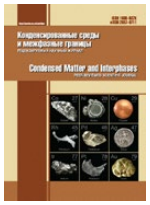

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Phase equilibria in the GeTe-Sb_2Te_3-Te system

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Abstract

Objectives: Germanium-antimony tellurides are of considerable practical interest as thermoelectrics with low thermal conductivity, topological insulators and phase memory materials. In this paper, the results of a study of phase equilibria in the region of GeTe-Sb_2Te_3-Te compositions of the Ge-Sb-Te system using the DTA, X-ray diffraction and SEM methods are we presents.

Experimental: The studied samples were synthesized using a special technique that allows them to be obtained in a state as close to equilibrium as possible.

Conclusions: A diagram of solid-phase equilibria at 300 K, a projection of the liquidus surface and some polythermal sections of the phase diagram are constructed. The fields of primary crystallization of phases are outlined, non- and monovariant equilibria are determined. According to the obtained picture of phase equilibria, the curves of monovariant equilibria originating from the peritectic and eutectic points of the boundary system GeTe-Sb_2Te_3 undergo transformations at certain transition points. In the region of compositions rich in tellurium, a number of invariant transition reactions occur, corresponding to the joint crystallization of two-phase mixtures of telluride phases and elemental tellurium.

Keywords: Layered germanium-antimony tellurides, Phase memory materials, Topological insulator, Phase diagram

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1. Introduction

Ternary compounds of the A^{IV}-B^V-Te systems (A^{IV}-Ge, Sn, Pb; B^V-Sb, Bi) with layered tetradymite-like structures have long been in the focus of researchers as thermoelectric materials with anomalously low thermal conductivity [1-6]. The discovery at the beginning of our century of a new quantum state of matter - a topological insulator [7, 8] gave a new powerful impetus to the study of these compounds and phases based on them. It turned out that compounds of the homologous series $A^{IV}Te{\cdot}mB^V_2Te_3$($A^{IV}B^V_2Te_4$, $A^{IV}B^V_4Te_7$, $A^{IV}B^V_6Te_{10}$, etc.) and solid solutions based on them are 3D topological insulators and are very promising for use in various areas of high technology, including spintronics, quantum computers, scanning devices used in security systems and medicine, etc. [9-17].

Recently, the special attention of researchers has been attracted by compounds and alloys of the GeTe-Sb_2Te_3 system with a reversible phase transition between the crystalline and amorphous states caused by very short (only a few tens of nanoseconds) laser radiation. These alloys, called phase memory materials, are already used as memory materials in rewritable optical disks and have great potential for creating a non-volatile alternative based on them to traditional flash memory [18–24].

At the initial of research stage on the development of new complex inorganic materials, particularly chalcogenide materials, it is essential to have reliable data on phase equilibria in the corresponding systems [25-29]. In the review article [26], based on a critical analysis of the available literature, it was shown that the data on the phase diagrams of most $A^{IV}Te$-$B^V_2Te_3$ type systems are contradictory and need to be clarified. Taking this into account, we have undertaken repeated detailed studies of phase equilibria in some $A^{IV}Te$-$B^V_2Te_3$ type systems using a specially developed technique for synthesizing equilibrium samples, as well as the thermodynamic properties of intermediate phases [30–37].

Numerous works [38–46] are devoted to the study of phase equilibria in the Ge–Sb–Te system, some of which are summarized in [43]. According to the data of [38], in the GeTe-Sb_2Te_3 quasi-binary system, ternary compounds $Ge_2Sb_2Te_5$, $GeSb_2Te_4$, $GeSb_4Te_7$ are formed, melting with decomposition according to peritectic reactions at 903, 888, and 875 K, respectively, as well as wide regions of solid solutions based on both initial compounds. The results of the study of phase equilibria in the GeTe– Sb_2Te_3–Te compositions region are presented in [39], and in [40, 41] in the Ge–GeTe–Sb_2Te_3–Sb compositions region. The results of the thermodynamic study of some ternary compounds of the GeTe– Sb_2Te_3 system by the calorimetric method are presented in [42].

The papers [44, 45], published at the beginning of our century, present the results of repeated studies of solid-phase equilibria in the Ge-Sb-Te system and crystal structures of germanium-antimony tellurides. The authors of [44] presented a compilation phase diagram of the GeTe- Sb_2Te_3 system, constructed based on the data of [38] with the addition of compositions of other known and suspected ternary compounds without specifying the nature and temperatures of their melting (Fig. 1a). Taking into account the compilation nature of this diagram, a new detailed study of this system was undertaken in [46]. It was shown that it is characterized by the presence of six ternary compounds: $Ge_4Sb_2Te_7$, $Ge_3Sb_2Te_6$ $Ge_2Sb_2Te_5$, $GeSb_2Te_4$, $GeSb_4Te_7$, and $GeSb_6Te_{10}$. The first two melt with decomposition by a solid-phase reaction, and the rest - by peritectic reactions at 863, 854, 848, and 843 K, respectively (Fig. 1). In addition, in [46] the refined parameters of the crystal lattices of all the indicated compounds are presented.

New data obtained in [46] for the key section GeTe- Sb_2Te_3 of the ternary system Ge-Sb-Te indicate the need to revise its complete T-x-y diagram and determine the primary crystallization fields of all identified ternary compounds.

