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SYNTHESIS AND CRYSTAL STRUCTURE OFA NEW 9*P*–TYPE LAYERED van der WAALSCOMPOUND $SnBi_4Te_4$

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Abstract: *Considering structural features of the already known tetradymite-like layered chalcogenide phases, we have attempt to synthesize a new mix-layered compound, $SnBi_4Te_4$. The newly synthesized alloy examined by means of differential thermal analysis, powder X-ray diffraction and scanning electron microscope techniques.The melting nature of the discovered phase is found to be incongruently at 831 K. The crystal structure of the $SnBi_4Te_4$ was elucidated from powder pattern by Rietveld method. The determined crystal structure was found to derived from tetradymite type and featured by the alternation of theseven-layered (septuple) blocks of $SnBi_2Te_4$ and bismuth bilayers. The result of this work, the existence of a new - $SnBi_4Te_4$ compound in the Sn–Bi–Te ternary systemcan shed light for the incoming research works to search for similar phases in the other releated A^{IV}–Bi–Te ($A^{IV} = Ge, Sn, Pb$) systems.*

Keywords:*Sn–Bi–Te ternary system, $SnBi_4Te_4$,novel layered chalcogenide, Bi-bilayers, van der Waals compounds, crystal structure, Rietveld method, topological insulator.*
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Introduction

The layered van der Waals (vdW) chalcogenides, in particular, tellurides of the group 15 metals have beenextensively studied during the last years as prospective thermoelectric materials and topological insulator for energy conversion and spintronic applications[1-3]. Tuning the band electronic properties of these materials are of interesting from the point of view of their applications in real optoelectronic and spintronic devices. The rational tuning of the electronic properties is possible by the doping, nanostructuring or heterostructuring by combination of various atomic blocks or layers. Thanks to the existingvdWgap in the mentioned materials, inserting the, e.g., atomic bilayers in rocksalt-type septuple blocks are always simple way to modify crystal structure and electronic properties [3-5].

Recently preparation of mixed-layered compounds having thermoelectric properties are considered to be a more effective method for material design[6-7]. The literature data shows that, the systems $A^{IV}B^{VI}$–$A^{V}_2B^{VI}_3$(A^{IV} = Ge, Sn, Pb; A^{V}=Sb, Bi; B^{VI}=Se, Te) host tetradymite-type layered ternary compounds and exhibit promising thermoelectric properties [7-14]. On the other hand, the discovery of the topological insulating properties in these compounds made themmuch more attractive in the last few years [15-20].

The Sn–Bi–Te ternary system[21-23]has been studied by various groups of authors so far [21-23]. According to Karpinski [21], this system includes three stable ternary compounds, namely $SnBi_2Te_4$, $SnBi_4Te_7$, $SnBi_6Te_{10}$ which are melt by peritectic reactions at 873, 863 and 855 K, respectively. Later, Kuropatwa [22] and Chiu [23] independently have reported an additional two ternary compounds - $Sn_2Bi_2Te_5$and $SnBiTe_2$. Literature data show that, in order to overcome metastable state, annealing at higher than 700

K is important in the compositional range of 30 and 53 mol % SnTe [21]. There by, it seems that very hard to obtain further stable homogeneous phases in the SnTe–Bi_2Te_3 system. May be very long annealing time could be helpful, but present reports on this system confirm that the phase diagram of this system is still contradictory and further thoroughly experimental investigations are necessary.

$SnBi_2Te_4$ is one of the main dominant phases in the SnTe–Bi_2Te_3system and, its septuplestructure is formed by the insertion of SnTe into rocksalt-type slabs of Bi_2Te_3. The crystal structure of this compound is a long-periodically stacking sequence of these septuples along the *c* axes. The crystal structure of the other two compounds $SnBi_4Te_7$ and $SnBi_6Te_{10}$ built-up alternation of quintuples of the Bi_2Te_3 and septuples of the $SnBi_2Te_4$ thus can be considered mixed-layer blocks according to -7-5-7-5-7-5- and -7-5-5-7-5-5- sequence, respectively. Crystal structure information of these compounds can be found in the Refs[21,24].

