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## Synthesis and Study of a Novel 9P-type Mixed Layered Tetradymite-Like $\text{GeBi}_4\text{Te}_4$ Compound in the Ge-Te-Bi System

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Taking as a base structural properties of the tetradymite-like layered chalcogenide compounds, a novel ternary  $\text{GeBi}_4\text{Te}_4$  phase was predicted and synthesized. The polycrystal of this compound was synthesized and its single-crystal was grown by the vertical Brigman-Stokbarger method. The phase composition of obtained samples was analyzed by differential thermal analysis (DTA), X-ray powder diffraction (XRD), and scanning electron microscope (SEM). It was determined that the novel phase melts peritectially at 538 °C and has the following lattice parameter values in a hexagonal configuration:  $a = 4.4071(6) \text{ \AA}$ ,  $c = 17.384(2) \text{ \AA}$  (sp. gr P3m1). This crystal structure is considered a derivative of tetradymite-like layered chalcogenides and consists of alternating Bi bilayers and  $\text{GeBi}_2\text{Te}_4$  septuple packets.

**Key words:** Ge-Bi-Te ternary system, new ternary compound,  $\text{GeBi}_4\text{Te}_4$ , tetradymite-like structure, Bi-bilayers, topological insulators.

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### Introduction

Chalcogenides are used as a main constituent in the design of such materials like solar panels, infrared detectors, new-generation refrigerators, semiconductors, thermoelectric materials etc. [1-4]. One of the contemporary methods in seeking new functional materials is preparation of phases with more complex and long-period mixed layered structures. Ternary compounds of the homologous series  $(\text{A}^{\text{IV}}\text{Te})_n(\text{B}_2^{\text{V}}\text{Te}_3)_m$  ( $\text{A}^{\text{IV}} = \text{Ge}, \text{Sn}, \text{Pb}$ ;  $\text{B}^{\text{V}} = \text{Sb}, \text{Bi}$ ) are long studied thermoelectric materials [5-12]. The thermal conductivity of such alloys possessing a large unit cell and heavy element atoms, is reduced due to the effective scattering of phonons, that causes to the increase of the thermoelectric effect. Last investigations demonstrated that these materials carry topological insulator properties and have wide potential application in optoelectronics, spintronics, and quantum computing [13-24].

In this context, interest to the study of the  $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$  ( $n = 1 - 9$ ,  $m = 1 - 4$ ) homologous series has been significantly increased. GeTe-rich ( $(n/m) \geq 1$ ) and  $\text{Bi}_2\text{Te}_3$ -rich ( $(n/m) < 1$ ) compounds substantially differ from each

other due to their structures [25-28]. Inclusion of the GeTe to the five-layer  $\text{Bi}_2\text{Te}_3$  slab yields the seven-layered  $\text{GeBi}_2\text{Te}_4$  packet with R-3m space group and congruent melting at 585 °C. Subsequent additions of GeTe bilayers increase the number of layers by two. As a result, the structure of  $\text{Ge}_2\text{Bi}_2\text{Te}_5$ ,  $\text{Ge}_3\text{Bi}_2\text{Te}_6$ , and  $\text{Ge}_4\text{Bi}_2\text{Te}_7$  [29] compounds consist of packages that are stacked along the  $c$  axis in 9, 11, and 13 layers respectively.  $\text{Bi}_2\text{Te}_3$ -rich ( $(n/m) < 1$ ) alloys demonstrate mixed-layered structures. Their crystal structure consists of two types of slabs: a five-layered tetradymite packet and a seven-layered  $\text{GeBi}_2\text{Te}_4$  packet.  $\text{GeBi}_4\text{Te}_7$  and  $\text{GeBi}_6\text{Te}_{10}$  compounds consist of five and seven-layered packets that are stacked in an ordered sequence and bonded with each other by the Van der Waals bonds. The general formula of the  $\text{Bi}_2\text{Te}_3$ -rich mixed-layered compounds can be represented as  $n\text{GeBi}_2\text{Te}_4 \cdot m\text{Bi}_2\text{Te}_3$ .

