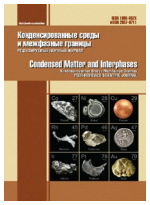

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A refined phase diagram of the GeTe-Bi_2Te_3 system

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Abstract

Updated phase diagram of the GeTe–Bi_2Te_3 system was constructed using differential thermal, X-ray diffraction analysis and scanning electron microscopy (SEM) results of alloys synthesized with specially developed technology. The refined version significantly differs from those reported so far. The presented phase diagram reflects six ternary compounds: $Ge_4Bi_2Te_7$, $Ge_3Bi_2Te_6$, $Ge_2Bi_2Te_5$, $GeBi_2Te_4$, $GeBi_4Te_7$, and $GeBi_6Te_{10}$.

The study determined that the first two compounds are formed as a result of solid-state reactions at temperatures of 750–800 K, and the latter four are formed as a result of peritectic reactions at 863, 854, 848, and 843 K, respectively. Wide homogeneity regions based on the initial binary compounds were also found. These regions reach 10 mol% at room temperature. The coordinates of eutectic point are 83 mol% Bi_2Te_3 and 838 K. It crystallises at 838 K. It was found that all the identified ternary compounds crystallise in a tetradymite-like layered structure. $Ge_4Bi_2Te_7$, $Ge_3Bi_2Te_6$, $Ge_2Bi_2Te_5$, and $GeBi_2Te_4$ compounds belong to the nGeTe·Bi_2Te_3 homologous series. Their crystal lattices are formed by the insertion of GeTe bilayers into the quintuple Bi_2Te_3 layers. $GeBi_4Te_7$ and $GeBi_6Te_{10}$ compounds are representatives of the GeTe·$m$$Bi_2Te_3$ homologous series and have a mixed-layer structure. The parameters of the crystal lattices of the compounds were determined by the Rietveld method based on their powder diffraction data.

Keywords: Germanium-bismuth tellurides, Phase diagram, Layered tetradymite-like structures, Solid solutions

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1. Introduction

In recent years, there has been a growth of interest in layered chalcogenides which serve as functional materials for various purposes [1-3]. Such valuable materials include ternary compounds of the $A^{IV}Te$-$B^V_2Te_3$ (A^{IV}-Ge, Sn, Pb; B^V-Sb, Bi) systems with a layered tetradymite-like structure. These compounds have long been the focus of research since they are thermoelectric materials with low thermal conductivity [2–8]. After the discovery of a new state of quantum matter - a topological insulator (TI) [9, 10], it was determined that compounds of the types $A^{IV}B^V_2Te_4$, $A^{IV}B^V_4Te_7$, $A^{IV}B^V_6Te_{10}$, etc. are three-dimensional TIs, which can have a variety of applications, including in spintronics, quantum computing, medicine, security systems, etc. [11-19]. In addition, it should be noted that Ge-B^V-Te alloys are widely used in optical storage devices and are currently considered to be the main class of materials with a reversible phase transition between amorphous and crystalline states [20–23].

The development of new methods for the directed synthesis of complex inorganic phases, in particular chalcogenide phases, is based on the data on the phase equilibrium and thermodynamic properties of the corresponding systems [15, 24]. The analysis of the existing literature regarding the phase equilibrium of $A^{IV}Te$-$B^V_2Te_3$ systems conducted in [15] showed that, despite the increased interest in the above mentioned ternary compounds, the phase diagrams of these systems are far from being perfect and need to be studied more thoroughly.

A specific feature of GeTe-$B^V_2Te_3$ systems, which makes them particularly interesting, is the fact that, besides the compounds of the GeTe·$mB^V_2Te_3$ homologous series, typical for all $A^{IV}Te$-$B^V_2Te_3$ systems, they also form compounds of the nGeTe·$B^V_2Te_3$ series [15, 25–29]. The information regarding the crystal structure and various physical properties of many of these ternary compounds is given in [15, 18, 25–31].

According to the available literature data, the quasi-binary system GeTe-Bi_2Te_3 has been investigated by a number of studies [25–27, 32]. The first phase diagram of the GeTe-Bi_2Te_3 system was constructed in 1965 [32]. According to [32], the system is characterized by the presence of compounds $Ge_3Bi_2Te_6$, $GeBi_2Te_4$, and $GeBi_4Te_7$ formed as a result of peritectic reactions, as well as by wide regions of solid solutions based on both of the initial binary compounds. [25–27] describe additional detailed XRD studies of the quasi-binary system GeTe-Bi_2Te_3 and present its compiled phase diagram taking into account the data from [32]. Besides the above listed ternary compounds, the phase diagram shows the presence of compositions of some other ternary compounds without specifying the nature and temperature of their formation.

