

HOMOLOGOUS SERIES OF LAYERED TETRADYMITE-LIKE COMPOUNDS IN Bi-Te AND GeTe-Bi₂Te₃ SYSTEMS

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Formation of the homologous series of layered compounds $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$ and $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ is analyzed. For both series, the crystal structure contains two-layer (Bi_2 or GeTe) and five-layer (Bi_2Te_3) packets perpendicular to the c axis. Unlike the Bi_2 packets, the GeTe packets do not retain their individuality during crystal structure formation; they are linked to the Bi_2Te_3 five-layer packets to form new multilayer packets leading to a considerable change in the character of interatomic interactions.

Bismuth-tellurium alloys possess interesting thermoelectric, galvano-, and thermomagnetic properties [1, 2]. This explains the interest of researchers in the phase diagram of the Bi-Te system and in the structural characteristics of crystalline compounds in this system. Experimental data were critically reviewed and a qualitative model of the diagram was constructed [3]; this led to a conclusion that intermediate phases with narrow homogeneity regions of Bi_2Te_3 and $\text{Bi}_{14}\text{Te}_6$ and of the solid solutions β and γ exist in the ranges 33.3-36.6 and 44.7-58.1 at. % Te, respectively. Data on $\text{Bi}_{2(n+m)}\text{Te}_{3m}$ (n and m are prime integers) [4-12] show that their composition corresponds either to the regions of existence of solid solutions or to the two-phase regions on the phase diagram. A similar situation takes place for the Bi_2Te_3 -GeTe system. Its phase diagram [13] indicates the presence of two compounds of constant composition, $\text{Ge}_3\text{Bi}_2\text{Te}_6$ and GeBi_2Te_4 , and of solid solutions based on GeBi_2Te_7 . Later it was shown that about a dozen constant-composition phases $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ are additionally formed in this system [14-21]. For most phases found up to now, n or m is unity. The compositions of these phases lie in the two-phase regions of the phase diagram described in [13]. Thus, in conditions of DTA experiment, not all compounds which are present in the systems show up on the phase diagrams. Consequently, the sections of the diagrams in the region of crystallization of the above homologous series constructed using traditional methods probably reflect the conditions of metastable equilibria, in which only few constant-composition phases and metastable solid solutions crystallize. The existence of a wide range of compounds not reflected on the diagrams justifies a revision of the latter. To analyze possible reasons for the discrepancy between the DTA data and the results of synthetic works for the systems under study, it would be appropriate to consider structural data for constant-composition crystalline compounds and solid solutions in Bi-Te and GeTe-Bi₂Te₃ systems. Therefore, the aim of the present work is to summarize crystal data on compounds and solid solutions in the homologous series $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$ and $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$. To explain the peculiarities of formation of these phases, it would be useful to know the tendencies of lattice parameter variation depending on the ratio between n and m described below.

HOMOLOGOUS SERIES OF LAYERED COMPOUNDS $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$

For compounds in this series, the composition is defined by two parameters, that is, all of these compounds belong to a homologous matrix composed of the homologous series satisfying the conditions $n = \text{const}$ or $m = \text{const}$.

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The compounds $\text{Bi}_{2(n+m)}\text{Te}_{3m}$ are constructed as ordered combinations of the fragments of the Bi_2Te_3 and bismuth structures. The former is based on the nine-layer rhombohedral packing of tellurium atoms with bismuth atoms filling the voids in such a way that two layers of voids are filled completely and one layer is empty [22, 23]. This structure may also be regarded as a packing of five-layer packets $\text{Te}(1)\text{BiTe}(2)\text{BiTe}(1)$. A comparison of the $\text{Bi}-\text{Te}(1)$ and $\text{Bi}-\text{Te}(2)$ bonds (0.324 and 0.304 nm, respectively) with the sums of the ionic and covalent radii leads one to conclude that the bonds are ionic and covalent [23]. The distance between the neighboring $\text{Te}(1)$ atoms in the lattice (0.373 nm) is much shorter than the van der Waals diameter of tellurium (0.44 nm); this implies the presence of a weak valence bond between the packets, with the partially occupied sp^3d^2 orbitals being responsible for the bond [23]. The rhombohedral bismuth lattice consists of double layers with each atom having three nearest neighbors from its own layer and three, lying slightly farther away, from the neighboring layer [23]. The distance between the neighboring bismuth atoms belonging to different layers is shorter than the van der Waals diameter of bismuth; therefore, we again have chemical binding between the layers [2]. The Bi_2Te_3 and bismuth structures may also be represented as a packing of 3^6 nets which are parallel to the base plane [2, 23]. This ensures compatibility between the Bi_2Te_3 tetradymite five-layer packets and the Bi_2 double layers and hence formation of mixed structures from these building units.