Literature data shows that in addition to the substitution of seven- and five-layered packets, there is extensive information about the existence of  $n\text{B}_2^{\text{V}} \cdot m\text{B}_2^{\text{V}}\text{X}_3$  homologous series [30-33]. Their structure research suggests that the crystal structure of these compounds consists of five-layered  $m\text{B}_2^{\text{V}}\text{X}_3$  and two-layered  $n\text{B}_2^{\text{V}}$

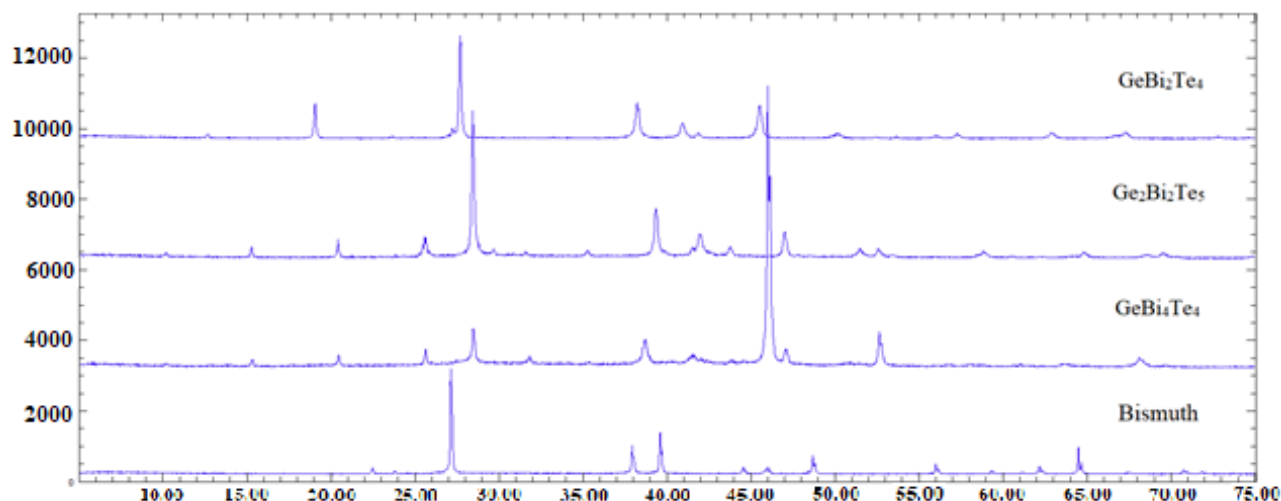


Fig. 1 . PXRD patterns of bismuth,  $\text{GeBi}_2\text{Te}_4$ ,  $\text{Ge}_2\text{Bi}_2\text{Te}_5$ , and  $\text{GeBi}_4\text{Te}_4$ .

packets that are stacked along the  $c$  axis in an ordered manner.

Data analysis indicates that in  $A^{\text{IV}} - B^{\text{V}} - \text{Te}$  systems, besides above mentioned homologous series, there can also exist phases relevant to  $m\text{Bi}_2 - A^{\text{IV}}B_2^{\text{V}}\text{Te}_4$  homologous series. The first two members of this series have been reported in recent years:  $\text{SnBi}_4\text{Te}_4$  [34] and  $\text{GeSb}_4\text{Te}_4$  [35]. Identification of these compounds increases the probability of such phases in a similar Ge – Bi – Te system. Taking into account mentioned facts in the presented paper, a new mixed layered phase consisting of the repetition of seven-layered  $\text{GeBi}_2\text{Te}_4$  and two-layered Bi packets was synthesized and investigated.

## I. Experimental part

High purity Ge (99.999 %, Alfa Aesar), Bi (99.999 %, Alfa Aesar), and Te (99.999 %, Alfa Aesar) elements were used to synthesize the  $\text{GeBi}_4\text{Te}_4$  polycrystalline sample and to prepare its single-crystalline ingot. According to stoichiometric amounts, 1 g of sample was sealed under the vacuum ( $10^{-2}$  Pa) in quartz ampoule and heated up to 800 °C, and kept at this temperature for 3 h. For better dissolving, the sample was mixed by shaking. The synthesized alloy was quenched in ice water and further annealed at 450 °C for 1000 h in order to reach the equilibrium state. Additionally, single-crystal with starting composition of  $\text{GeBi}_4\text{Te}_4$  was grown from the melt using the vertical Bridgman-Stockbarger method. Initially, conical-bottom quartz ampoule was filled with 8 g of the stoichiometric mixture and sealed under the vacuum ( $10^{-2}$  Pa). This ampoule was kept in the hot zone (630 °C) of the two-zone furnace for 3 h to ensure that the sample was completely liquefied. Then, the ampoule was descended at the rate of 1mm/h from the hot zone to the cold zone (430 °C). The obtained ingots were studied using DTA, PXRD, and SEM methods.

