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Article

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Synthesis and study of a new mixed-layered compound $GeBi_3Te_4$ belonging to the $n$$Bi_2$–$m$$GeBi_2Te_4$ homologous series

In light of the structural properties of tetradymite-like layered chalcogenide compounds, the mixed-layered compound $GeBi_3Te_4$ was predicted and synthesized for the first time, which belongs to the $n$$Bi_2$–$m$$GeBi_2Te_4$ homologous series in the Ge-Te-Bi system. A polycrystal of a new phase was synthesized, and its single crystal was grown by the Bridgman–Stockbarger method. The obtained samples were investigated by differential thermal analysis (DTA) and powder X-ray diffraction (XRD). It was found that the compound melts peritectically at 563 °C and has a rhombohedral lattice-type structure with the following lattice parameters: a = 4.3625 (5) Å, c = 31.381 (2) Å (sp. gr R3m). The crystal structure of the layered van der Waals compound $GeBi_3Te_4$ consists of a repetition of seven-layer $GeBi_2Te_4$ packets and two-layer Bi packets in the form of -7-2-7-7-2-7-7-2-7- which differ from the previously discovered $GeBi_4Te_4$ phase, which consists of unit cells from only one seven-layer packet. The discovery of a new mixed-layered compound indicates the possibility of the formation of similar compounds in A^{IV}–B^{V}–Te (A^{IV} = Ge, Sn, Pb; B^{V} = Sb, Bi) systems.

Keywords: Ge-Bi-Te ternary system, $n$$Bi_2$–$m$$GeBi_2Te_4$ homologous series, $GeBi_3Te_4$, $GeBi_4Te_4$, tetradymite-like structure, Bi-bilayers, crystal structure, topological insulators.

Introduction

In recent years, researchers have intensively studied the members of the homologous series $(A^{IV}Te)_n(B_2^{V}Te_3)_m$ (A^{IV} = Ge, Sn, Pb; B^{V} = Sb, Bi) due to their extraordinary properties. These tetradymite-type layered ternary phases are potentially attractive thermoelectric materials with low thermal conductivity [1–6]. In addition, homologous members of $(A^{IV}Te)_n(B_2^{V}Te_3)_m$ have been confirmed as three-dimensional topological insulators (TI) [7–11], which gave impetus to the study of the A^{IV}–B^{V}–Te systems and the search for new layered compounds in the indicated systems. Since topological insulators can demonstrate many exotic properties, scientists believe that these materials have a huge perspective in the use of spintronics, quantum computers, medicine, protection systems, etc. [12–15].

An interesting feature of the Ge–B^{V}–Te systems is that compounds belonging to the $n\mathrm{GeTe}\cdot B_2^{V}Te_3$ homologous series are formed in the A^{IV}–B^{V}–Te systems in addition to $A^{IV}\mathrm{Te}\cdot mB_2^{V}Te_3$ homologous series. The crystal structure of Bi_2Te_3-rich and GeTe-rich members of $n\mathrm{GeTe}\cdot m\mathrm{Bi_2Te_3}$ differ significantly from each other due to their structures [16–19]. The ternary compounds with GeTe-rich phase made up of identical slabs in which introduction of one GeTe bilayer unit to seven-layer packed increases the number of layers by two, giving 9-, 11-, and 13-layer slabs ($Ge_2Bi_2Te_5$, $Ge_3Bi_2Te_6$, and $Ge_4Bi_2Te_7$) [20]. Compounds with a high Bi_2Te_3 content are also built of two types of slabs: Seven-layer packets typical to $GeBi_2Te_4$, which comprises four anionic and three cationic layers and five-layered tetradymite. The general formula for these mixed layers can be written as $n\mathrm{GeBi_2Te_4}\cdot m\mathrm{Bi_2Te_3}$, where n and m are the numbers of seven-layer and five-layer packets per unit cell, respectively. The slabs are bonded with each other by weak van der Waals forces.

The existence of another type of mix-layered compounds belonging to $n\mathrm{B}_2^{\mathrm{V}}\cdot m\mathrm{B}_2^{\mathrm{V}}\mathrm{X}_3$ homologous series is also confirmed [21–23]. The crystal structure of this type of homologous series consists of repeating five-layered $\mathrm{B}_2^{\mathrm{V}}\mathrm{X}_3$ and two-layered $\mathrm{B}_2^{\mathrm{V}}$ packets connected by the van der Waals forces that are stacked along the *c* axes in an ordered manner.

