. However, coordinates of this transformation are not experimentally fixed due to a narrow temperature range. Solidus surface consists of two areas corresponding to the completion of crystallization α- and δ-phases.

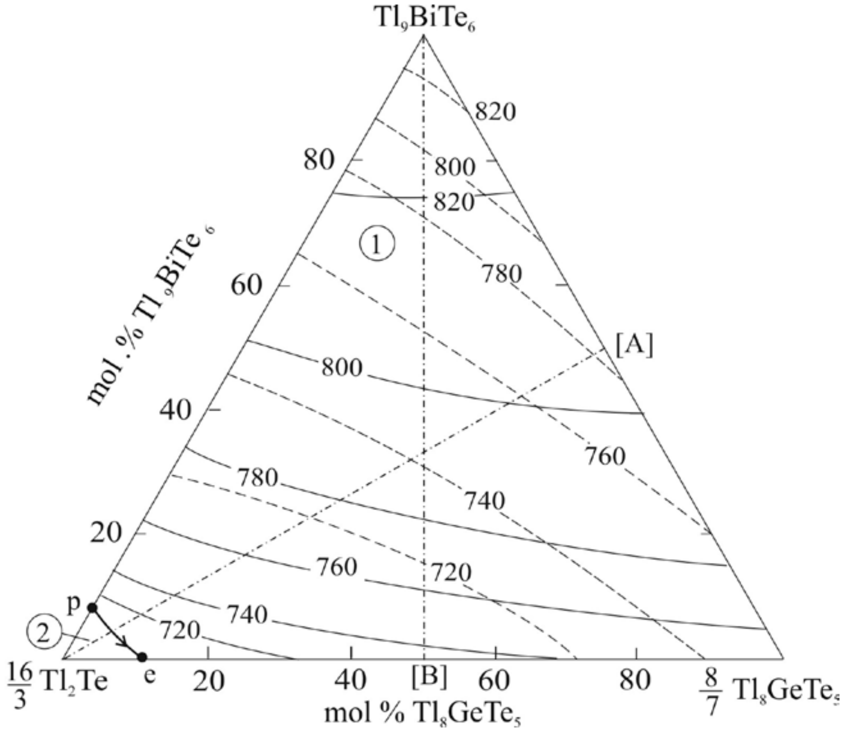
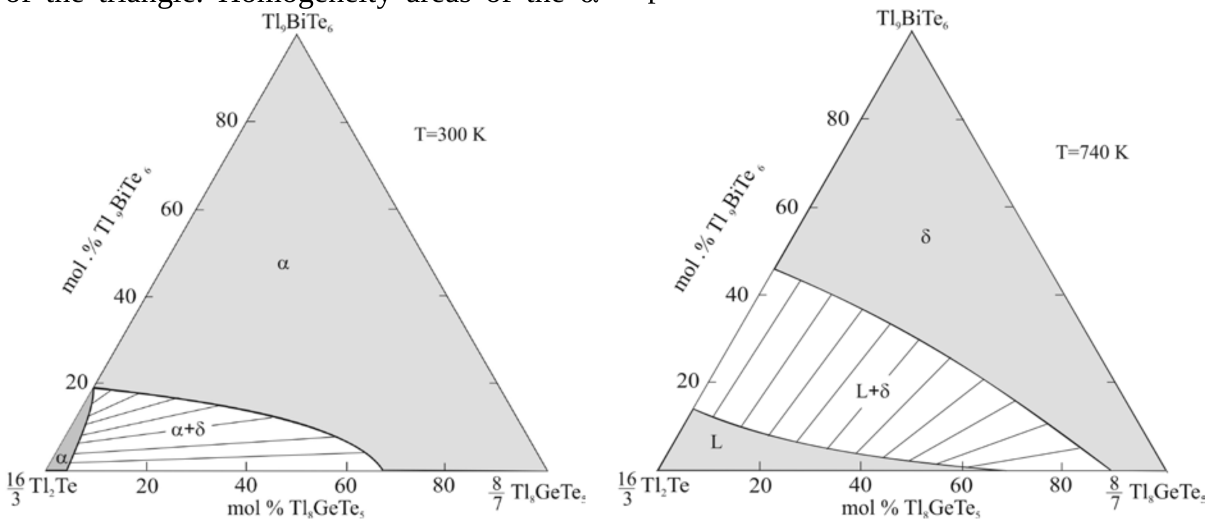


Fig.3. Projection of the liquidus and solidus (dashed lines) surface of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system. Primary crystallization fields of phases: 1-δ; 2-α. Investigated sections are shown by dashed lines. [A] and [B] are equimolar alloys from the respec tive boundary systems.