Table 1 lists the crystal data and the conditions of preparation and thermal treatment of layered phases in the $\text{Bi}-\text{Te}$ system. Lattice parameters are given for a hexagonal structure. This description provides information about the mutual arrangement of atomic layers and ensures easy determination of atomic coordination, interatomic distances, etc. The number of layers in the unit cell is related to the composition of the compounds by the equation

$$N = Z(2n + 5m). \quad (1)$$

If $(2n + 5m)$ is a multiple of three, $Z = 1$ (space group $P3m1$); otherwise, $Z = 3$ (space group $R3m$).

Superposition of the two types of layer packet in the structure of $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$ leads to mutual distortion of the packets. As a consequence, the a parameter monotonically increases as the phase composition changes from Bi_2Te_3 to Bi . Figure 1 shows that this dependence is linear if the $x = m/(n + m)$ coordinate is chosen to be the relative number of Bi_2Te_3 packets.

The molar fraction of tellurium in the compounds is defined by the expression $z = 3m/(2n + 5m) = 3x/(3x + 2)$. For an arbitrary z specified with finite accuracy, one can always select the values of m and n strictly or roughly satisfying the formula. In this case, however, N changes nonmonotonically with growth of z , leading to nonmonotonic variation in the c parameter. For example, for the compounds Bi_8Te_9 and $\text{Bi}_{26}\text{Te}_{30}$ with close compositions, the number of layer packets in the unit cell differs threefold. Several layered structures were found (Table 1) whose c parameter is up to several dozens nanometers and which contain up to 258 atomic layers in a cell [10]. Therefore, it would be more correct to use packets of intermediate thickness and $c' = c/(n + m)$. Figure 1 shows the linear dependences of c' on x . The existence of the linear dependences $a = f(x)$ and $c' = f(x)$ reflects the general principle of crystal structure formation for $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$, namely, the additivity of superposition for the two types of layer packet differing in size: two-layer Bi_2 and five-layer Bi_2Te_3 . This relationship between the c parameter and the composition was used by Imamov and Semiletov to predict the structural characteristics of layered phases in $\text{A}^{\text{V}}-\text{B}^{\text{VI}}$ systems [9]. Note that the XRD data [3-10] for compounds with different backgrounds are adequately described by the general linear dependences.

Prolonged annealing and crystal growing from melt and gas phase are the basic procedures for the preparation of compounds in the series under analysis. It is noteworthy that phases with a large c parameter were obtained by the first method. It was used by Brebrick to prepare melts with compositions from 50.0 to 57.0 at. % using homogenizing annealing at 450°C every 1 at. % (that is, in the region slightly lower than the solidus line); he noted that this interval contains no two-phase regions [10]. He concluded that a continuous sequence of ordered phases is formed which he interpreted as solid solutions existing in the composition interval under study. For formation of solid solutions, it is not necessary to assume formation of ordered phases for arbitrary n and m . It was also suggested [10] that antistructural defects in the form of tellurium atoms may arise in the bismuth layers of Bi_4Te_5 . These or other defects must lead to a homogeneity region in the compounds. If there is a series of compounds where these regions overlap for compounds with close compositions, a sequence of phases of variable composition with narrow two-phase regions between them may be formed. If the widths of the regions are comparable within the error of composition determination for the samples, the sequence may be interpreted as a continuous series of solid solutions. Formation of this series requires

TABLE 1. Crystal Data for $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$