Taking into account the above, we have undertaken a re-examination of phase equilibria in the Ge-Sb-Te system. In this paper, a new refined picture of phase equilibria of the indicated system in the GeTe -Sb_2Te_3-Te compositions range is presented, including the liquidus surface projection, the isothermal section at 300 K, and some polythermal sections of the phase diagram.

2. Experimental

2.1. Synthesis

The alloys for the study were prepared in 2 stages. At the first stage, the initial binary tellurides GeTe and Sb_2Te_3 were synthesized

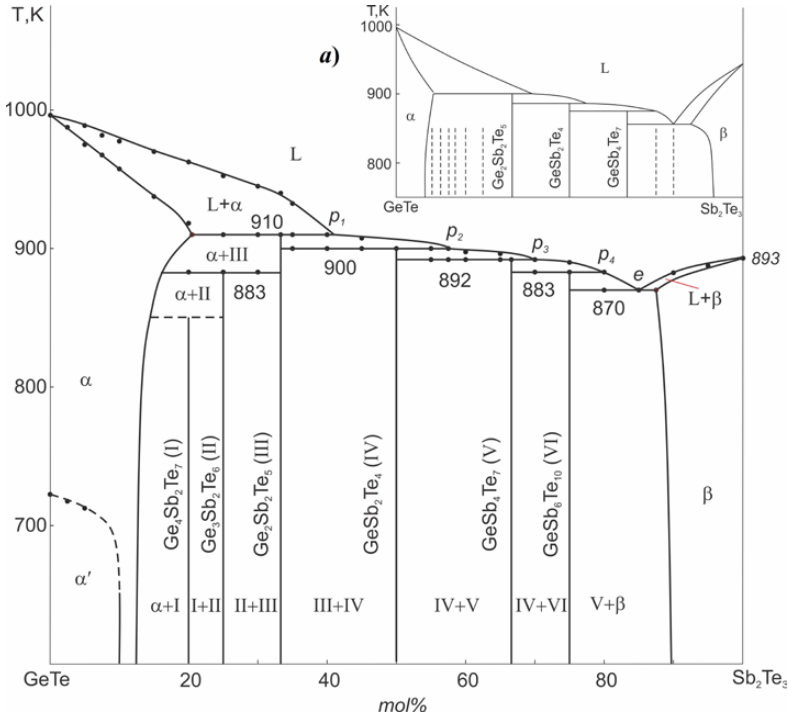

Fig. 1. Phase diagram of the GeTe-Sb_2Te+ system [46]. a) Compilation phase diagram according to [44, 45]

and identified by DTA and X-ray diffraction techniques. The synthesis was carried out by melting high-purity elemental components in quartz ampoules evacuated to a residual pressure of ~10^{-2} Pa. At the second stage, intermediate alloys of the GeTe-Sb_2Te_3-Te system were obtained by fusing the obtained tellurides, as well as elemental tellurium in various stoichiometric ratios, also under vacuum conditions.

At the second stage of synthesis, the results of works [46–48] were taken into account, which showed that even long-term (up to 3000 h) thermal annealing of bulk samples of layered tetradymite-like phases obtained by the traditional method of alloying does not lead to reaching the equilibrium state. According to the authors of the mentioned works, this is due to weak diffusion between the layers in the layered structure of the phases. Taking into account the results of these works, the alloys after alloying were quenched by throwing them into ice water with subsequent homogenizing annealing. Quenching was carried out in the temperature range of 900-1050 K depending on the composition, and homogenizing annealing was carried out at 620 K for 1000 h. Then the alloys were cooled in the switched-off furnace mode.

2.2. Methods

Differential thermal analysis (DTA), X-ray diffraction analysis (XRD), and scanning electron microscopy (SEM) were used for the alloys investigations.

Thermal heating curves were recorded on a differential scanning calorimeter DSC NETZSCH 404 F1 Pegasus system and on a multichannel DTA setup assembled based on an electronic data recorder “TC-08 Thermocouple Data Logger”. Powder diffraction patterns were obtained on a Bruker D8 diffractometer with CuK_α radiation, and SEM images were collected on a Tescan Vega 3 SBH scanning electron microscope.

3. Results and discussion

Analysis of the set of obtained experimental results of annealed samples along different sections of the GeTe-Sb_2Te_3-Te concentration triangle using literature data on the системам GeTe-Te [49, 50], Sb_2Te_3-Te [50] and GeTe-Sb_2Te_3 [46] boundary systems allowed to obtain a mutually consistent picture of phase equilibria in the studied system (Fig. 2-8, Table). In the text, figures and table we have adopted the following designations of phases: α- and α′-solid solutions based on high-temperature (HT) and low-temperature (RT) modifications of GeTe,

