

REFINEMENT OF THE CRYSTAL STRUCTURE OF MnBi_2Te_4 I.R. AMIRASLANOV, P.A. ASKEROVA, Z.S. ALIYEV, Y.R. ALIYEVA,
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Interest in magnetic topological insulators is growing every day. Among topological insulators, MnBi_2Te_4 is considered more promising. Due to its antiferromagnetic properties, it can be used in spintronic and quantum electronics. The authors of this work were the first to grow a single-phase ingot of MnBi_2Te_4 , refined the crystal structure, and examined the mutual solubility in the cationic sites of Mn and Bi. It is shown that such solubility is optional and depends on technological procedures. In addition to the seven-layer package characteristic of MnBi_2Te_4 , a new site was also found to be partially present.

Key words: Topological insulator, phase transition, structure.

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1. INTRODUKTION

The integration of ferromagnetism in layered chalcogenide semiconductors with the properties of topological insulators (*TI*) and thermoelectric materials (*TE*) has attracted much attention in recent years. *TI* are insulators in bulk, but have metallic conductivity on the surface due to the presence of clearly defined topological surface states [1]. The charge carriers have spin polarization and are completely protected from defect scattering due to time reversal symmetry (*SOW*), which leads to almost non-dissipative currents. The aforementioned quantum effects occur in magnetic topological insulators (*MTI*), when a magnetic ion destroys and opens the energy gap in the surface state [2]. In the context of *TI*, the compounds MnBi_2Se_4 and MnBi_2Te_4 have recently been the cause of great research activity. The ferromagnetic seven-layer films of these compounds were grown by various authors either by molecular beam epitaxy alone or on the surface of a tetradymite-like *TI* [3], also by intercalation between five-layer *TI* packets [4-6], which are promising platforms for realizing quantized anomalous Hall effects [7,8], magnetoelectric effects [9-11] and the state of the axion insulator [12, 13]. MnBi_2Te_4 was described as the first antiferromagnetic *TI* [14,15], the observation of which can lead to such exotic phenomena as axion electrodynamics [16] and hinged Majorana modes [17]. Due to the growing *MTI* boom, detailed studies of ternary compounds in *MTM-A^V-Chalcogenide* systems (*MTM*=magnetic transition metal $3d3-6$; A^V =Sb, Bi; Chalcogenide=Se, Te) are of significant interest in the context of chemical and structural modeling of new *MTI* and *TE*. The great interest in these systems is due to the hope of obtaining a number of homologous compounds with controlled compositions and properties. It is known that several layered ternary phases are formed in the Mn-Bi-Te system [18]. The crystal structure of Bi_2Te_3 , solved in the middle of the last century, is also layered and is characterized by the structural type of tetradymite [19, 20]. The five-story packages (or slabs) of this structure are composed of five atomic layers: Te-Bi-Te-Bi-Te. The alternation of these packets along the c axis form Bi_2Te_3 (-5-5-5-) crystals. The addition of Mn atoms to

the composition promotes the formation of seven-story layers of the type Te-Bi-Te-Mn-Te-Bi-Te. Accordingly, the crystal structure of MnBi_2Te_4 is formed by alternating similar layers along to the c axis (-7-7-7-). The crystal structure of MnBi_2Te_4 was solved by Korean scientists based on X-ray powder data [21]. However, obtaining high-quality crystals of this compound in monophasic form is not an easy task. Usually the x-ray analysis of the ingots obtained by melting the elements taken in the ratios corresponding to MnBi_2Te_4 showed that the final product consists of a mixture of several phases. Studies have shown that these phases correspond to compounds of the mixed layer type, which are formed from five and seven layer slabs in different ratios. Therefore, it was necessary to study the phase formation in the Mn-Bi-Te system. For this purpose, in our previous work [18], we carried out syntheses in various stoichiometric ratios in the range Bi_2Te_3 - MnBi_2Te_4 and refined the crystal structures of the homologous phases MnBi_2Te_4 , MnBi_4Te_7 and $\text{MnBi}_6\text{Te}_{10}$ by the Rietveld method. In all cases, the morphological characteristics of the obtained crystals indicate their belonging to the layered structures of the Van der Waals type. Numerous articles published in recent years on Mn-containing *TIs* show that not many still manage to isolate single-phase pieces of at least a few millimeters in size [22, 23]. Also, the quality of crystals grown by the Bridgman method did not correspond to obtaining high quality single-crystal diffraction data. As noted above, the magnetic properties of MnBi_2Te_4 are currently widely studied both experimentally and theoretically. Correlation between these results requires more accurate structural data. One of these parameters is the interchange of metal atoms Mn and Bi, which is necessary for an accurate assessment of magnetic properties, for example, phase transitions of the paramagnetic-antiferromagnetic type. However, in the aforementioned work [21], the degree of mutual solubility in cationic positions was not determined, but it was considered that they were occupied by one type of atoms. In fact, for various reasons, they can partially deal with other atoms involved in synthesis. Such reasons may be the proximity of atomic or ionic radii, the presence of free positions in the structure, better