Considering the above, we undertook a new study of the phase equilibrium in the GeTe–Bi_2Te_3 system using a specially developed technique for the synthesis of the samples. The resulting new version of the T-x diagram in the composition range of 0–50 mol% Bi_2Te_3 was presented in [33].

We have now completed our study of the phase equilibria in the GeTe-Bi_2Te_3 system and constructed its complete T-x diagram. The results are presented in this article.

2. Experimental

2.1. Materials and synthesis

The alloys of the studied system were synthesised in two stages. First, binary compounds GeTe and Bi_2Te_3 were synthesised by melting high purity elemental germanium (CAS 7440-56-4), bismuth (CAS 7440-69-9), and tellurium (CAS 13494-80-9) in evacuated (~10^{-2} Pa) quartz ampoules at temperatures of ~50 °C higher than their melting points. The binary compounds were identified using the differential thermal analysis (DTA) and the X-ray diffraction analysis (XRD) methods. Then, we obtained the alloys of the GeTe-Bi_2Te_3 system by fusing the initially synthesized and identified binary compounds in evacuated quartz ampoules with various ratios. The synthesized alloys was examined by means of the DTA and XRD techniques.

When designing the second stage of the synthesis, we took into account the previously published data [26, 34, 35], according to which bulk samples of layered tetradymite-like phases, obtained by the well-known fusion method, do not reach the equilibrium state even after being subjected to thermal annealing for a long time (2000-3000 h). Apparently, this is accounted for by the fact that, in contrast to standard bulk

phases, van der Waals phases obtained under nonequilibrium crystallisation conditions (i.e. standard cooling of the melt), practically do not change during further thermal annealing due to very low diffusion level between layers.

Taking this into account, in order to ensure a high degree of dispersion of the alloys containing layered phases, in [36–39] the fused samples were quenched from the liquid state by dropping ampoules into cold water followed by stepwise annealing.

In this study, we applied the same technique. After the fusion, the samples were quenched from a liquid state (950 K) in iced water and then subjected to thermal annealing at 800 K for 1000 h.

2.2. Research methods

In our study, we used DTA, XRD, and SEM methods.

The DTA was performed using a DSC NETZSCH 404 F1 Pegasus differential scanning calorimeter and a multi-channel DTA device based on an electronic TC-08 Thermocouple Data Logger. Powder diffraction patterns of the initial compounds and intermediate alloys were recorded on a Bruker D8 diffractometerwith CuK_α-radiation within an angle range of 2θ = 10÷80°. The diffraction patterns were indexed and the lattice parameters were calculated using Topas 4.2 software by the *Le Bail method*. The EDX (energy dispersive X-ray spectroscopy) analysis was performed on a HITACHI SU8030 scanning electron microscope with a Bruker-EDX detector system.

3. Results and discussion

XRD study of annealed alloys with compositions oF > 50 mol. % Bi_2Te_3 showed that samples correspond to $GeBi_4Te_7$ and $GeBi_6Te_{10}$ stoichiometric compositions, as well as with sample with 90 mol.% Bi_2Te_3 composition were single phased. Powder diffraction patterns of the mentioned alloys are given in Fig. 1a-c. An analysis of the powder diffraction patterns showed that they were completely indexed in