Formula	a, nm	c, nm	N	Procedure	Refs.
Bi_2	0.45461	1.18623	6		[4]
$\text{Bi}_{14}\text{Te}_{16}$ ($5\text{Bi}_2 \cdot 2\text{Bi}_2\text{Te}_3$)	0.447	11.904	60	Zone melting	[5]
Bi_2Te ($2\text{Bi}_2 \cdot \text{Bi}_2\text{Te}_3$)	0.449	1.089	9	Calculation	[9]
Bi_4Te_3 ($\text{Be}_2 \cdot \text{Bi}_2\text{Te}_3$)	0.443	4.189	21	Zone melting	[8]
Bi_4Te_3 ($\text{Bi}_2 \cdot \text{Bi}_2\text{Te}_3$)	0.4451	4.1888	21	Annealing at 733 K for 53 days	[11]
Bi_6Te_5 ($4\text{Bi}_2 \cdot 5\text{Bi}_2\text{Te}_3$)	0.445	6.675	33	Calculation	[9]
Bi_8Te_7 ($5\text{Bi}_2 \cdot 7\text{Bi}_2\text{Te}_3$)	0.445	9.108	45	Calculation	[9]
$\text{Bi}_{22}\text{Te}_{21}$ ^a ($4\text{Bi}_2 \cdot 7\text{Bi}_2\text{Te}_3$)	0.44324	25.799	129	Powder annealing with 50 at. % Te at 723 K for 170 h	[10]
Bi_2Te_2 ($\text{Bi}_2 \cdot 2\text{Bi}_2\text{Te}_3$)	0.440	2.397	12	Cooling in a melt at a rate of 5 deg/h	[5]
Bi_2Te_2 ($\text{Bi}_2 \cdot 2\text{Bi}_2\text{Te}_3$)	0.4423	2.4002	12	Annealing at 823 K for 14 days	[11]
Bi_2Te_2 ($\text{Bi}_2 \cdot 2\text{Bi}_2\text{Te}_3$)	0.44296	2.4017	12	Powder annealing with 51 at. % Te at 723 K for 170 h	[10]
$\text{Bi}_{32}\text{Te}_{33}$ ^b ($5\text{Bi}_2 \cdot 11\text{Bi}_2\text{Te}_3$)	0.44264	39.0434	195	Powder annealing with 52 at. % Te at 723 K for 370 h	[10]
$\text{Bi}_{14}\text{Te}_{15}$ ^c ($2\text{Bi}_2 \cdot 5\text{Bi}_2\text{Te}_3$)	0.44249	17.4329	87	Powder annealing with 53 at. % Te at 723 K for 370 h	[10]
$\text{Bi}_{26}\text{Te}_{29}$ ^d ($10\text{Bi}_2 \cdot 29\text{Bi}_2\text{Te}_3$)	0.44215	33.0936	165	Powder annealing with 54 at. % Te at 723 K for 370 h	[10]
Bi_8Te_9 ($\text{Bi}_2 \cdot 3\text{Bi}_2\text{Te}_3$)	0.441	~ 10.3	51	Single crystal plates, transport with iodine	[12]
$\text{Bi}_{26}\text{Te}_{30}$ ^e ($3\text{Bi}_2 \cdot 7\text{Bi}_2\text{Te}_3$)	0.44178	33.7286	168	Powder annealing with 55 at. % Te at 723 K for 170 h	[10]
Bi_6Te_7 ($2\text{Bi}_2 \cdot 7\text{Bi}_2\text{Te}_3$)	0.4421	7.8201	39	Powder annealing with 55 at. % Te at 798 K for 160 h	[10]
$\text{Bi}_{32}\text{Te}_{39}$ ^f ($3\text{Bi}_2 \cdot 13\text{Bi}_2\text{Te}_3$)	0.44134	42.842	213	Powder annealing with 56 at. % Te at 723 K for 170 h	[10]
Bi_4Te_5 ($\text{Bi}_2 \cdot 5\text{Bi}_2\text{Te}_3$)	0.44108	5.4331	27	Powder annealing with 57 at. % Te at 798 K for 170 h	[10]
Bi_4Te_5 ($\text{Bi}_2 \cdot 5\text{Bi}_2\text{Te}_3$)	0.44114	5.4318	27	Powder annealing with 57 at. % Te at 823 K for 170 h	[10]
$\text{Bi}_{38}\text{Te}_{48}$ ^g ($3\text{Bi}_2 \cdot 16\text{Bi}_2\text{Te}_3$)	0.44085	51.9735	258	Powder annealing with 57 at. % Te at 723 K for 330 h	[10]
Bi_2Te_3	0.43835	3.0487	15	Films	[21]

^{a-g} Brebrick phases are quoted because of a certain indeterminacy of their composition associated with the ambiguity of indexation of powder X-ray diffractograms for long-spacing structures.