Analysis of the literature shows that in the $\mathrm{A^{IV}}$–$\mathrm{B^{V}}$–Te systems, along with the homologous series $(\mathrm{A^{IV}Te})_n(\mathrm{B}_2^{\mathrm{V}}\mathrm{Te}_3)_m$, there also exist ternary phases corresponding to the $n\mathrm{B}_2^{\mathrm{V}}–m\mathrm{A^{IV}}\mathrm{B}_2^{\mathrm{V}}\mathrm{Te}_4$ homologous series. The formation of such kinds of members is confirmed in numerous works: $\mathrm{SnBi_4Te_4}$ [24], $\mathrm{GeSb_4Te_4}$ [25], and $\mathrm{GeBi_4Te_4}$ [26]. The existence of these compounds, in particular $\mathrm{GeBi_4Te_4}$, increases the probability of formation of other members of $n\mathrm{Bi_2}–m\mathrm{GeBi_2Te_4}$ homologous series in the Ge-Te-Bi system. Considering foresaid, in this paper, for the first time, a new van der Waals type of mixed-layered compound $\mathrm{Bi_2{\cdot}2(GeBi_2Te_4)}$ was synthesized and studied, which comprises seven-layer $\mathrm{GeBi_2Te_4}$ packets and two-layer Bi packets repeating along the *c* axis in the form of -7-2-7-7-2-7-7-2-7-.

Experimental

For synthesis $\mathrm{GeBi_3Te_4}$ compound, high purity elements Ge (99.999 %, Alfa Aesar), Bi (99.999 %, Alfa Aesar), and Te (99.999 %, Alfa Aesar) (Table 1) were melted in a quartz ampoule according to stoichiometric amounts under the vacuum condition (10^{-2} Pa) at 800 °C for 3 hours and quenched in ice water. Then annealing was carried out at 450 °C for 1000 h to reach an equilibrium state. In the second part of the work, a single-crystal sample with $\mathrm{GeBi_3Te_4}$ composition was grown by the vertical Bridgman–Stockbarger method. For this, a quartz ampoule with a conical bottom was sealed (10^{-2} Pa) and passed through the hot zone (650 °C) of the two-zone furnace into the cold zone (450 °C) at the 1.0 mm/h speed. As a result, bulk single-crystal ingots 2.5 cm in length and 0.8 cm in diameter were grown by the vertical Bridgman–Stockbarger method. The obtained samples were investigated by DTA and XRD methods.

X-ray diffraction analysis was performed at room temperature in the range $2\theta = 5–75$ degrees on a Bruker D2 PHASER diffractometer ($\mathrm{CuK_{\alpha 1}}$ radiation). The “NETZSCH 404 F1 Pegasus” system was used for differential thermal analysis. DTA of the annealed alloy was carried out from room temperature to 800 °C with a heating and cooling rate of 5 °C $\mathrm{min^{-1}}$. The crystal lattice parameters were calculated using the TOPAS V3.0 program.

Table 1

Information about initial elements

Element	CAS number	Source	Purity	Form
Germanium	7440-56-4	Alfa Aesar	99.999 %	Pieces
Tellurium	13494-80-9	Alfa Aesar	99.999 %	Lump
Bismuth	7440-69-9	Alfa Aesar	99.998 %	Polycrystalline lump

Results and Discussion

The polycrystalline sample of $\mathrm{GeBi_3Te_4}$ was analyzed by powder X-ray diffraction method and obtained XRD patterns were compared with bismuth, $\mathrm{GeBi_2Te_4}$, and $\mathrm{GeBi_4Te_4}$ (Figure 1). XRD pattern of GeBi4Te4 was taken from [26]. Comparison of diffraction lines of the synthesized polycrystalline sample with the bismuth, $\mathrm{GeBi_2Te_4}$, and $\mathrm{GeBi_4Te_4}$ data shows that new diffraction lines appear on the diffraction pattern of the $\mathrm{GeBi_3Te_4}$ sample. Using TOPAS V3.0 software, the XRD result of the new phase was indexed and identified as a $\mathrm{GeBi_3Te_4}$ compound with a tetradymite-like layered structure and has the lattice parameter values $a = 4.3625\ (5)$ Å, $c = 31.381\ (2)$ Å (sp. gr R3m1).