satisfaction of local valence balances (*LVB*), etc. There are similar reasons in the structure of the tetradymite type. For example, in the Bi_2Te_3 structure, Bi atoms are noticeably shifted from the center of the octahedrons.

Apparently, the main reason for this shifting is an improvement in *LVB* values. In the idealized structure of Bi_2Te_3 , the *LVB* value for tellurium atoms in the central layer is 3 electrons, and for the outer layers of blocks, 1.5e. The shifting of Bi atoms towards Te atoms in the outer layers reduces this large difference in real structures. In seven-layer packets, the presence of more divalent Mn^{+2} atoms provide additional opportunities for improving TWT. In this case, the substitution of some of the Bi^{+3} atoms by the Mn^{+2} atoms lead to a similar result.

In recently published papers [18, 24], this issue was discussed. The authors show that such a cationic substitution does exist. They experimentally established that the central cationic layer of the seven-story package of MnBi_2Te_4 is populated with 85% Mn + 15% Bi atoms, and in the other cationic layer 10% of Bi atoms are replaced by Mn atoms. Nevertheless, it is still impossible to say that the noted values of mutual solubility are optimal for 7-storey blocks, or does it depend on the technological conditions of synthesis? Therefore, it is impossible to consider the issue of solubility in cationic positions solved, and obtaining new data on the basis of various samples is necessary.

2. THE EXPERIMENTAL PART

2.1. Material preparation

First, the binary compounds MnTe and Bi_2Te_3 were synthesized from bismuth, manganese, and tellurium elements (all 99.999 wt%) purchased from Alfa Aesar. The synthesis was carried out in sealed quartz ampoules by melting elements taken in stoichiometric ratios at 1180 and 630°C, respectively. Avoid to the reaction of manganese with silicon dioxide during melting, the inner wall of the ampoule was previously coated with graphite by thermal decomposition of acetone in a medium with a low oxygen content. And MnBi_2Te_4 was synthesized from previously prepared MnTe and Bi_2Te_3 by direct melting at 980°C for 8 hours. After that, polycrystalline alloy samples were pulverized, pressed into tablets, and annealed at 575°C for 750 hours. As a result, a single-phase polycrystalline MnBi_2Te_4 was obtained.

2.2. Refinement of the crystal structure of MnBi_2Te_4

The crystal structure was refined by the Rietveld method based on X-ray powder diffraction data obtained on a “D2 Phaser” diffractometer, and all calculations were performed using the Topas 4.2 software (Bruker, Germany). The results obtained are shown in tables 1-3 and in fig. 1-3.