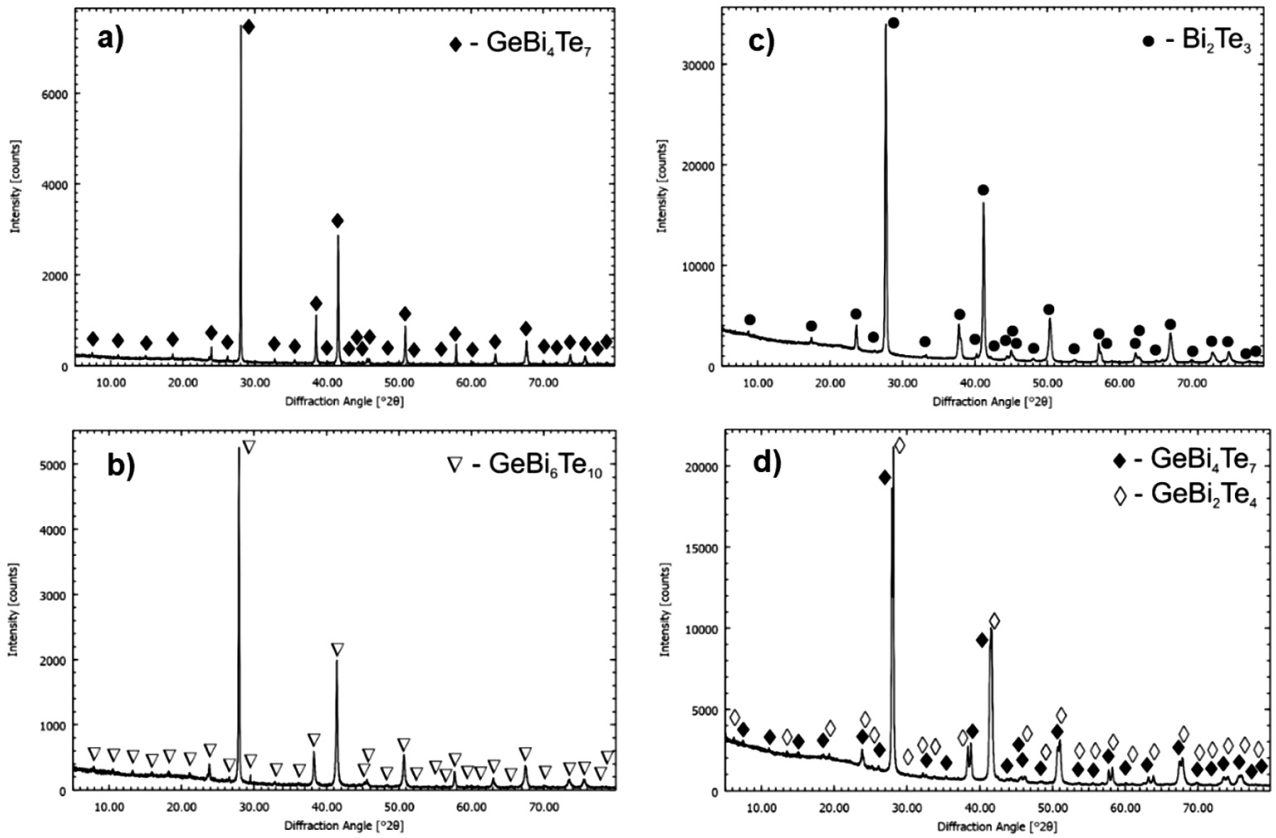

Fig. 1. X-ray powder diffraction patterns of $GeBi_4Te_7$ (a), $GeBi_6Te_{10}$ (b), 90 mol% Bi_2Te_3 (c), and 57.5 mol% Bi_2Te_3 (d)

a tetradymite-like hexagonal structure. The lattice parameters calculated by the Rietveld method are given in Table 1. The table also gives the crystallographic parameters of the synthesised GeTe and Bi_2Te_3, as well as of other ternary compounds of the GeTe-Bi_2Te_3 system according to the data obtained in our earlier study [33].

The XRD data also confirmed the phase compositions of the alloys from two-phase regions $GeBi_2Te_4$–$GeBi_4Te_7$, $GeBi_4Te_7$–$GeBi_6Te_{10}$, and $GeBi_6Te_{10}$–β. As an example, Fig. 1d shows the diffraction pattern of an alloy with a 57.5 mol% Bi_2Te_3 composition. As we can see, the sample consists of a two-phase mixture $GeBi_2Te_4$+$GeBi_4Te_7$.

The results of SEM correlated with the XRD data. Fig. 2 demonstrates the SEM images of compounds $GeBi_2Te_4$, $GeBi_4Te_7$, and $GeBi_6Te_{10}$. These results confirm that all the samples are single-phase and have a layered structure. Fig. 3 and Table 2 show the results of the elemental microanalysis of one of these compounds, namely $GeBi_6Te_{10}$, which appeared in the phase diagram of the GeTe-Bi_2Te_3 system for the first time. As can be seen from Table 2, the elemental composition