The combination of the elemental bismuth or antimony bilayers and quintuple blocks of Bi_2Te_3 (orSb_2Te_3 and Bi_2Se_3) and the septuple blocksof the $GeBi_2Te_4$, $PbBi_2Te_4$ ternaries are also found to be stable structures [6]. Taking into account alternation of quintuple, septupleand, mixed-layered structures exist in the$(A^{IV}Te)_n\cdot(Bi_2Te_3)_m$($A^{IV}$ = Ge, Sn, Pb) homologous series, there is a possibility to design $(A^{IV}Te)_n\cdot(Bi_2Te_3)_m\cdot(Bi_2)_k$ layered phases where there is an alternation of *k*Bi bilayers, *n*A^{IV}Te quintuplesand *m*$A^{IV}Bi_2Te_4$septuples.

Here we present the synthesis and elucidation of a crystal structure of 9*P*-type heterostructured new ternary compound - $SnBi_4Te_4$, which is consists of alternating bismuth bilayers and $SnBi_2Te_4$ septuple packets. The melting nature and temperature were also presented here.

Experimental part

Elemental Tin, Bismuth, and Tellurium (99.999% purity, Alfa Aeser company) were used as starting components to synthesize polycrystalline $SnBi_4Te_4$. The stoichiometric mixture of elements was sealed in evacuated (10^{-2} Pa) quartz ampule and heated up to 1000 K and kept at this temperature for 5 hand thenwater quenched. In order to achieve complete homogenization, the sample annealed for ~700h at 700 K.

The sorted-outingot was examined by differential thermal analysis and powder X-ray diffraction techniques. DTA measurement was performed using a NETZSCH 404 F1 Pegasus system at a heating rate of 10 $K\cdot min^{-1}$, while PXRD was donein a Bruker D2 PHASER diffractometer with CuK_α radiation within 2θ = 5-100 range at room temperature.The crystal structure refinement was performed using the EVA and Topas V4.2 softwares by Bruker.The microstructures and equilibrium composition of the title sample was determined by Tescan Vega 3 SBH scanning electron microscope equipped with ThermoScientific UltraDry Compact EDS detector.

Results and discussion

Fig.1 shows the XRD pattern of $SnBi_4Te_4$ in comparison with initial $SnBi_4Te_4$ and Bismuth. It is clearly seen that $SnBi_4Te_4$ has a quite identical diffraction pattern with typical peaks those do not come from initial constituents. The obtained pattern fully indexed with a rhombohedral *P-3m1* (#156)lattice.The crystal structure of the obtained phase was refined by the Rietveld method and results will be discussed below.

The DTA heating thermogram for $SnBi_4Te_4$ is given in Fig. 2 with two endothermic effects at 831 K and 906 K. We assume that the first sharp endothermic thermal event corresponding to the peritectic decomposition of $SnBi_4Te_4$ phase according toreaction.