“NETZSCH 404 F1 Pegasus” system was used for differential thermal analysis. Powder X-ray phase analysis was performed at room temperature in the range of  $2\theta = 5 - 75$  degrees with Bruker D2 PHASER X-ray diffractometer ( $\text{CuK}\alpha_1$  radiation). Lattice parameters were

calculated with the help of TOPAS V3.0 software. SEM analysis was determined by the HITACHI SU8030 system.

## II. Results and discussion

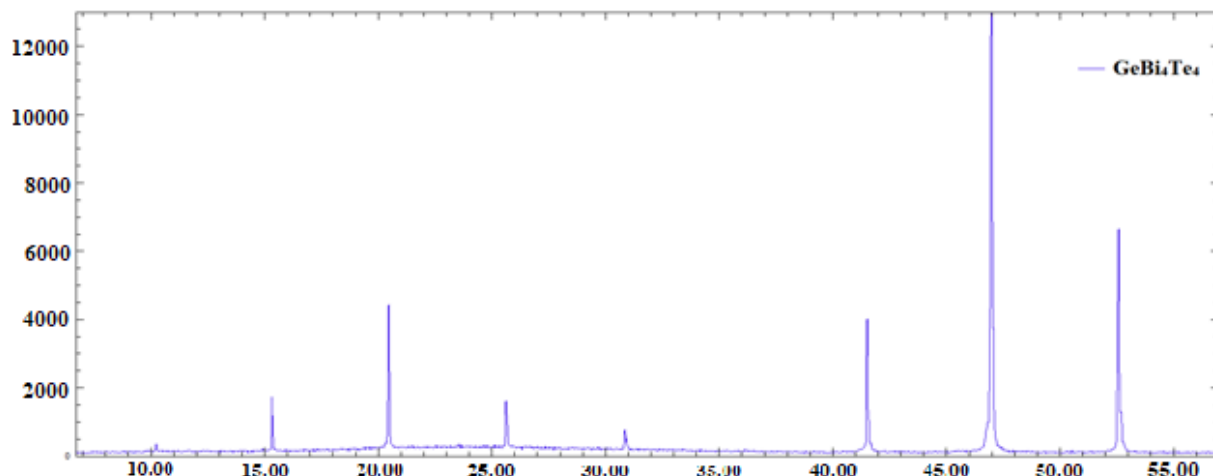
The powder XRD pattern of the obtained polycrystalline sample  $\text{GeBi}_4\text{Te}_4$  is compared with bismuth,  $\text{GeBi}_2\text{Te}_4$ , and  $\text{Ge}_2\text{Bi}_2\text{Te}_5$  (Fig. 1). Comparison of the diffraction data shows that, there are new diffraction lines in the diffraction pattern of the synthesized  $\text{GeBi}_4\text{Te}_4$  sample that are not typical for bismuth and  $\text{GeBi}_2\text{Te}_4$ . The XRD result of the new phase was indexed with the help of TOPAS V3.0 software and it was identified to be a 9P-type  $\text{GeBi}_4\text{Te}_4$  compound with tetradymite-like layered structure.

It should be noted that, composition of the 9P- $\text{GeBi}_4\text{Te}_4$  ( $a = 4.40$  Å,  $c = 17.38$  Å) and 9P- $\text{Ge}_2\text{Bi}_2\text{Te}_5$  ( $a = 4.29$  Å,  $c = 17.35$  Å) compounds are different, however both of them consist of a nine-layer packages. For this reason,  $c$  parameter in their crystal structures is very close to each other. This causes the diffraction peaks to overlap at lower angles.