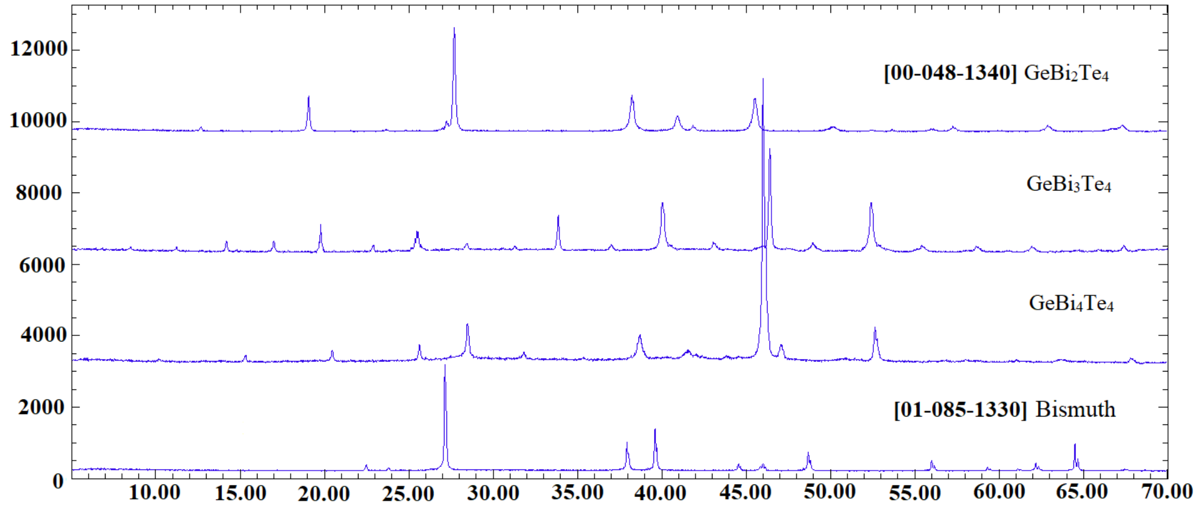


Figure 1. PXRD patterns of Bismuth, $GeBi_2Te_4$, $GeBi_3Te_4$, and $GeBi_4Te_4$

In Figure 2, the Rietveld refinement profile for the new synthesized $GeBi_3Te_4$ phase was shown. It is seen that all peak positions of the PXRD pattern are perfectly indexed with calculated lattice parameters.

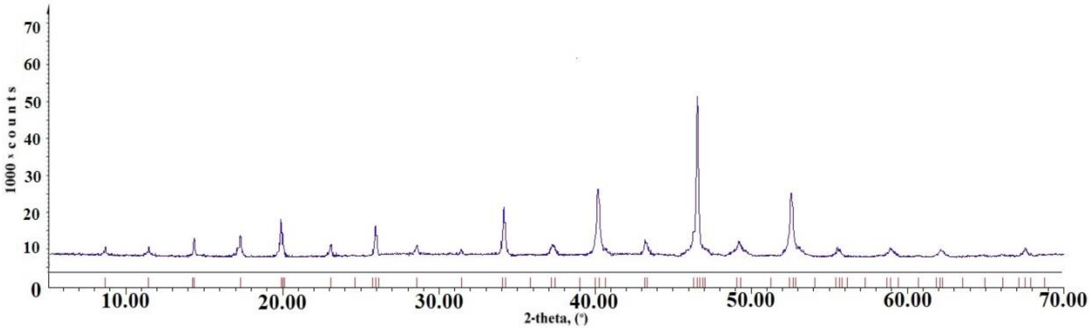
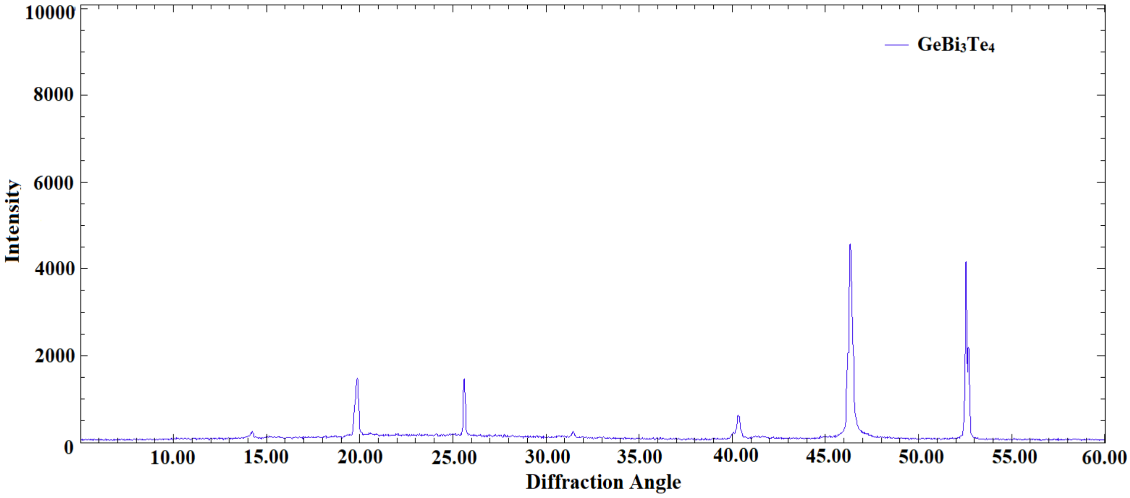