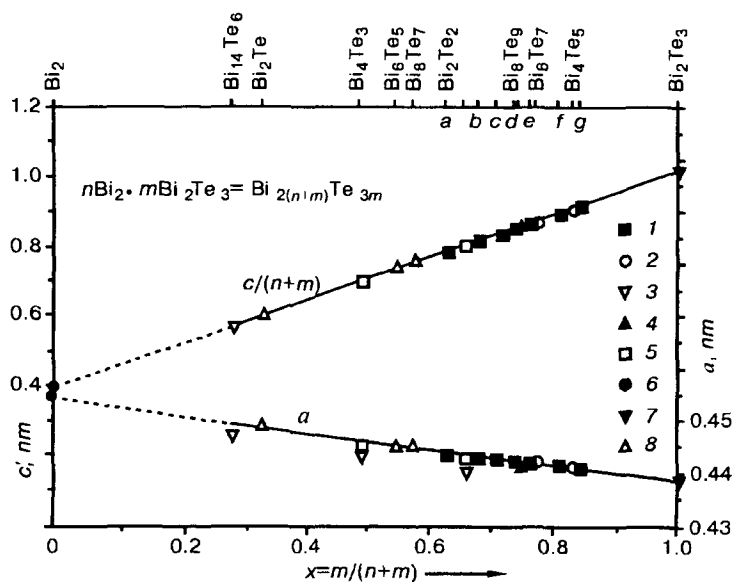


Fig. 1. Plot of the lattice parameters a and c' ($c' = c/(n+m)$), where $(n+m)$ is the total number of layer packets per unit cell vs the relative number of five-layer packets Bi_2Te_3 $x = m/(n+m)$ in the structure of $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3 = \text{Bi}_{2(n+m)}\text{Te}_{3m}$. 1) [10] annealing at 723 K, 2) [10] annealing at 798 K, 3) [8], 4) [12], 5) [11], 6) [4], 7) [21], 8) [12].

a finite set of coefficients m and n ; the wider the homogeneity region, the smaller the set. The available data indicate that only minor deviations from stoichiometry may take place; therefore, the lattice parameters of the compounds are almost constant within the homogeneity region. The above-formulated additivity rule is satisfied when this condition is met.

Zone melting [8], slow cooling of melt [5], or gas transport reactions [12] lead to formation of phases containing up to four two- and five-layer packets in the unit cell. An exception is the $\text{Bi}_{14}\text{Te}_6$ phase, which seems to be stable since it is present on the phase diagram obtained by the DTA method [3] and occurs in nature as a mineral [9]. These facts may be explained as follows. Formation of layered phases by annealing at temperatures below the solidus leads to compounds whose composition is equivalent to the general composition of the starting mixture. This brings about a virtually continuous series of constant-composition phases whose set may be regarded as solid solutions. The case is similar for fast crystallization of melt used to obtain the cooling thermogram. Sample preparation by hardening followed by annealing used for determining the solidus from the heating thermogram lead to the same result. Note that homogenizing annealing of solid solutions cannot lead to decomposition into a mixture of constant-composition phases with lower Gibbs energies as this would require a complete rearrangement of the crystal lattice, which is only possible in the presence of a melt or an active gas phase. When zone melting is conducted in typical conditions, the sample cooling rate is approximately one order lower than in DTA. In these conditions, phases are formed which are in thermodynamic equilibria with the melt. An analogous situation takes place when selective crystallization is used, which is typically realized in slow cooling conditions. Gas phase crystallization also provides nearly equilibrium conditions. Thus one can speak about two phase diagrams of the Bi-Te system. The first diagram, corresponding to DTA or solid state synthesis conditions, contains extensive regions of solid solution and is metastable. The second corresponds to thermodynamic equilibrium conditions; it was not yet studied in the region of layered phase formation. Its construction requires synthesis of a complete set of equilibrium compounds in this system as well as DTA and XRPA *in situ* investigations of decomposition on heating for these compounds or for samples hardened against temperatures near thermal effects.