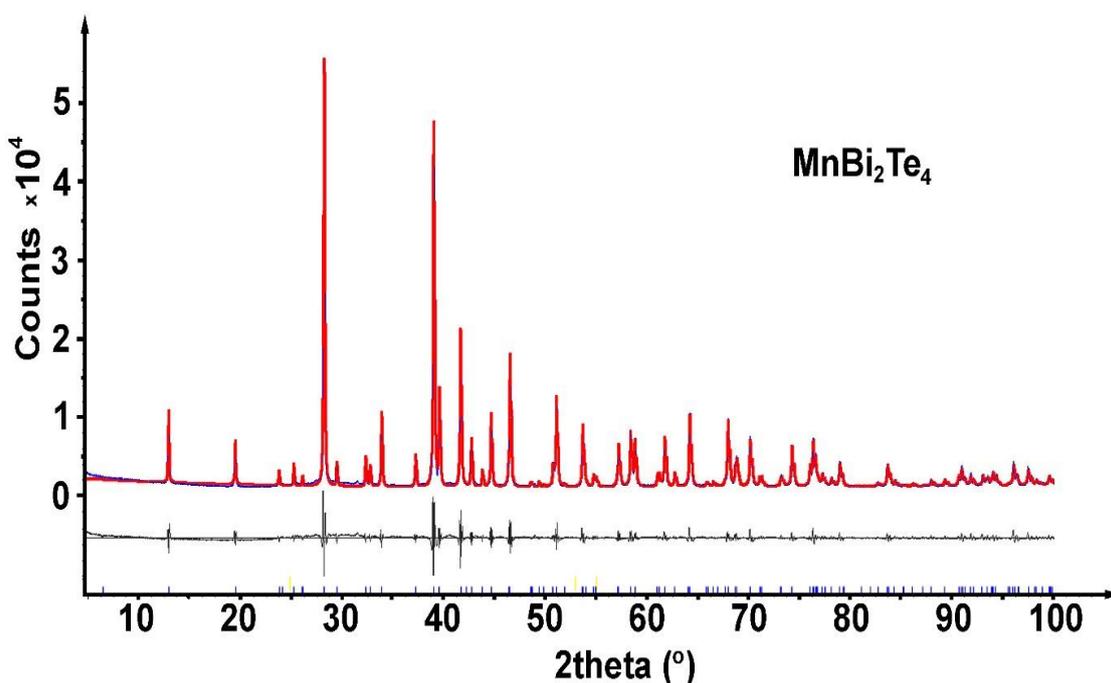


Fig. 1. Experimental, calculated by Rietveld (almost identical upper profiles of blue and red) and difference diffraction profiles (below) of MnBi_2Te_4 crystals.

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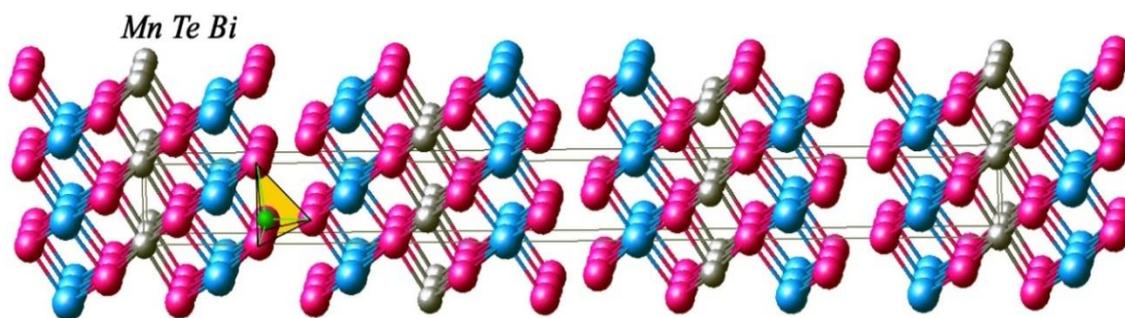


Fig. 2. Crystal structures of MnBi₂Te₄: projection of the structure onto the (100) plane. Interlayer tetrahedral position highlighted in yellow

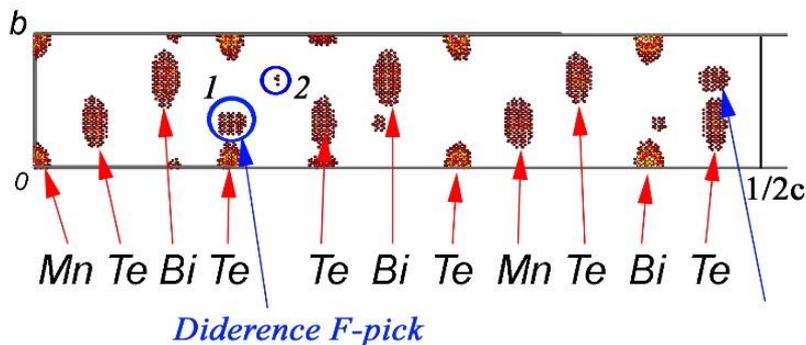


Fig 3. The position of difference flourier picks in F-map

Table 1.