$$L + X \leftrightarrow SnBi_4Te_4$$

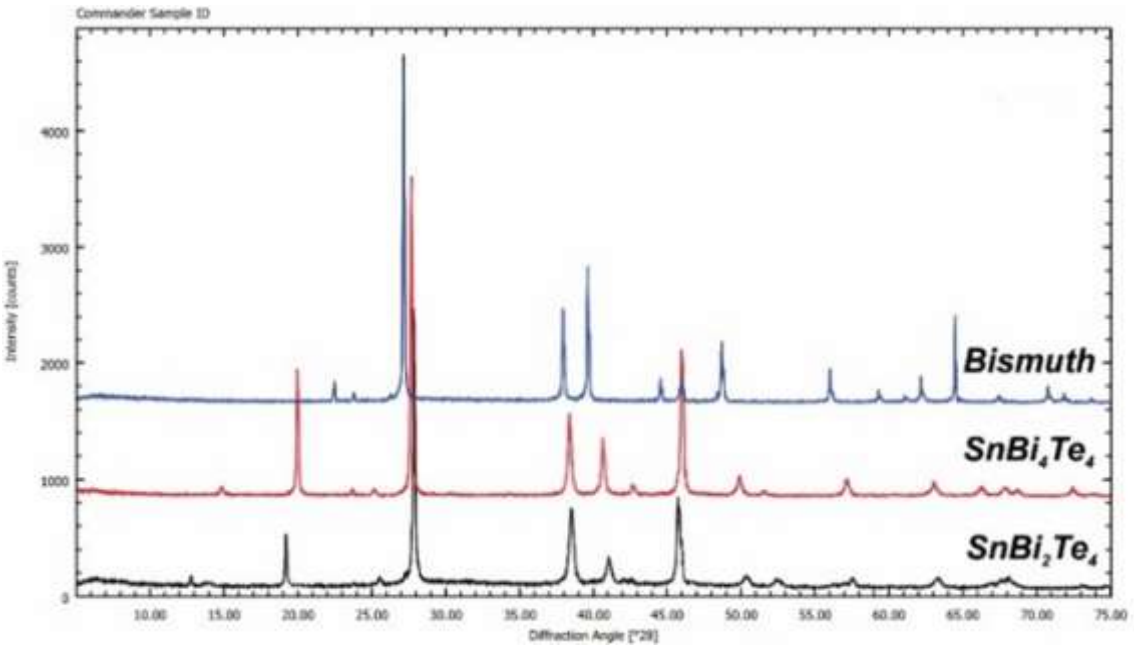

Fig. 1. PXRD patterns of Bismuth, $SnBi_4Te_4$, and $SnBi_2Te_4$.

The literature data on Sn–Bi–Te ternary system showed that *X* phase may tin telluride which is in equilibrium with liquid phase at above peritectic temperature. Nevertheless, further experimental results are strongly necessary for the conclusion.The second wide thermal effect confirmsthat the melting process starts at the end of the first effect whereas,the effect at 906 K conforms to finish of the melting process and can be considered as liquidus point.

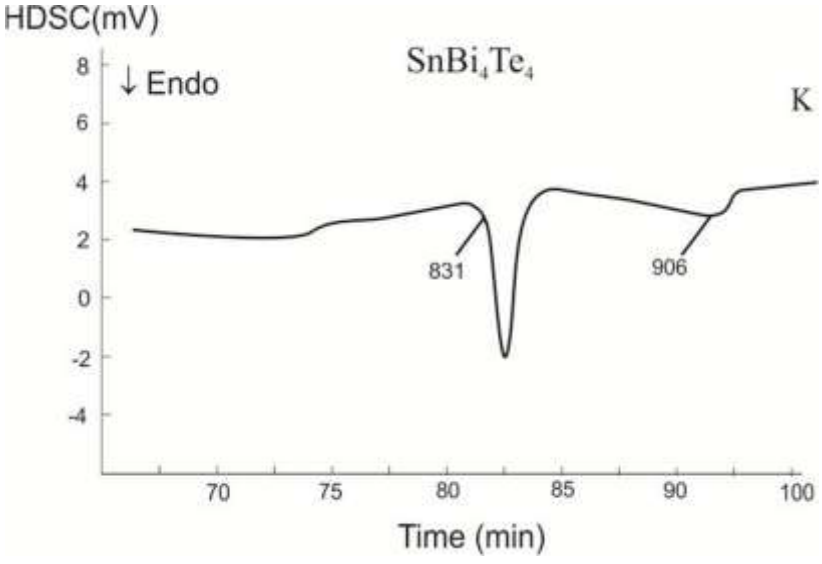

Fig. 2. DTA heating thermogram for the $SnBi_4Te_4$.

The further confirmation of the existence and chemical composition of the synthesized alloy comes from SEM-EDS measurements. Fig. 3 illustrates the homogenous microstructure of the $SnBi_4Te_4$ alloy, where as its EDS spectrum and equilibrium composition are given in Fig. 4. The layered texture of the alloy is also clearly

seen from micrograph. Obviously, the sample agrees well with the formula $SnBi_4Te_4$. chemical composition of the synthesized