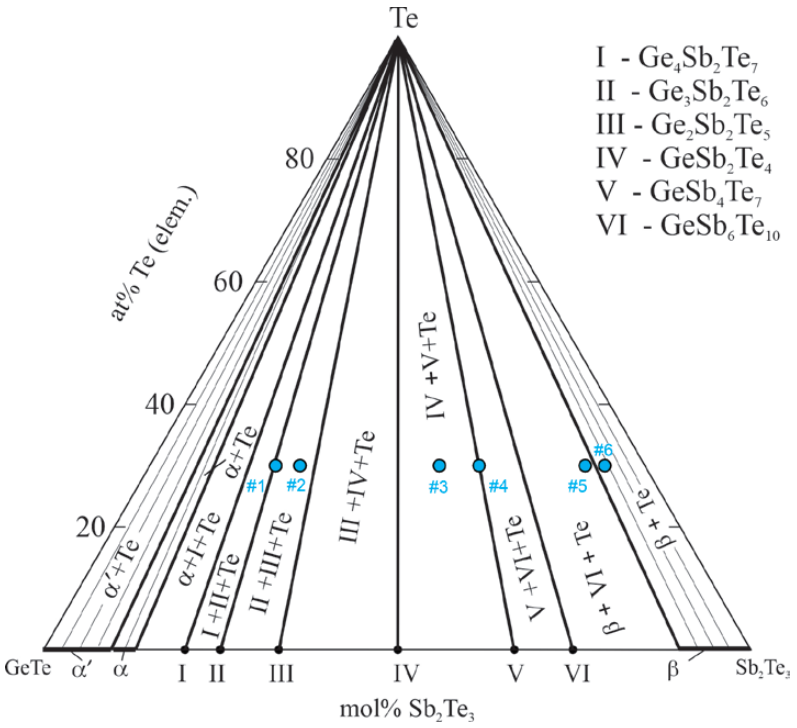

Fig. 2. Solid-phase equilibria diagram of the GeTe-Sb_2Te_3-Te system at 300 K

β-solid solutions based on Sb_2Te_3, I-VI – ternary compounds $Ge_4Sb_2Te_7$, $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $GeSb_2Te_4$, $GeSb_4Te_7$ and $GeSb_6Te_{10}$, respectively (Fig. 2).

3.1. Solid-phase equilibria diagram

Fig. 2 shows an isothermal section of the phase diagram at 300 K. As can be seen, it is characterized by the presence of stable tie-lines between elemental tellurium and all crystalline phases of the GeTe-Sb_2Te_3 side system. The two-phase regions α′+Te and β+Te occupy a significant part of the area of the concentration triangle. Other possible two-phase regions are practically degenerated into tie-lines between ternary compounds and elemental tellurium, which is due to the insignificance of their homogeneity regions.

All phase regions in Fig. 2 are confirmed by X-ray diffraction and SEM methods. As can be seen from Fig. 3, the powder diffraction patterns of alloys, which are on the tie-lines in composition, consist of reflection lines of the corresponding ternary compounds and elemental tellurium, and the diffraction patterns of alloys from the $Ge_3Sb_2Te_6$-$Ge_2Sb_2Te_5$-Te and $GeSb_2Te_4$-$GeSb_4Te_7$-Te three-phase regions contain diffraction reflections of the corresponding three phases.

The SEM patterns were also in accordance with the solid-phase equilibria diagram. As an example, Fig. 4 shows the SEM patterns of two alloys (samples 5 and 6 in Fig. 2), which clearly show the interface between the β+Te and $GeSb_6Te_{10}$+β+Te phase regions.

3.2. Liquidus surface

Fig. 5 shows the projection of the liquidus surface of the GeTe-Sb_2Te_3-Te system. As can be seen, it consists of the fields of primary crystallization of seven phases: α- and β-solid solutions, ternary compounds $Ge_2Sb_2Te_5$, $GeSb_2Te_4$, $GeSb_4Te_7$, $GeSb_6Te_{10}$, and elemental tellurium. All liquidus surfaces of telluride phases have the form of stripes from the GeTe-Sb_2Te_3 side system towards the tellurium angle of the concentration triangle.

The primary crystallization fields of phases are delimited by a series of curves of monovariant equilibria, which originate from various points of nonvariant equilibria of the boundary systems. The indicated curves, intersecting near the tellurium angle of the concentration triangle, form a series of points with nonvariant transition (U_1-U_4) and eutectic (E) equilibria. The types and temperatures of all non- and monovariant equilibria are given in Table.