HOMOLOGOUS SERIES OF LAYERED COMPOUNDS $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$

The structural similarity between the compounds in the Bi–Te system and in the homologous series $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ is due to the existence of the low-temperature modification α -GeTe with a structure related to the bismuth structure. The phase is rhombohedral of α -As type (space group $R\bar{3}m$) with parameters $a = 0.5986$ nm, $\alpha = 88.35^\circ$ [24] or $a = 0.5977$ nm, $\alpha = 88.30^\circ$ [25] ($a = 0.4163$ nm and $c = 1.0657$ nm for the hexagonal setting). The lattice is of distorted NaCl type in which the Ge and Te sublattices are shifted relative to each other along the $\langle 111 \rangle$ axis [24, 25]. This gives rise to two-layer packets which are analogous to those observed in the Bi structure but have stronger interatomic interactions inside the packets compared to interpacket interactions.

The compounds $\text{Ge}_3\text{Bi}_2\text{Te}_6$, GeBi_2Te_4 , and GeBi_4Te_7 found in a phase diagram study for the GeTe– Bi_2Te_3 quasibinary system [13] are formed by peritectic reactions at 923, 857, and 837 K, respectively. The crystal structures were determined by thin film electron diffraction analyses [14–16] and by powder and single crystal XRD analyses [17, 18]. The layered structure of the ternary compounds is cubic closest packing of Te layers with Ge and Bi atoms engaged in the octahedral voids. The cations occupy only some of the octahedral voids of the anionic sublattice. The void layers alternate with the germanium, bismuth, and tellurium multilayer packets formed due to the ionic and covalent interatomic bonds. The weaker interpacket bonds are due to both van der Waals interactions and partially occupied sp^3d^2 orbitals.

The unit cell of $\text{Ge}_3\text{Bi}_2\text{Te}_6$ consists of three eleven-layer packets $\text{TeGeTeBiTeBiTeGeTeGeTe}$, the unit cell of GeBi_2Te_4 contains three seven-layer packets TeBiTeGeTeBiTe , and the structure of GeBi_4Te_7 involves one seven-layer packet and one five-layer packet $\text{TeBiTeBiTe} \square \text{TeBiTeGeTeBiTe}$. The rectangle denotes the void layer in the anion packing. Note that, according to [14–16], the cation layers of Ge or Bi atoms exist only in the structures of thin films. In the structures of single crystals obtained from melts, there are mixed cationic layers [18].

A homologous series of layered compounds $n\text{GeTe} \cdot \text{Bi}_2\text{Te}_3$ ($n = 1, \dots, 9$ and possibly up to 18) was found in electron diffraction and high-resolution electron microscopy studies [19] on samples annealed at temperatures of 570–620 K for 300–500 h. In addition to the homologous series $n\text{GeTe} \cdot \text{Bi}_2\text{Te}_3$, layered compounds $\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ ($m = 1, \dots, 4$ and possibly $m > 4$) were found [20]. The existence of the $\text{Ge}_2\text{Bi}_2\text{Te}_3$ phase with a nine-layer lattice and of the $\text{Ge}_4\text{Bi}_2\text{Te}_7$ phase with a 39-layer lattice was confirmed in an X-ray diffraction study [28].

As in the case of $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$, the crystal structure of $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ consists of two- and five-layer packets, but the two-layer packets of bismuth are replaced by the same packets of GeTe. The number of layers in the unit cell of $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ is also specified by Eq. (1), given above for $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$. An essential difference between the crystal structures of the two homologous series lies in the fact that in $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ the GeTe packets do not retain their individuality as the BiBi packets do but are linked to the five-layer packets to form new multilayer packets. As a result, the character of interatomic interaction changes dramatically. In the structures of $n\text{Bi}_2 \cdot m\text{Bi}_2\text{Te}_3$, the octahedral void layers of the anionic packing separate the BiBi and Bi_2Te_3 packets, but in the structures of $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ they separate the new multilayer packets. This is illustrated by Fig. 2 showing the structures of Bi_4Te_3 [11] (a) and GeBi_2Te_4 [18] (b) projected the (1120) plane. The number of atomic layers in the unit cell of the two compounds is the same ($N = 21$) but, as follows from the given interatomic distances, the chemical bonding in Bi_4Te_3 and GeBi_2Te_4 differs significantly. In the structure of Bi_4Te_3 (Fig. 2a), the two- and five-layer packets alternate (525252...) down the c axis. The distance between the packets (0.3401 nm) is far longer than the interatomic distances within the five-layer packets or within the Bi–Bi packets (0.3098 nm). In the structure of GeBi_2Te_4 (777...) (Fig. 2b), there are no individual two-layer GeTe packets or five-layer Bi_2Te_3 packets. The unit cell contains three seven-layer packets $\text{Te}_3\text{Me}_2\text{Te}_4\text{Me}_1\text{Te}_4\text{Me}_2\text{Te}_3$ (Me1, Me2 are mixed Ge,Bi-cationic layers) with weak interpacket bonds. The interpacket distance (0.365 nm) is much longer than the distances in the packets.