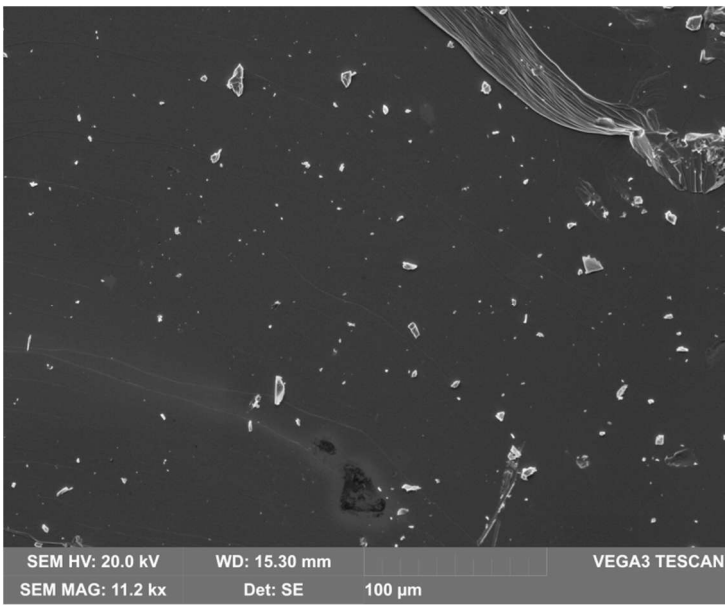

Fig. 3.SEM micrograph of the $SnBi_4Te_4$.

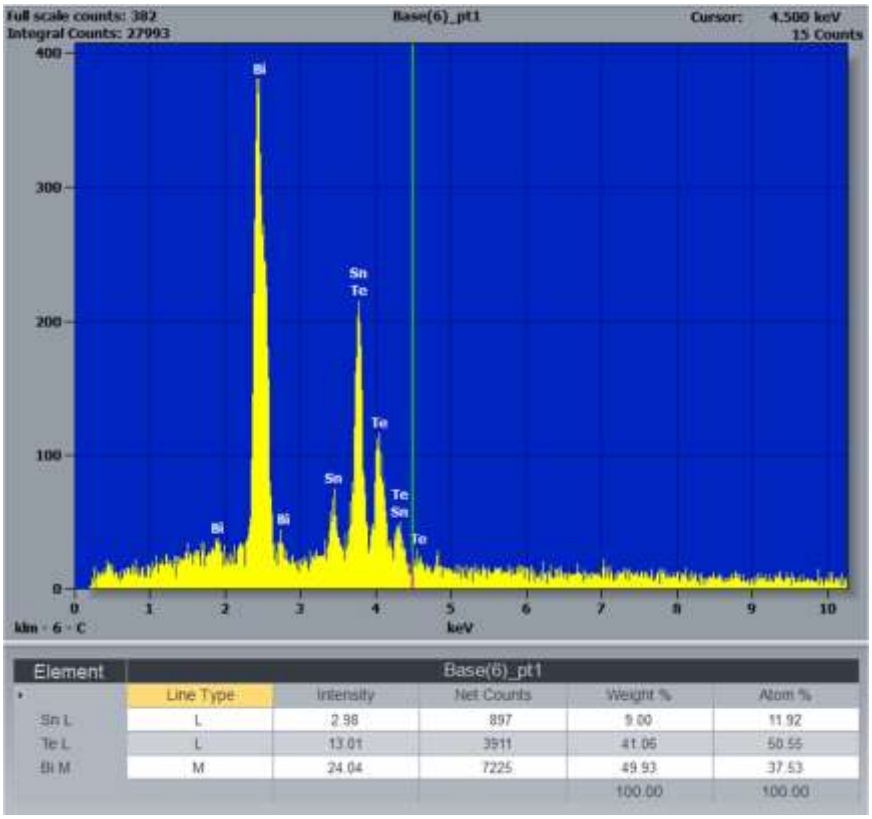

Fig. 4.EDS spectrum and element analysis result for the $SnBi_4Te_4$.