Table. Non- and monovariant equilibria in the GeTe-Sb_2Te_3-Te system

Points and curves in Fig. 5	Equilibrium	*T*, K
p_1	$L + \alpha \leftrightarrow Ge_2Sb_2Te_5$	910
p_2	$L + Ge_2Sb_2Te_5 \leftrightarrow GeSb_2Te_4$	900
p_3	$L + GeSb_2Te_4 \leftrightarrow GeSb_4Te_7$	892
p_4	$L + GeSb_4Te_7 \leftrightarrow GeSb_6Te_{10}$	883
e_1	$L \leftrightarrow GeSb_6Te_{10} + \beta$	873
e_2	$L \leftrightarrow \alpha' + Te$	653
e_3	$L \leftrightarrow \beta + Te$	695
U_1	$L + \beta \leftrightarrow GeSb_6Te_{10} + Te$	688
U_2	$L + GeSb_6Te_{10} \leftrightarrow GeSb_4Te_7 + Te$	677
U_3	$L + GeSb_4Te_7 \leftrightarrow GeSb_2Te_4 + Te$	665
U_4	$L + GeSb_2Te_4 \leftrightarrow Ge_2Sb_2Te_5 + Te$	651
E	$L \leftrightarrow \alpha' + Ge_2Sb_2Te_5 + Te$	640
p_1K_1	$L + \alpha_1 \leftrightarrow Ge_2Sb_2Te_5$	910–825
p_2K_2	$L + Ge_2Sb_2Te_5 \leftrightarrow GeSb_2Te_4$	900–830
p_3K_3	$L + GeSb_2Te_4 \leftrightarrow GeSb_4Te_7$	892–840
p_4K_4	$L + GeSb_4Te_7 \leftrightarrow GeSb_6Te_{10}$	883–850
e_1K_5	$L \leftrightarrow GeSb_6Te_{10} + \beta$	873–855
K_5U_1	$L + \beta \leftrightarrow GeSb_6Te_{10}$	855–688
K_4U_2	$L + GeSb_6Te_{10} \leftrightarrow GeSb_4Te_7$	850–677
K_3U_3	$L + GeSb_4Te_7 \leftrightarrow GeSb_2Te_4$	840–665
K_2U_4	$L + GeSb_2Te_4 \leftrightarrow Ge_2Sb_2Te_5$	830–651
K_1E	$L \leftrightarrow \alpha_1(\alpha_2) + Ge_2Sb_2Te_5$	835–640
e_3U_1	$L \leftrightarrow \beta + Te$	695–688
U_1U_2	$L \leftrightarrow GeSb_6Te_{10} + Te$	688–677
U_2U_3	$L \leftrightarrow GeSb_4Te_7 + Te$	677–665
U_3U_4	$L \leftrightarrow GeSb_2Te_4 + Te$	665–651
U_4E	$L \leftrightarrow Ge_2Sb_2Te_5 + Te$	651–640
e_2E	$L \leftrightarrow \alpha_2 + Te$	653–640

According to Fig. 5, the curves emanating from the peritectic (P_1-P_4) and eutectic (e_1) points of the GeTe-Sb_2Te_3 boundary system undergo transformations at certain transition points K_1-K_5. These transformations can be explained based on phase diagrams of the boundary components of the studied system. Thus, in the side system GeTe- Sb_2Te_3, the temperatures of the peritectic (P_1-P_4) and eutectic (e_1) equilibria decrease in the direction from germanium telluride to Sb_2Te_3, i.e. from left to right in Fig. 5. At the same time, in the side system GeTe-Te, the temperature of the eutectic e_2 (653 K) is significantly lower than that of the eutectic e_3 (695 K) in the other boundary system Sb_2Te_3-Te, i.e. in this part of the phase diagram, the temperatures of the invariant equilibria decrease in the opposite direction. The