Table 1. Crystallographic parameters of the phases in the GeTe–Bi_2Te_3 system

Composition	Crystal system, space group, and lattice parameters, Å
GeTe	Trigonal, *R*3*m*, *a* = 4.1628(3), *c* = 10.6675(8)
$Ge_4Bi_2Te_7$	Trigonal, *R*3*m*, *a* = 4.2638(2), *c* = 73.271(3)
$Ge_3Bi_2Te_6$	Trigonal, *R*3*m*, *a* = 4.2730(3), *c* = 62.634(4)
$Ge_2Bi_2Te_5$	Trigonal, *P*-3*m*1, *a* = 4.2986(2), *c* = 17.335(3)
$GeBi_2Te_4$	Trigonal, *R*-3*m*, *a* = 4.3176(3), *c* = 41.259(5)
$GeBi_4Te_7$	Trigonal, *P*-3*m*1, *a* = 4.3556(2), *c* = 23.928(4)
$GeBi_6Te_{10}$	Trigonal, *R*-3*m*, *a* = 4.3572(3), *c* = 101.911(2)
90 mol. % Bi_2Te_3	Trigonal, *R*-3*m*, *a* = 4.3693(2), *c*= 30.2132(2)

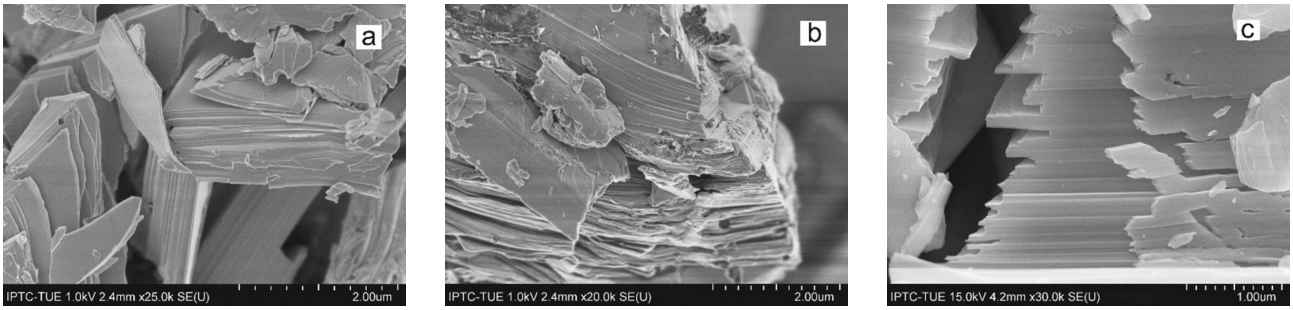

Fig. 2. SEM images of compounds $GeBi_2Te_4$(a), $GeBi_4Te_7$, (b) and $GeBi_6Te_{10}$ (c)

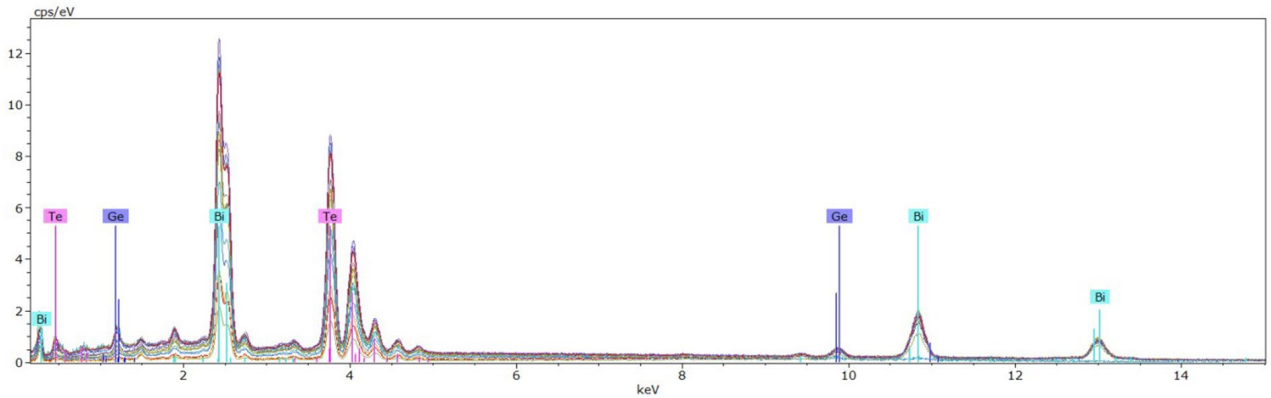

Fig. 3. EDX spectrum of a single crystal $GeBi_6Te_{10}$

corresponds to the stoichiometry of the said compound.