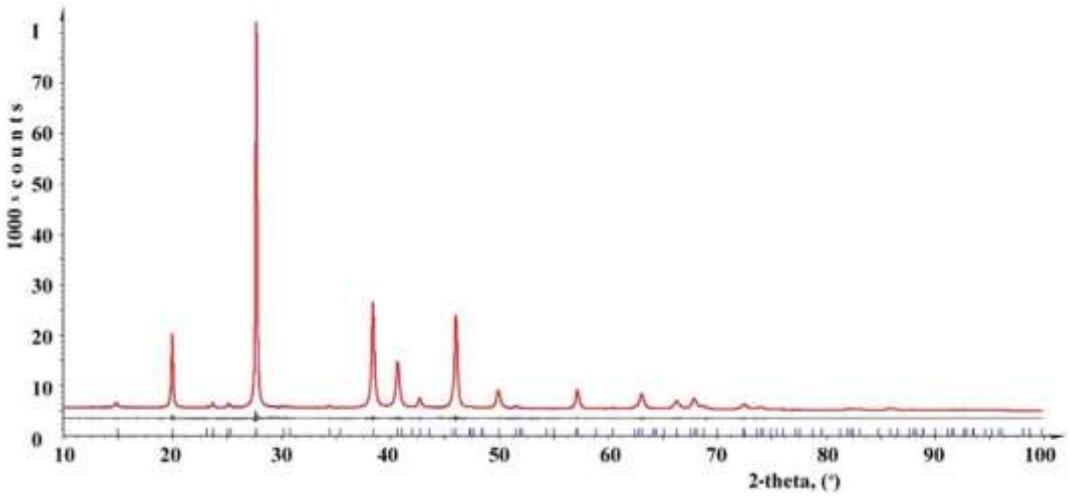

Fig. 5. XRD pattern for the $SnBi_4Te_4$.

The crystal structure of the title compound was refined from powder XRD pattern recorded in the range 2θ = 5-100 (Fig. 5). Below the XRD pattern black curve shows the difference of intensities between the experimental and calculated by Rietveld. A 3D side view of the obtained crystal structure illustrated in Fig. 6.

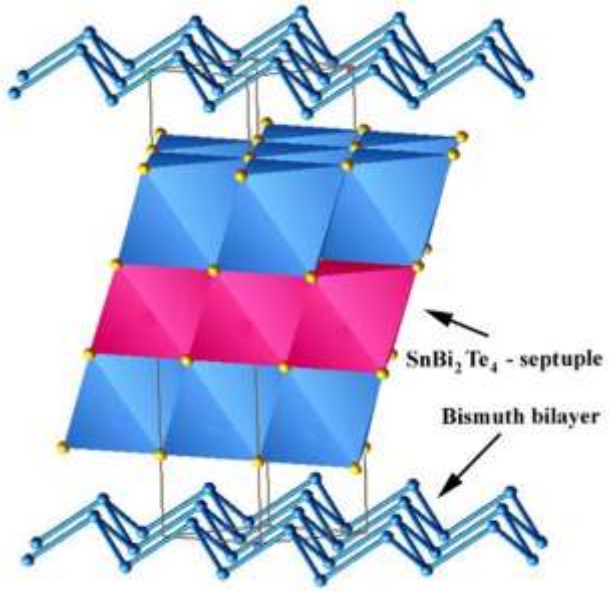

Fig. 6. A 3D side view of the refined crystal structure for the $SnBi_4Te_4$.

The refined unit cell parameters, atomic positions, and interatomic distances are shown in Tables 1, 2, and 3.

Table 1. Refined structure parameters for $SnBi_4Te_4$.

Space group	***P-3m1***
Unit cell parameters at298 K: a (Å) c (Å)	 4.43306 (57) 17.7396 (57)
Cell Volume ($Å^3$)	302.01 (12)
Crystal Density (g/cm^3)	8.0550 (33)
R-Bragg (%)	0.20

Table 2. Atomic positional parameters in $SnBi_4Te_4$.

Site	N_p	x	y	z	Atom	Occ		B_{eq}
						Single positions	Mixed positions	
Bi1	2	1/3	2/3	0.0451(12)	Bi^{+3}	1	1	1.32
Te1	2	0	0	0.1790(23)	Te	1	1	1.32
Bi2	2	2/3	1/3	0.2706 (13)	Bi^{+3} Sn^{+2}	1 -	0.76 0.24	1.32
Te2	2	1/3	2/3	0.3938(30)	Te	1	1	1.32
Sn	1	0	0	0.5	Sn^{+2} Bi^{+3}	1 -	0.52 0.48	1.32

Table 3. Interatomic distances in $Bi_2 \cdot SnBi_2Te_4$.