The isothermal sections of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system at 300, 740 and 800 K (Fig.4) consist of three phase areas. At 300 K, over 80% of the concentration triangle is occupied by δ-solid solutions with Tl_5Te_3 structure. Tl_2Te-based α-phase has a narrow homogeneity area in the corresponding angle of the triangle. Homogeneity areas of the α- and δ-phases are separated by α+δ two-phase region. It should be noted that comparison of the isopleth sections (Fig.1) and isothermal sections at 740 and 800 K(Fig.4) shows that the directions of the tie-lines in the two-phase area L+δ deviate from the *T–x* planes of the above-mentioned sections and vary with temperature.



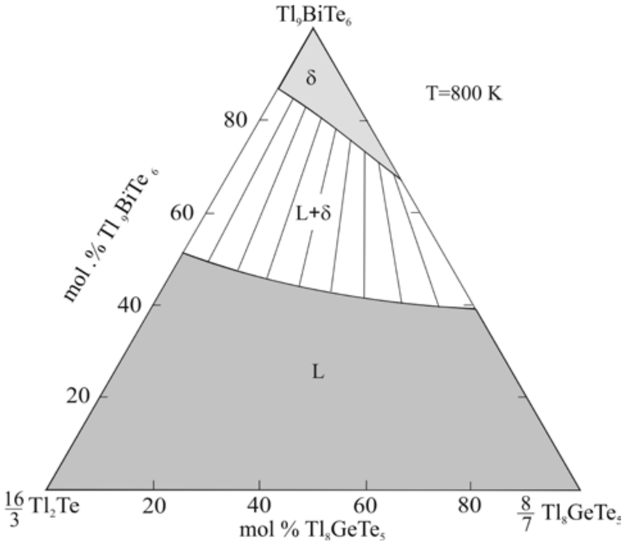


Fig.4. Isothermal section of the phase diagram of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system at 300, 740 and 800 K.

CONCLUSION

A complete T-x-y diagram of the Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 system has been constructed, including some isopleth and isothermal sections at 300, 740 and 800 K as well as projections of liquidus and solidus surfaces. The analyzed system is characterized by the formation of the wide field of δ-solid solutions with the Tl_5Te_3 structure, occupying more than 80% of the concentration triangle. Experimental data obtained can be used for choosing the composition of solution-melt and for determining of temperature conditions for growing crystals of δ- phase with a given composition.

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СИСТЕМА Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5

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Методами ДТА и РФА изучены фазовые равновесия в четверной системе Tl-Ge-Bi-Te в области концентраций Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5. Построены некоторые политермические сечения фазовой диаграммы, изотермические сечения при 300, 740 и 800 К, а также проекции поверхностей ливидуса и солидуса. Установлено образование широкой области твердых растворов со структурой Tl_5Te_3 (δ-фаза), занимающей более 80% площади концентрационного треугольника. На основе Tl_2Te обнаружена узкая область твердых растворов (α-фаза) вдоль боковой системы Tl_2Te-Tl_9BiTe_6.

Ключевые слова: *теллуриды таллия-германия, теллуриды таллия-висмута, фазовые равновесия, твердые растворы, кристаллическая структура.*

Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 SİSTEMİ

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DTA və RFA üsulları ilə Tl-Ge-Bi-Te sisteminin Tl_2Te-Tl_9BiTe_6-Tl_8GeTe_5 tərkib sahəsində faza tarazlıqları öyrənilmişdir. Faza diaqramının bəzi politermik kəsikləri, 300, 740 və 800 K-də izotermik kəsikləri, həmçinin likvidus və solidus səthlərinin proyeksiyaları qurulmuşdur. Sistemdə Tl_5Te_3 tipli tetraqonal quruluşda kristallaşan və qatılıq üçbucağının sahəsinin 80 %-dən artığını əhatə edən δ bərk məhlul sahəsi aşkar edilmişdir. Tl_2Te əsasında α-fazanın homogenlik sahəsinin Tl_2Te-Tl_9BiTe_6 yan sistemi boyunca nazik zolaq şəklində olması göstərilmişdir.

***Açar sözlər**: tallium–germnium telluridləri tallium–bismut telluridləri, faza tarazlıqları, bərk məhlullar, kristal quruluş.*

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