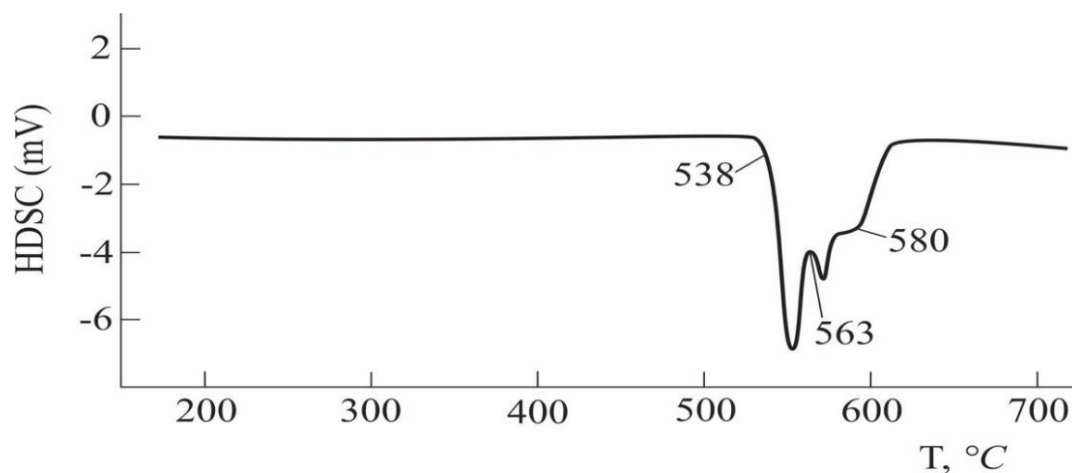
A single-crystalline ingot of the synthesized phase was used for XRD, DTA and SEM measurements. It is clearly seen that diffraction patterns of both samples are identical (Fig. 2).

The heating thermogramme of the  $\text{GeBi}_4\text{Te}_4$  phase is given in Figure 3. As can be seen from the figure, it contains three endothermic effects. The first endothermic effect observed at 538 °C refers to the peritectic decomposition of the  $\text{GeBi}_4\text{Te}_4$  compound. We assume that the second endothermic effect (at 563 °C) belongs to the decomposition of the Ge-rich phase in the  $m\text{Bi}_2 - \text{GeBi}_2\text{Te}_4$  homologous serie. For accurate results, additional studies are needed. Finally, the endothermic effect at 580 °C indicates the end of the melting process.

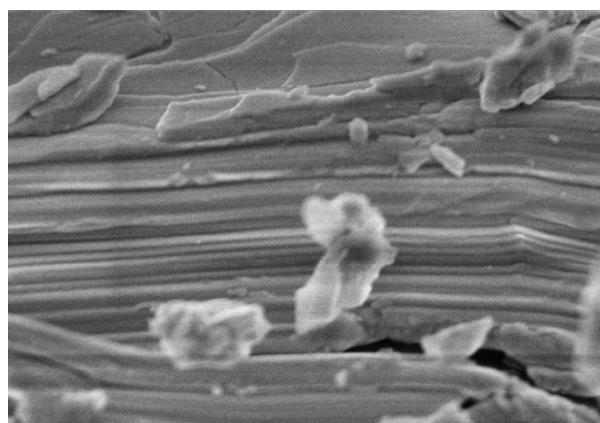
SEM and microstructure images of the  $\text{GeBi}_4\text{Te}_4$  compound are given in Figure 4. It is obvious from the



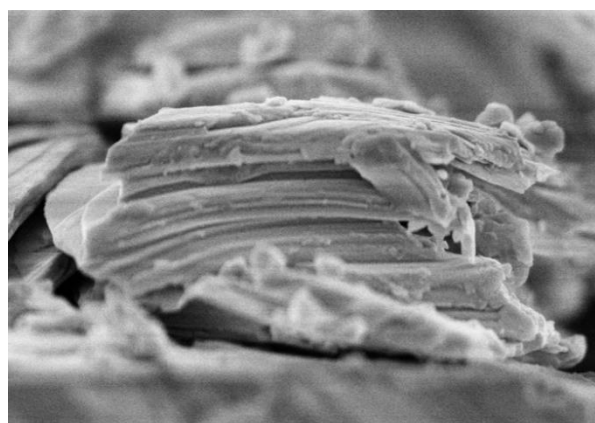
**Fig. 2.** XRD pattern of a sample from a surface of the  $\text{GeBi}_4\text{Te}_4$  single-crystal ingot.