Based on the DTA data and the results of XRD and SEM, we constructed a T-*x* diagram of the system GeTe-Bi_2Te_3 (Fig. 4). A part of the phase diagram in the region of 0–50 mol% Bi_2Te_3 composition was adopted from [33]. The diagram presented in Fig. 4 shows the presence of six new ternary compounds, four of which are formed as a result of the following peritectic reactions:

$L+\alpha_1 \leftrightarrow Ge_2Bi_2Te_5$ (p_1, 863 K) (1)

$L+ Ge_2Bi_2Te_5 \leftrightarrow GeBi_2Te_4$ (p_2, 854 K) (2)

$L+ GeBi_2Te_4 \leftrightarrow GeBi_4Te_7$ (p_3, 848 K) (3)

$L+ GeBi_4Te_7 \leftrightarrow GeBi_6Te_{10}$ (p_4, 843 K) (4)

At the peritectic points, the compositions are the following: 52 (p_1), 60 (p_2), 73 (p_3), and 77 mol% Bi_2Te_3 (p_4) respectively.

The system has eutectic equilibrium (E) with the coordinates of the eutectic point being 83 mol% Bi_2Te_3 and 838 K.

The data on the GeTe - $GeBi_2Te_4$ subsystem is presented and discussed in detail in [33]. A characteristic feature of the phase equilibria in this system is the incongruent nature of melting

Table 2. Elemental composition of $GeBi_6Te_{10}$ according to EDX

Element	Series [wt %]	Non standard C [wt %]	Standard C [wt %]	Atom C [at %]	Error (3 sigma) [wt %]
Germanium	K-series	2.51	2.69	5.65	0.28
Bismuth	L-series	43.84	47.07	34.33	3.33
Tellurium	L-series	46.79	50.24	60.02	4.10
	Total	93.14	100.00	100.00	