Atoms		Distance
Sn	Te(2)	6 x 3.178(31) Å
Bi(1)	Bi(1)	3 x 3.019(24) Å
Bi(2)	Te(1) Te(2)	3 x 3.033(25) Å 3 x 3.366(32) Å

The values presented in Table 2 (except the "*mixed positions*" column) were obtained for the condition where each crystallographic position was completely occupied by one type of atoms. However, a structural study of compounds containing similar septuple slabs shows that they are characterized by the substitution of metal atoms in atomic layers[25]. Therefore, we also refined the occupation coefficients in this structure in case of the initial composition of $SnBi_4Te_4$ is preserved. The occupation results obtained inthis case are shown inTable 2, in the "*mixed position*" column. According to the results of the refinement, the Sn/Bi occupation ratio is found to be 52/48in the central layer. At the same time, in the Bi(2) site, the Bi/Sn ratio is 76/24.

Conclusion

In this report, we have synthesized a new ternary tetradymite typelayered compound - $SnBi_4Te_4$in the Sn–Bi–Te ternary system.The obtained phasehas a layered structure with rocksalt-type septuple blocks of $SnBi_2Te_4$ and Bi-bilayers. Thermal analysis result reveals that the newly found compound melts peritectically at 831 K. The existence of nonuple packets in the Sn–Bi–Te ternary system gives possibility to expect similar phases in the other relatedA^{IV}–B^{V}–Te (A^{IV}=Ge, Sn, Pb; B^{V}= Sb, Bi) ternary systems.

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YENİ 9P-TİP LAYLI $SnBi_4Te_4$ van der VAALS BİRLƏŞMƏSİNİN SİNTEZİ VƏ KRİSTAL QURULUŞU

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Mövcud tetradimitəbənzər laylı xalkogenid fazalarının quruluş xüsusiyyətlərini araşdırmaqla $SnBi_4Te_4$tərkibli qarışıq laylı birləşmənin istiqamətli sintezi həyata keçirilmiş, alınan polikristallik nümunə DTA, RFA vəSEM üsulları ilə tədqiq olunmuşdur. Müəyyən edilmişdir ki, birləşmə 831 K-də peritektik reaksiya ilə parçalanmaqla əriyir.Nümunənin ovuntu rentgenoqramının Rietveld metodu ilə tədqiqi göstərir ki, birləşmə tetradimitəbənzər laylı quruluşlu olub, Bi_2layları və $SnBi_2Te_4$7-laylı paketlərinin təkrarlanmasından ibarətdir. Sn–Bi–Te üçlü sistemində belə birləşmənin olması,A^{IV}–Bi–Te ($A^{IV} = Ge, Sn, Pb$) sistemlərində də oxşar tərkibli fazaların mövcud ola biləcəyini ehtimal etməyə əsas verir.

Açar sözlər: *Sn–Bi–Te üçlü sistemi,$SnBi_4Te_4$, yeni laylı xalkogenid, Bi_2 layları, van der Waals birləşmələri, kristal quruluş, Rietveld metodu, topoloji izolyator.*

СИНТЕЗ И КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА НОВОГО СЛОИСТОГО ВАН-ДЕР-ВААЛЬСОВОГО СОЕДИНЕНИЯ $SnBi_4Te_4$9 Р-ТИПА

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Учитывая структурные особенности уже известных тетрадимитоподобных слоистых халькогенидных фаз, нами былпроведен направленный синтез нового смешанно-слойного соединения $SnBi_4Te_4$. Полученный полукристаллический образец был исследован методами дифференциального термического и рентгенофазового анализов, а также сканирующей электронной микроскопии.Установлено, что полученное соединение плавится инконгруэнтно при 831 К. Из порошковой рентгенограммы методом Ритвельдаопределена кристаллическая структура соединения $SnBi_4Te_4$и выявлено, что она относится к тетрадимитному типу и характеризуется чередованием семислойных блоков $SnBi_2Te_4$ и бислоёв висмута.Существование нового соединения $SnBi_4Te_4$ в тройной системе Sn–Bi–Tедает основание для поиска аналогичных фаз в других подобныхсистемахA^{IV}–Bi–Te (A^{IV} = Ge, Sn, Pb).

***Ключевые слова**: тройная система Sn–Bi–Te, $SnBi_4Te_4$, новый слоистый халькогенид, Bi-бислои,ван-дер-ваальсовые соединения, кристаллическая структура, метод Ритвельда, топологический изолятор.*