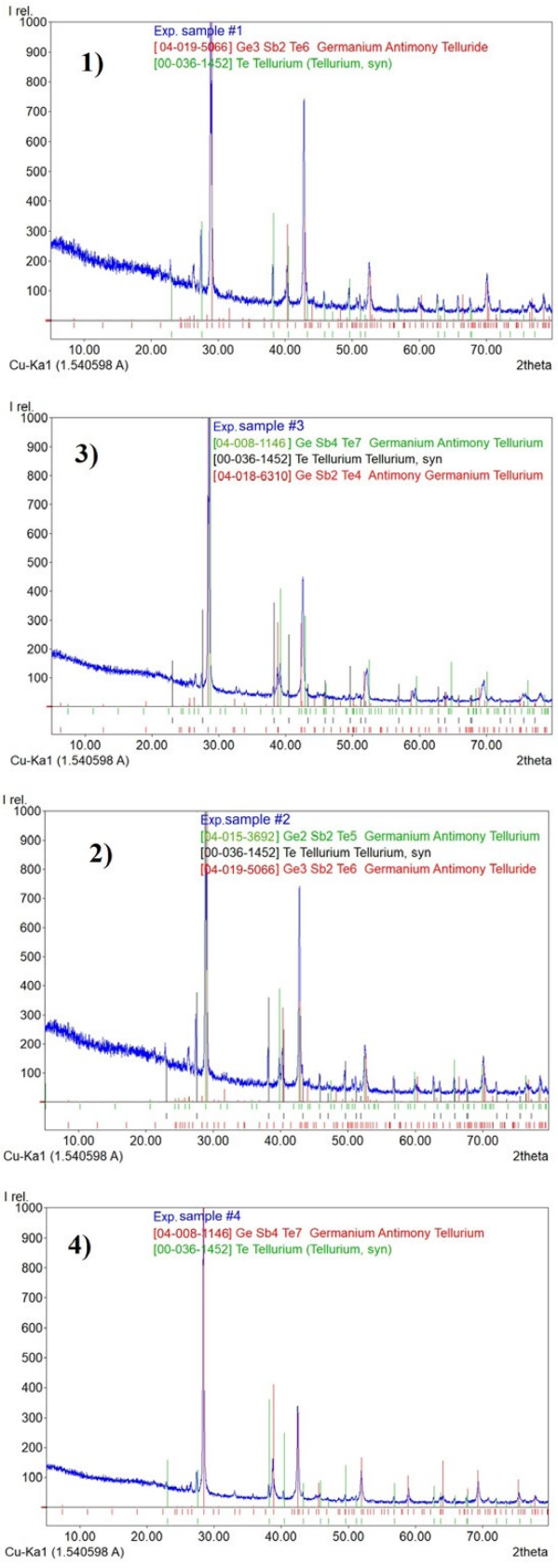

Fig. 3. Powder diffraction patterns of alloys 1-4, shown in Fig. 2

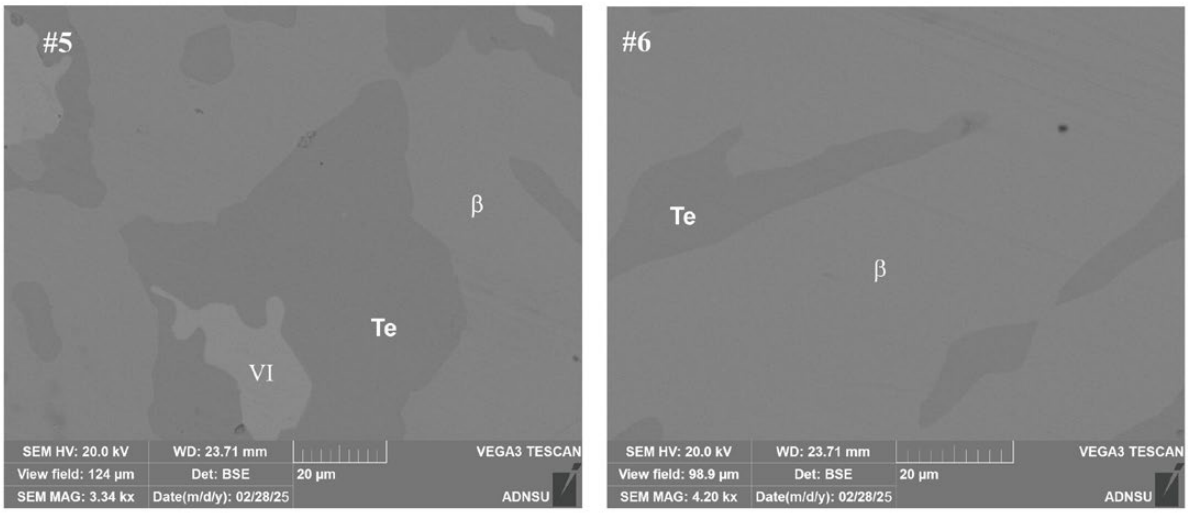

Fig. 4. SEM patterns of alloys 5 and 6, shown in Fig. 2

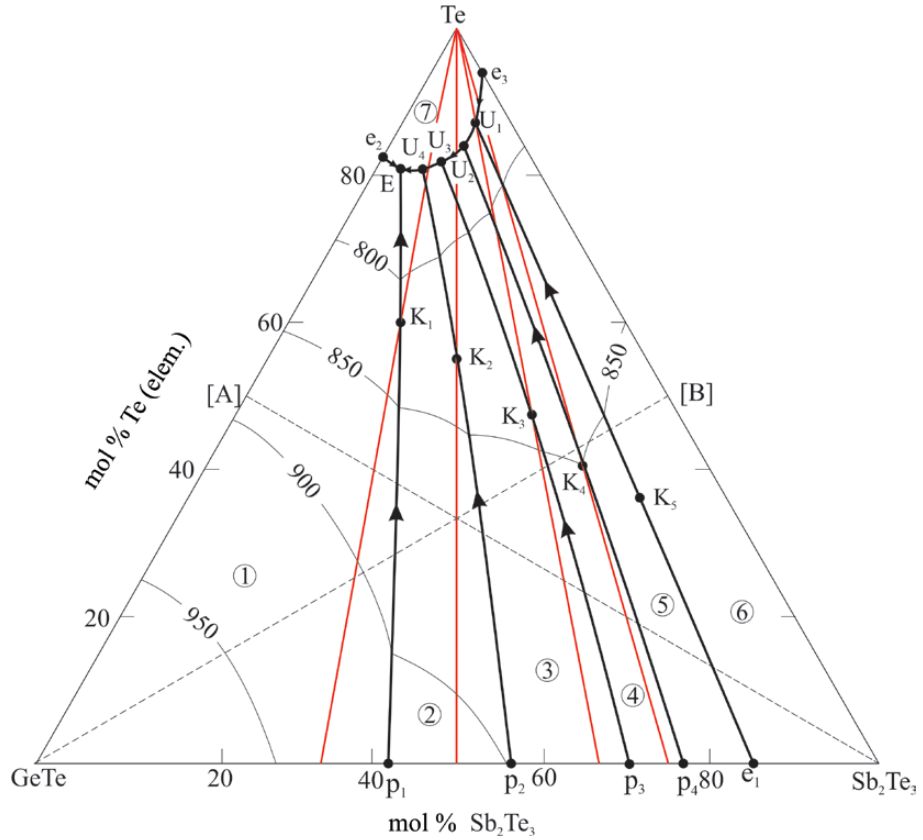

Fig. 5. Projection of the liquidus surface of the GeTe-Sb_2Te_3-Te system. Primary crystallization fields: 1 – α; 2 – $Ge_2Sb_2Te_5$; 3 – $GeSb_2Te_4$; 4 – $GeSb_4Te_7$; 5 – $GeSb_6Te_{10}$; 6 – β; 7 – Te

experimental DTA data obtained by us showed that the temperatures of nonvariant transition equilibria (U_1-U_4) also decrease in the direction from the eutectic e_3 to the ternary eutectic point E (640 K) (Fig. 5, Table). Similar opposite directions of changes in the temperatures of nonvariant equilibria in the boundary system GeTe- Sb_2Te_3 and in the regions of compositions rich in tellurium lead to the transformation of the above-mentioned monovariant equilibria [51, 52]. In the case of peritectic equilibrium curves, similar transformations occur at the intersection points (K_1-K_4) of the pointed curves with the corresponding stable sections of the "ternary compound-elementary tellurium" type (Fig. 5). Therefore, in the Table, the pointed curves are

presented as two series, transforming into each other at the transition points K_1-K_5 (Fig. 5).