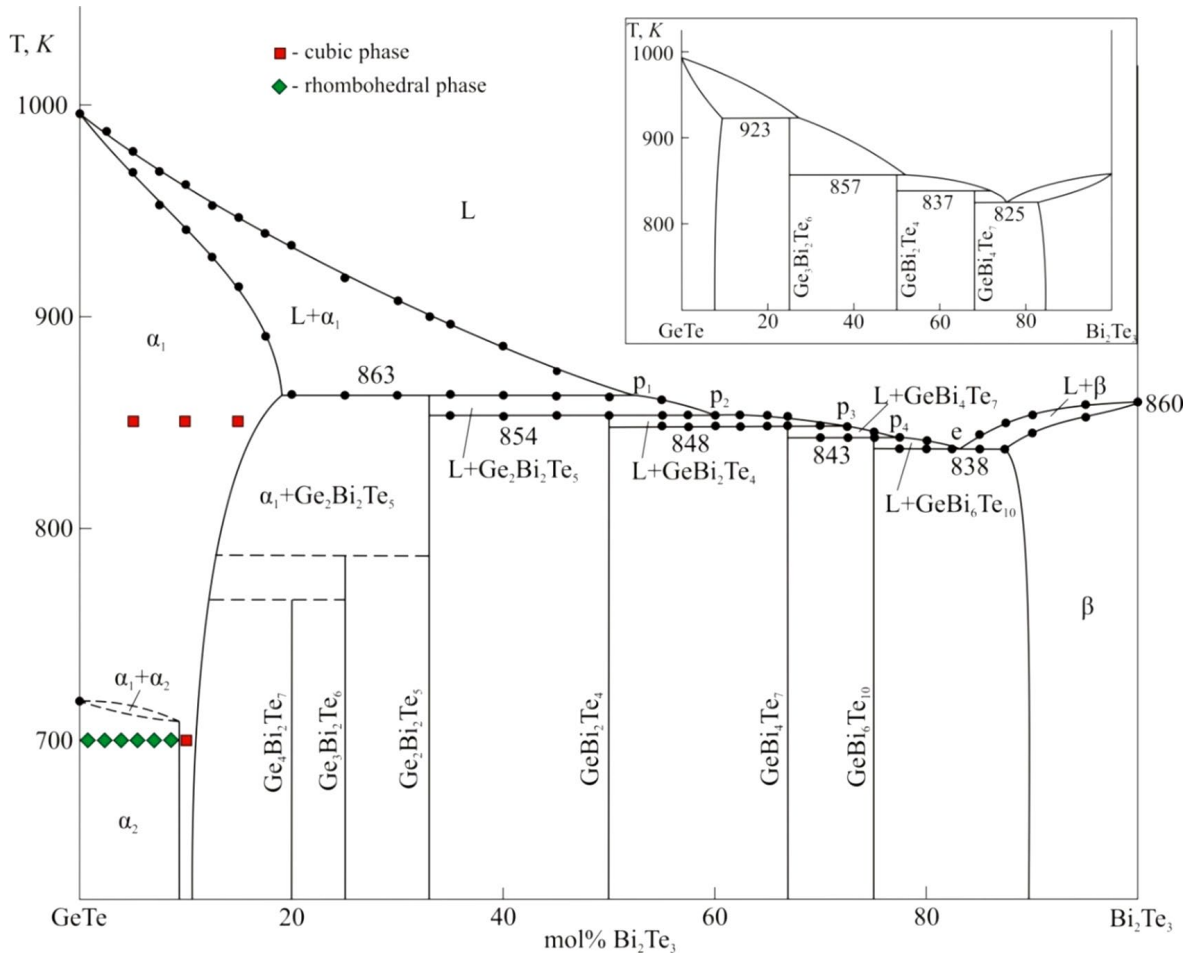

Fig. 4. Phase diagram of the GeTe-Bi_2Te_3 system. A *T*–*x* diagram based on the data from [32] is given in the right-hand upper corner.

of the compounds and small difference (5–8°) in the temperatures of peritectic reactions. We registered thermal effects with similar temperatures on the DTA curves of the samples weighing 0.05–0.1 g. For heavier samples these peaks overlap forming one large peak. Fig. 5 demonstrates the DTA heating curves for the samples with a 55 mol% Bi_2Te_3 composition weighing 0.5 and 0.1 g. It is obvious that the sample weighing 0.5 g has 1 endothermic peak covering the temperature range of 848–860 K, while the thermogram of the sample weighing 0.1 g clearly shows three endothermic effects at 848, 854, and 860 K. According to Fig. 4, the first two endothermic effects correspond to peritectic reactions (2) and (1), and the third effect corresponds to the end of melting.

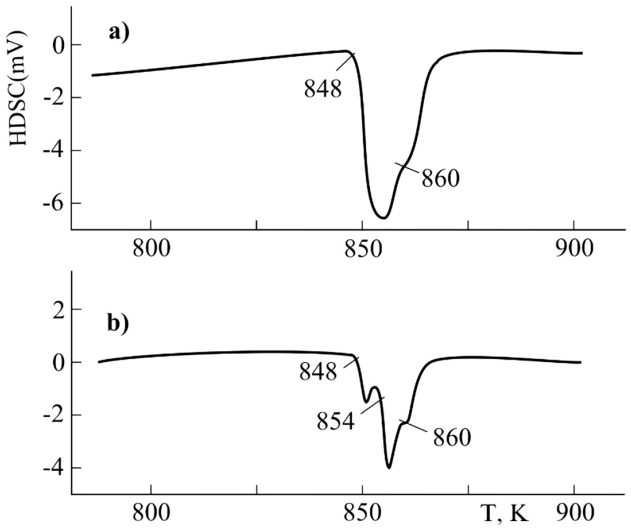

Fig. 5. DTA heating curves of the samples of 55 mol% Bi_2Te_3 weighing 0.5 (a) and 0.1 g (b)

An updated version of the GeTe-Bi_2Te_3 phase diagram differs significantly from that presented in [25, 32] in the number of ternary compounds and the nature and temperature of their formation (Fig. 4). We assume that this may be due to the nonequilibrium of the samples obtained in [25, 32], since the homogenization is hindered due to their layered structure.

3. Conclusions

Based on the results of DTA, XRD, and SEM analyses of carefully homogenized alloys synthesized by means of a specially developed technique, a new version of the phase diagram of the GeTe-Bi_2Te_3 system was constructed. It shows the presence of six ternary compounds, $Ge_4Bi_2Te_7$, $Ge_3Bi_2Te_6$, $Ge_2Bi_2Te_5$, $GeBi_2Te_4$, $GeBi_4Te_7$, and $GeBi_6Te_{10}$, in the system formed as a result of solid-phase (the first two compounds) and peritectic reactions. The study also revealed wide homogeneity regions based on Bi_2Te_3 and both modifications of GeTe. The constructed phase diagram differs significantly from the ones presented in earlier studies.

It was found that all the identified ternary compounds crystallise in a tetradymite-like layered structure. The first three compounds belong to the nGeTe·$B^V_2Te_3$ homologous series, and the rest of them belong to the GeTe·$m B^V_2Te_3$ series. The parameters of the crystal lattices of the identified ternary compounds were calculated using the Rietveld method based on their powder diffraction patterns. We do not exclude the possibility of existence of other representatives of both homologous series, although we did not observe any in the synthesised samples.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

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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