Figure 2. PXRD pattern for the $GeBi_3Te_4$

Analyses performed on the cleaved surface of the single-crystal sample, obtained by the Bridgman–Stockbarger method (nominal composition of $GeBi_3Te_4$), show that crystal comprises several phases along with the sample (Figure 3). The XRD results show that the primary crystallization phase is $GeBi_3Te_4$, then comes a mix of two phases $GeBi_3Te_4$ and $GeBi_4Te_4$, and finally pure phase of $GeBi_4Te_4$. Subsequent research shows that no other ternary mixed-layered compounds were found.



a)

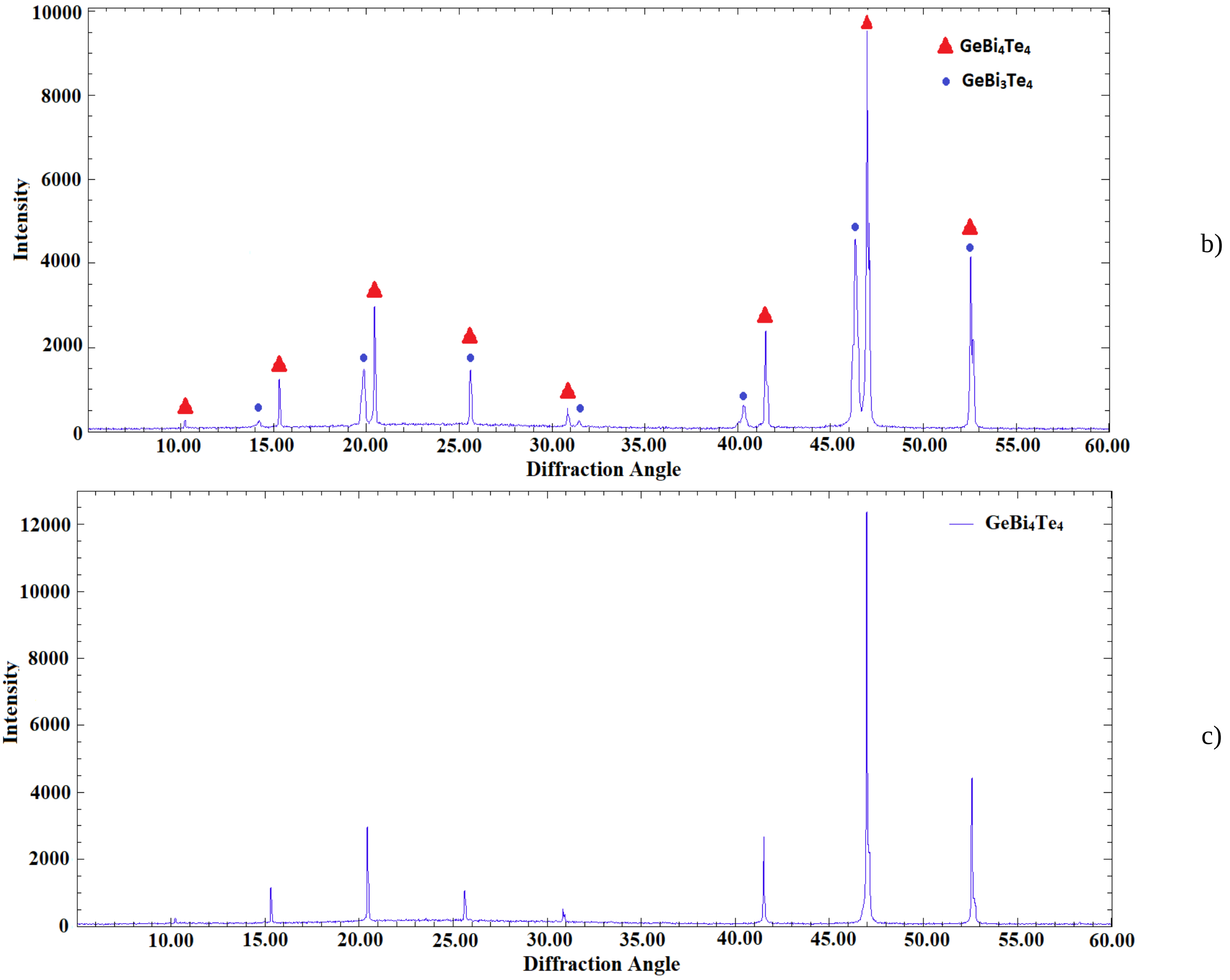


Figure 3. XRD pattern of a sample from the cleaved surface of the single-crystal a) $GeBi_3Te_4$, b) $GeBi_3Te_4$ + $GeBi_4Te_4$, c) $GeBi_4Te_4$

The novel synthesized compound belongs to the tetradymite-type layered structure family where crystal structure consists of stacked together two rocksalt-type septuple blocks of Te-Bi-Te-Ge-Te-Bi-Te ($GeBi_2Te_4$, sp. gr R-3m) and bismuth bilayer Bi-Bi (Figure 4) repeating along the c axis. Each atomic layer is strongly bonded with each other by covalent bonds, while weak van der Waals forces exist between blocks.

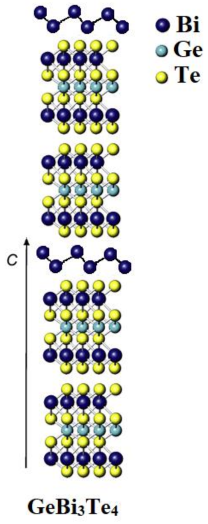


Figure 4. Crystal structure of $GeBi_3Te_4$

Figure 5 shows DTA results of the newly synthesized $GeBi_3Te_4$ phase which was analyzed from the powder sample. As can be seen, two endothermic effects are observed in the thermogram. The first and intensive endothermic effect noted at 563 °C belongs to the peritectic decomposition of the $GeBi_3Te_4$ compound, while the second endothermic effect at 585 °C refers to the end of melting. No additional effects are detected in DTA analysis which confirms that the synthesized sample is phase pure and does not contain any traces of other phases alongside $GeBi_3Te_4$.

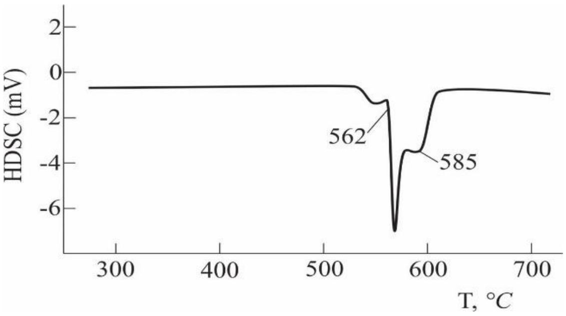


Figure 5. Heating thermogram of the $GeBi_3Te_4$ phase

Finding one more compound alongside $GeBi_4Te_4$ in nBi$_2$–mGeBi$_2$Te$_4$ homologous series opens to researchers great opportunities for searching new mixed layered ternary compounds in another homologous series such as $n\,B_2^{V}–m\,A^{IV}B_4^{V}Te_7$ and $n\,B_2^{V}–m\,A_2^{IV}B_2^{V}Te_5$. New ternary materials with more complex and long-period mixed layered structures will potentially show more extraordinary properties.

Conclusions

In this paper, for the first time, the mixed-layered compound $GeBi_3Te_4$ was synthesized and analyzed which belongs to nBi$_2$-mGeBi$_2$Te$_4$ homologous series in the Ge-Te-Bi system. Novel ternary compound melts peritectically at 563 °C and crystallizes: a = 4.3625 (5) Å, c = 31.381 (2) Å (sp. gr R3m). The structure of the novel phase is consists of a repetition of seven-layer $GeBi_2Te_4$ and Bi bilayer packets in the -7-7-2-7-7-2-7-7-2- form. Finding a second ternary compound in nBi$_2$ — mGeBi$_2$Te$_4$ increases the probability of the existence of other mixed-layered ternary compounds in $n\,B_2^{V}–m\,A^{IV}B_2^{V}Te_4$ homologous series. Synthesized novel phase has potential application as topological insulators.