Using the curve P_1E as an example, we will consider one of the above transformations. This curve, before intersecting with the stable section $Ge_2Sb_2Te_5$-Te (P_1K_1), reflects the peritectic equilibrium L + α ↔ III. At the intersection point (K_1), this equilibrium is transformed into the eutectic L ↔ α + III (curve K_1E). Similar transformations take place on the P_2U_4, P_3U_3, P_4U_2 and e_1U_1 curves.

3.3. Polythermal sections of the phase diagram

Below some polythermal sections of the *T*-*x*-*y* phase diagram of the GeTe-Sb_2Te_3-Te system (Fig. 6–8) are presented, which reflect the crystallization processes in more detail and made it possible to clarify the location of the curves of monovariant equilibria and the coordinates of the invariant points.

Four ($Ge_2Sb_2Te_5$-Te, $GeSb_2Te_4$-Te, $GeSb_4Te_7$-Te and $GeSb_6Te_{10}$-Te) of the six polythermal sections considered are stable in the subsolidus. Two other

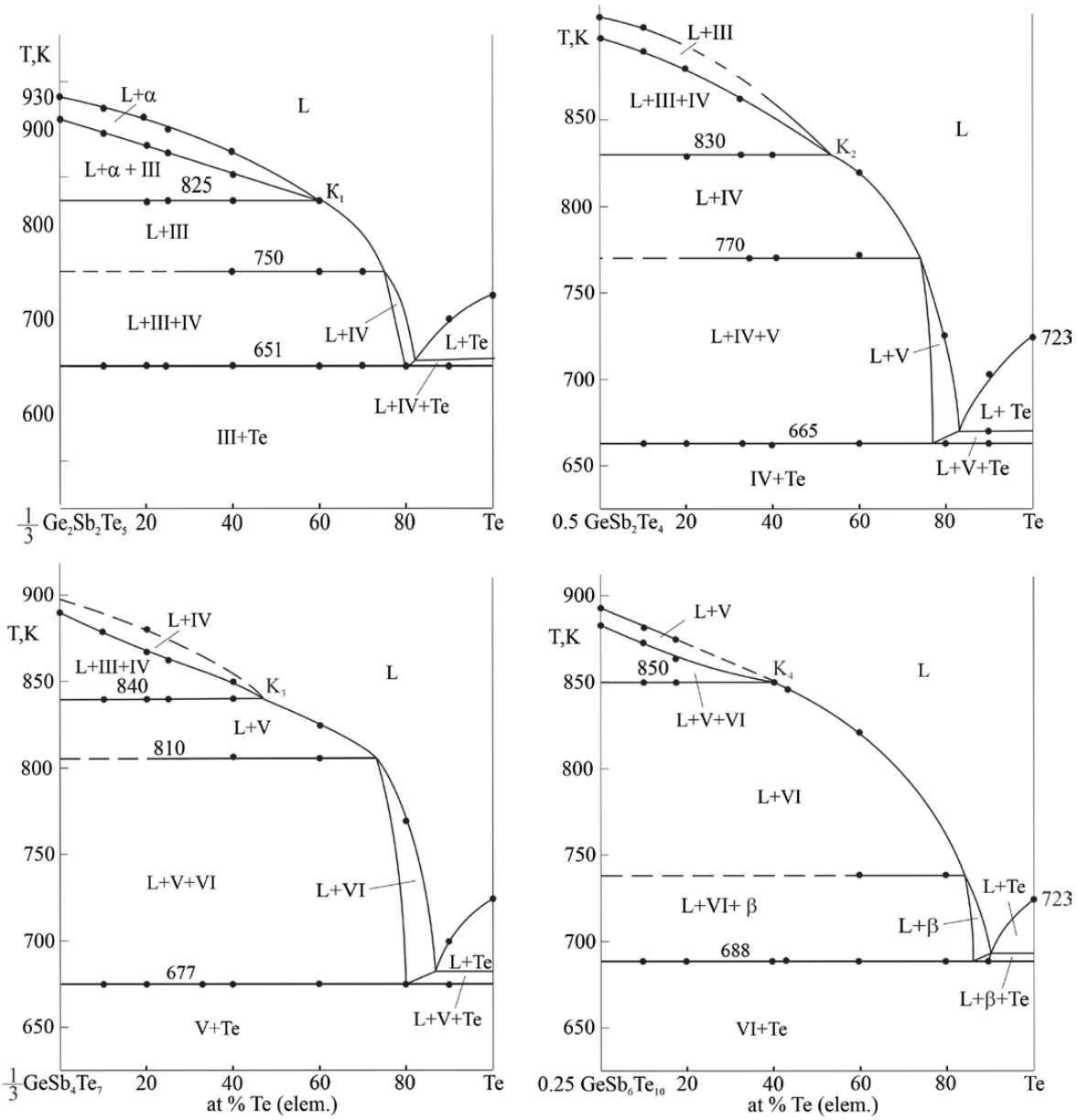

Fig. 6. Polythermal sections of $Ge_2Sb_2Te_5$-Te, $GeSb_2Te_4$-Te, $GeSb_4Te_7$-Te и $GeSb_6Te_{10}$-Te of the phase diagram of the GeTe-Sb_2Te_3-Te system

sections GeTe-[B] and [A]-Sb_2Te_3 ([A] and [B] are alloys with equimolar ratios of components of the boundary systems GeTe-Te and Sb_2Te_3-Te, respectively) intersect almost all fields of primary crystallization of phases and reflect most heterogeneous equilibria.