**Fig. 3.** DTA heating thermogramme of the  $\text{GeBi}_4\text{Te}_4$  phase.



**a**



**b**

**Fig. 4.** SEM images of the  $\text{GeBi}_4\text{Te}_4$  phase.

image that the compound has a mixed layered structure. The EDS balance is very close to the stoichiometric composition of  $\text{GeBi}_4\text{Te}_4$ .

The crystal structure of  $\text{GeBi}_4\text{Te}_4$  is given in Figure 5.

The structure of  $\text{GeBi}_4\text{Te}_4$  can be described as an ordered stacking sequence of Bi bilayers and rocksalt-type  $\text{GeBi}_2\text{Te}_4$  blocks which are connected by the Van der Waals bonds.

## Conclusion

A novel 9P-type tetradymite-like mixed layered  $\text{GeBi}_4\text{Te}_4$  compound was synthesized and identified in Ge-Te-Bi ternary system. This compound melts incongruently at 538 °C and crystallizes in the hexagonal lattice:  $a = 4.4071(6)$  Å,  $c = 17.384(2)$  Å (sp. gr P3m1). This phase consists of alternating Bi bilayers and  $\text{GeBi}_2\text{Te}_4$  septuple packets. Existence of this type compound in Ge-Te-Bi ternary system increases the probability of similar complex structural phases in  $\text{mBi}_2 - A^{IV}B_2^V\text{Te}_4$  homologous series. Obtained novel compound tempts attention as potential topological insulators.

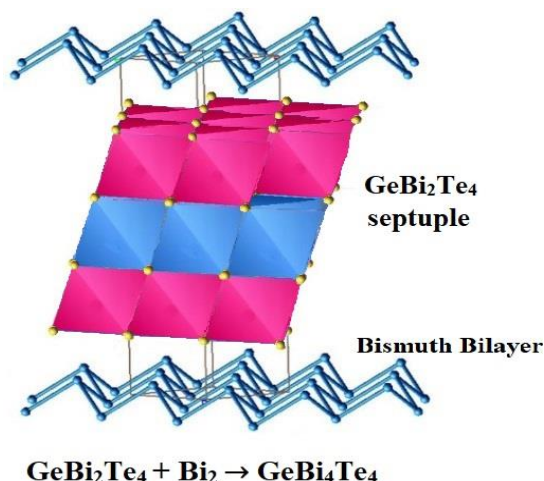


Fig. 5. Crystal structure of  $\text{GeBi}_4\text{Te}_4$ .

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## Синтез та дослідження нової змішаної шаруватої 9R-типу тетрадимітоподібної сполуки $\text{GeV}_4\text{Te}_4$ у системі Ge-Te-Vi

Азербайджанський державний університет нафтової промисловості, Баку, Азербайджан, [fariz\\_ar@hotmail.com](mailto:fariz_ar@hotmail.com)

Взявши за основу структурні властивості тетрадимітоподібних шаруватих халькогенідних сполук, було передбачено та синтезовано нову потрійну фазу  $\text{GeV}_4\text{Te}_4$ . Синтезовано полікристалічну сполуку, а монокристал вирошено вертикальним методом Бриджмена-Стокбаргера. Фазовий склад отриманих зразків аналізували за допомогою диференціального термічного аналізу (DTA), X-променевої порошкової дифракції (XRD) та скануючого електронного мікроскопа (SEM). Встановлено, що нова фаза перитодійно плавиться при  $538^\circ\text{C}$  і володіє наступними значеннями параметрів ґратки в гексагональній конфігурації:  $a = 4,4071(6) \text{ \AA}$ ,  $c = 17,384(2) \text{ \AA}$  (sp. Gr  $P3m1$ ). Така кристалічна структура вважається похідною тетрадимітоподібних шаруватих халькогенідів і складається із змінних бішарів Vi та септулетних пакетів  $\text{GeV}_2\text{Te}_4$ .

**Ключові слова:** потрійна система Ge-Vi-Te, нова потрійна сполука,  $\text{GeV}_4\text{Te}_4$ , тетрадимітоподібна структура, шари Vi, топологічні ізолятори.