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$n\mathrm{Bi_2}$–$m\mathrm{GeBi_2Te_4}$ гомологтық қатарына жататын $\mathrm{GeBi_3Te_4}$ жаңа аралас-қатпарлы қосылыстарын синтездеу және зерттеу

Бұрыннан белгілі тетрадимит тәрізді қабаттасқан халькогенидті қосылыстардың құрылымдық қасиеттерін ескере отырып, Ge-Te-Bi жүйесінде $n\mathrm{Bi_2}$–$m\mathrm{GeBi_2Te_4}$ гомологтық қатарына жататын жаңа тетрадимит тәрізді аралас-қатпарлы $\mathrm{GeBi_3Te_4}$ қосылысы болжанып, синтезделді. Жаңа фазалық поликристал синтезделіп, оның монокристалы Бригман–Стокбаргер әдісімен алынды. Алынған үлгілер дифференциалды термиялық талдау (ДТТ) және рентгендікфазалық талдау (РФТ) арқылы зерттелді. Қосылыс 563 °C температурада перитектикалық балқитыны анықталды және тор параметрлерінің мынадай мәндері бар: a = 4,3625(5) Å, c = 31,381(2) Å (sp. gr R3m). $\mathrm{GeBi_3Te_4}$ Ван дер Ваальс қатпарлы қосылысының кристалдық құрылымы қабатты -7-2-7-7-2-7-7-2-7- түріндегі $\mathrm{GeBi_2Te_4}$ жеті қабатты пакеттері мен Bi екі қабатты пакеттерінің қайталануынан тұрады. Ол бұрын ашылған элементарлы ұяшықта тек бір ғана жеті қабатты пакетті бірлік ұяшықтан тұратын $\mathrm{GeBi_4Te_4}$ фазасынан басқаша болады. Жаңа аралас-қабатты қосылыстың ашылуы AIV–BV–Te (AIV = Ge, Sn, Pb; BV = Sb, Bi) жүйелерінде ұқсас қосылыстардың болуы мүмкіндігін көрсетеді.

Кілт сөздер: Ge-Bi-Te үштік жүйесі, $n\mathrm{Bi_2}$–$m\mathrm{GeBi_2Te_4}$ гомологиялық қатар, $\mathrm{GeBi_3Te_4}$, $\mathrm{GeBi_4Te_4}$, тетрадимиттәрізді құрылым, Bi-биқабаттар, кристалдық құрылым, топологиялық изоляторлар.

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Синтез и исследование нового смешанно-слоистого соединения $\mathrm{GeBi_3Te_4}$, принадлежащего к $n\mathrm{Bi_2}$–$m\mathrm{GeBi_2Te_4}$ гомологическому ряду

Учитывая структурные свойства уже известных тетрадимитоподобных слоистых халькогенидных соединений, в системе Ge–Te–Bi было предсказано и синтезировано новое тетрадимитоподобное смешанно-слоистое соединение $\mathrm{GeBi_3Te_4}$, относящееся к $n\mathrm{Bi_2}$–$m\mathrm{GeBi_2Te_4}$ гомологическому ряду. Поликристалл новой фазы был синтезирован, а его монокристалл выращен методом Бригмана–Стокбаргера. Полученные образцы исследовали методами дифференциального термического анализа (ДТА) и рентгенофазового анализа (РФА). Было обнаружено, что соединение плавится перитектически при температуре 563 °C и имеет следующие значения параметров решетки: a = 4,3625(5) Å, c = 31,381(2) Å (sp. gr R3m). Кристаллическая структура слоистого соединения Ван-дер-Ваальса $\mathrm{GeBi_3Te_4}$ состоит из повторения семислойных пакетов $\mathrm{GeBi_2Te_4}$ и двухслойных пакетов Bi в форме -7-2-7-7-2-7-7-2-7-, которая отличается от обнаруженной ранее фазы $\mathrm{GeBi_4Te_4}$, состоящей в элементарной ячейке всего лишь из одного семислойного пакета. Открытие нового смешанно-слоистого соединения указывает на возможность существование подобных соединений в $\mathrm{A^{IV}}$–$\mathrm{B^{V}}$–Te ($\mathrm{A^{IV}}$ = Ge, Sn, Pb; $\mathrm{B^{V}}$ = Sb, Bi) системах.

Ключевые слова: тройная система Ge–Bi–Te, гомологический ряд $n\mathrm{Bi_2}$–$m\mathrm{GeBi_2Te_4}$, $\mathrm{GeBi_3Te_4}$, $\mathrm{GeBi_4Te_4}$, тетрадимитоподобная структура, Bi-бислои, кристаллическая структура, топологические изоляторы.

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