$Ge_2Sb_2Te_5$-Te section (Fig. 6) passes through the fields of primary crystallization of the α-phase, $Ge_2Sb_2Te_5$ and $GeSb_2Te_4$ compounds as well as elemental tellurium. Below the α-phase liquidus, crystallization proceeds according to the L + α ↔ $Ge_2Sb_2Te_5$ peritectic reaction (Fig. 5, curve P_1K_1), resulting in the formation of a three-phase field L + α + $Ge_2Sb_2Te_5$. In this reaction, the α-phase is completely consumed and at 825 K the system passes into a two-phase state L + $Ge_2Sb_2Te_5$. Starting from 750 K, crystallization continues according to the peritectic reaction L + $GeSb_2Te_4$ ↔ $Ge_2Sb_2Te_5$ (Fig. 5, curve K_2U_4), as a result of which a three-phase region L+$Ge_2Sb_2Te_5$+$GeSb_2Te_4$ is formed.

Near the tellurium angle, tellurium crystallizes primarily from the melt, then the monovariant eutectic process L ↔ $GeSb_2Te_4$+Te begins (Fig. 5, curve U_3U_4). Complete crystallization of the alloys of this section occurs at 651 K according to the invariant transition reaction U_4 and a two-phase mixture $GeSb_2Te_4$+Te is formed. The crystallization processes along the other three sections connecting the compositions of ternary compounds with elemental tellurium (Fig. 6) can be followed by comparing them with Figs. 2 and 5. As can be seen from the T-diagrams, despite the stability of these sections below the solidus, the crystallization processes in them are complex and multi-stage.

The GeTe-[B] section (Fig. 7) passes through the fields of primary crystallization of all phases except elemental tellurium (Fig. 5). In the subsolidus it crosses all phase regions of the system (Fig. 2). In this diagram, the liquidus curves of different phases are marked taking into account Fig. 5. Pairs of conjugate curves emanating from the intersection points of the liquidus lines reflect the beginning and the

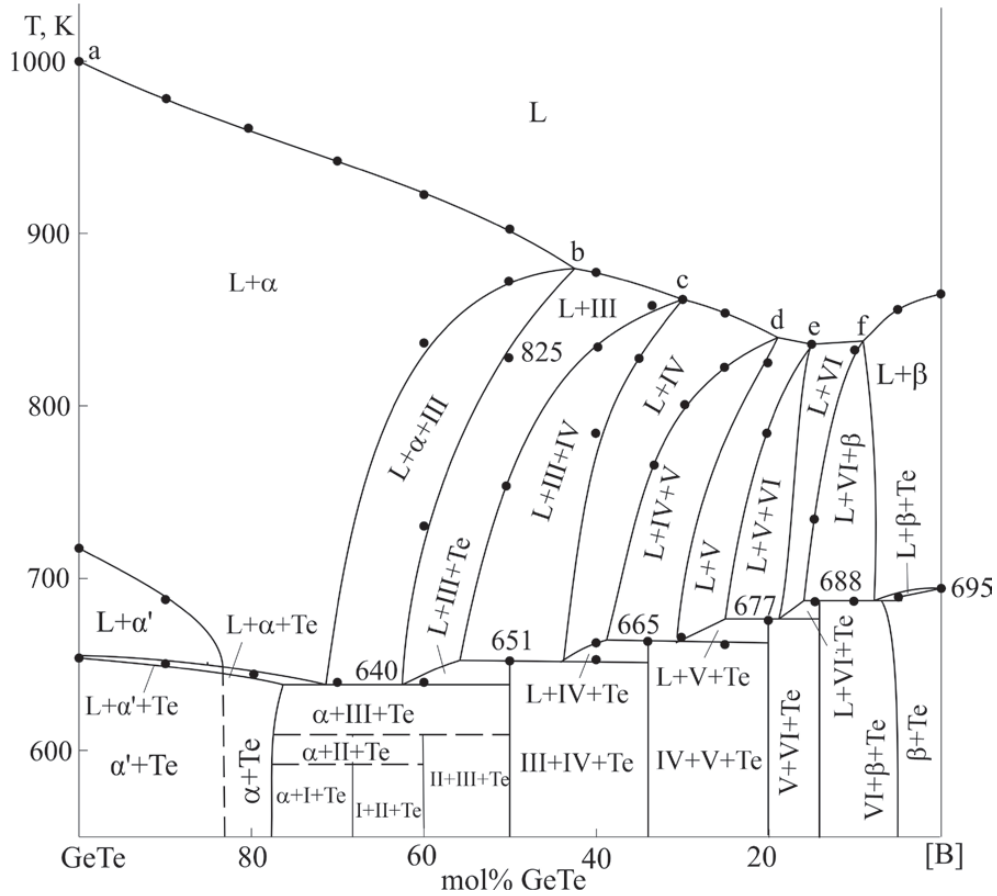

Fig. 7. Polythermal section of GeTe-[B] of the phase diagram of the GeTe-Sb_2Te_3-Te system