Crystallographic data of the crystal structure of MnBi₂Te₄

Characteristic	Value
M (q/mol)	983.298
Z	3
Syngonia	Trigonal
Prost. Group (No.)	R-3m (166)
Radiation	Cu-K α_1 ($\lambda = 1.540596 \text{ \AA}$)
2 θ interval ($^\circ$)	$5 \leq 2\theta \leq 100$
R-Bragg (%)	1.542
Cell Parameters:	
a (\AA)	4.3304(1)
c (\AA)	40.956(2)
Cell Volume (\AA^3)	664.87(2)
X-ray density (g / sm ³)	7.32(5)

Table 2.

Refined coordinates of atomic positions and inter-atomic distances of MnBi₂Te₄ crystals.

Site	Np	X	Y	Z	Atom	Occ	Beq
Mn	3	0	0	0	Mn ⁺²	1.02(3)	0.5
Bi	6	0	0	0.4230(2)	Bi ⁺³	0.98(2)	0.5
Te (1)	6	0	0	0.1344(2)	Te	1	0.5
Te (2)	6	0	0	0.2924(3)	Te	1	0.5
Interatomic distances:						(Å)	
Mn – Te (2)						3.010(8)	
Bi – Te (1)						3.101(9)	
Bi – Te (2)						3.199(10)	

Table 3.

Refined coordinates of atomic positions and inter-atomic distances of MnBi₂Te₄ crystals, taking into account the occupation of the inter-slab's tetrahedral positions.

Site	Np	X	Y	Z	Atom	Occ	B _{eq}
Mn	3	0	0	0	Mn ⁺²	0.878(46)	1
Bi	6	0	0	0.4228(3)	Bi ⁺³	0.942(32)	1
Te(1)	6	0	0	0.1348(3)	Te	1	1
Te(2)	6	0	0	0.2923(4)	Te	1	1
Mn*	6	0	0	0.804(10)	Mn ⁺³	0.058(32)	1
Bi*	3	0	0	0	Bi ⁺³	0.122(46)	1
Interatomic distances:					(Å)		
Mn – Te(2)					3.012(8) x 6		
Bi – Te(1)					3.115(9) x 3		
– Te(2)					3.192(12) x 3		
Mn* – Te(1)					2.490		
– Te(2)					2.502 x 3		

The obtained diffraction pattern is uniquely indexed with the parameters of the rhombohedral cell of MnBi₂Te₄. On the other hand, the presence or absence of other homologous compounds (MnBi₄Te₇, MnBi₆Te₁₀, ...) in the sample is very easily determined by the *00l* type reflections using powder diffraction pattern. The fact is that a small value of the parameters *a* and *b*, as well as a multiply large value of *c*, always leads to the appearance of non-superimposed and sufficiently strong peaks of the *00l* type in the initial region of the diffraction pattern ($Cu, k\alpha; 5^\circ \leq 2\theta \leq 100^\circ$), which make it possible to unambiguously determine the phase sample composition. In the noted system, in addition to ternary homologous phases, binary compounds MnTe and MnTe₂ can also form. However, a detailed examination of the diffraction image did not confirm the presence of these phases. Thus, the sample under study consists exclusively of MnBi₂Te₄ crystals and the results of structure refinement presented in table 2. It can be seen from this table that, within the error, no substitution at cation positions (Mn↔Bi) is observed.

3. RESULTS AND DISCUSSIONS

The atomic coordinates given in table 2 were used to calculate the difference Fourier synthesis. On the

obtained Fourier map two peaks with a certain electron density were clearly seen. Both peaks are located in the inter-layer van der Waals space. The intensity of the first peak is several times stronger than the background level, while the second one is noticeably weak and should be ignored. In fig.3, these positions are indicated by numbers 1 and 2. Interestingly, peak-1 is tetrahedral surrounded by tellurium atoms. Previously, such a partial filling of the van der Waals space between blocks was established in a tetradymite-like structure gamma-In₂S₃, stabilized by the addition of As or Sb [25]. Consequently, the formation of such tetrahedrons in the MnBi₂Te₄ structure looks quite possible. Therefore, we are inclined to believe that, in fact, a previously unobserved new cation position is formed in MnBi₂Te₄ crystals. The refinement of the structure with the addition of Mn atoms to this position corresponded to their approximately six percent occupation. These results are shown in table 3.

Apparently, the occupancy factors of cationic positions depend on the technological process and, to a certain extent, can be used to control the properties of these materials. Thus, new syntheses and further research on this issue are still needed.

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