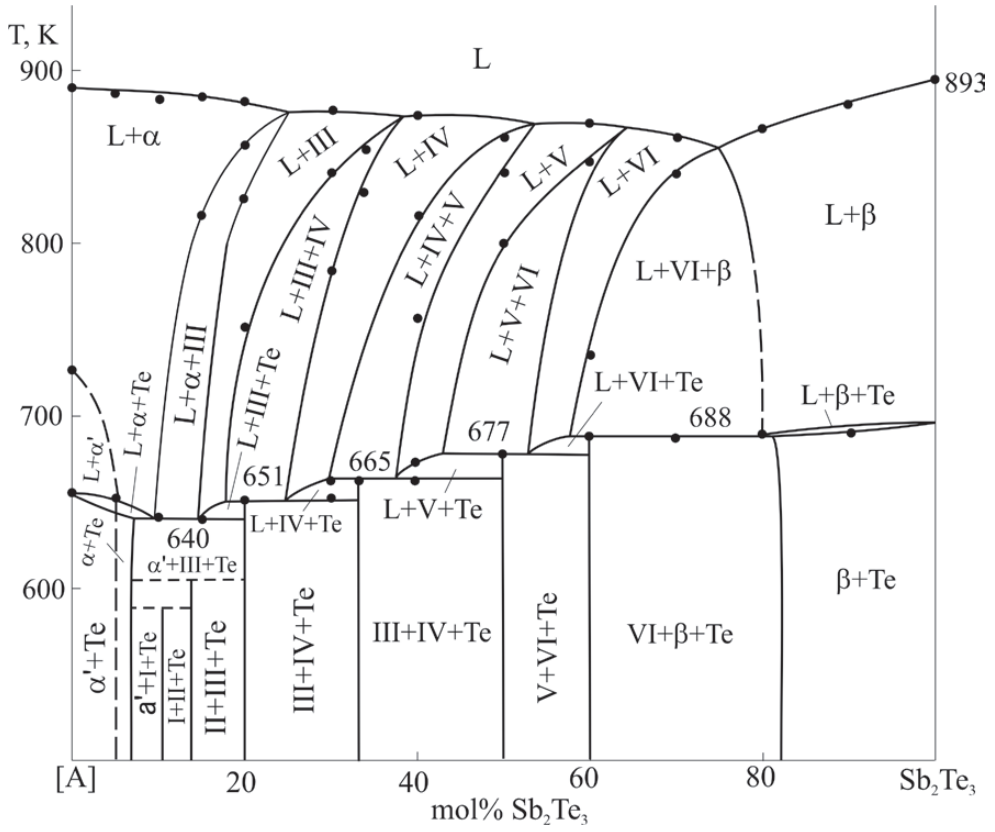

Fig. 8. Polythermal section of [A]-Sb_2Te_3 of the phase diagram of the GeTe-Sb_2Te_3-Te system

end of monovariant equilibria along the curves P_1K_1E (*b*), $P_2K_2U_4$ (*c*), $P_3K_3U_3$ (*d*), $P_4K_4U_2$ (*e*), $P_1K_5U_1$ (*f*). The fields between the indicated pairs of curves correspond to the two-phase areas L+III (IV, V, VI) and L + β. These pairs of curves in the temperature range of 640-688 K reach the curves of monovariant equilibria originating from the eutectic points e_2 and e_3 of the side systems and form a series of transition points (U_1, U_2, U_3, U_4) and eutectic (E) equilibria (Fig. 5). The horizontals at 688, 677, 665, 651 and 640 K in Fig. 7 reflect these nonvariant equilibria.

Section [A]-Sb_2Te_3 (Fig. 8). Phase equilibria along this section are qualitatively similar to those in Fig. 7 and differ from them only in temperature-concentration intervals.

4. Conclusion

Based on the experimental data obtained by studying carefully homogenized equilibrium alloys using the DTA, XRD and SEM methods, a new refined picture of phase equilibria in the GeTe-Sb_2Te_3-Te system was obtained, which significantly differs from the previously known one. A solid-phase equilibria diagram at 300 K and a projection of the liquidus surface, as well as a number of polythermal sections of the phase diagram, were constructed. The fields of primary crystallization of seven phases, including ternary compounds $Ge_2Sb_2Te_5$, $GeSb_2Te_4$, $GeSb_4Te_7$ and $GeSb_6Te_{10}$ were determined, non- and monovariant equilibria were established. It was shown that monovariant equilibria on the curves of monovariant equilibria undergo transformations at certain transition points. The interaction of the indicated curves with the eutectic curves emanating from the lateral systems GeTe-Te and Sb_2Te_3-Te leads to a cascade of invariant transition reactions characterizing the joint crystallization of two-phase mixtures III(IV, V, VI)+Te.

The results obtained in the work can be used to obtain poly- and single crystals of the above-mentioned ternary compounds, which are promising as topological insulators, thermoelectrics and materials with phase memory.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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