The violated additivity of contributions of the two- and five-layer packets to the c constant in GeBi_2Te_4 leads to a smaller c constant ($c = 4.127$ nm [18]) for this compound compared to Bi_4Te_3 ($c = 4.1888$ nm [11]). This is explained not only by the greater radius of Bi compared to Ge but also by the different numbers of “gaps” between the packets in the unit cells of Bi_4Te_3 (six gaps) and GeBi_2Te_4 (three gaps).

Figure 3a presents the dependence of c/N on the relative number of Bi_2Te_3 packets in the structures of $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$. The parameter c/N is the “average” thickness of the atomic layer, which depends on the contribution of the cationic and anionic layers as well as of the interpacket gaps to the c constant. The nonlinearity of the dependence $c/N = f(x)$ [$x = m/(n + m)$] reflects the nonadditivity of addition of the two- and five-layer packets in the structure

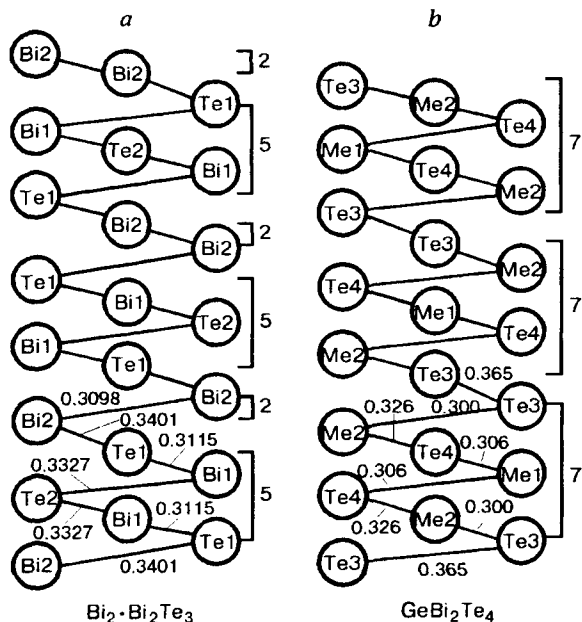


Fig. 2. Structures of Bi_4Te_3 (a) [11] and GeBi_2Te_4 (b) [18] projected on the (1120) plane. The five-, two-, and seven-layer packets are denoted by 5, 2, and 7, respectively.

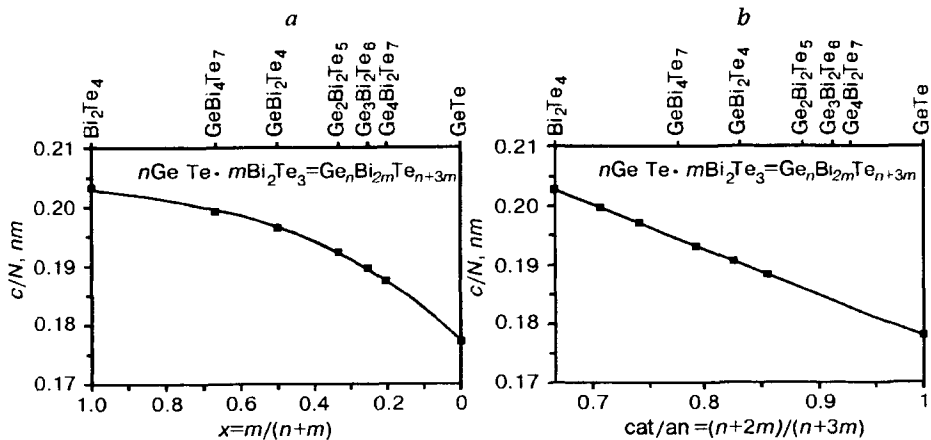


Fig. 3. Dependence of the average thickness of the atomic layer c/N (N is the number of layers per unit cell) on the relative number of five-layer packets $x = m/(n+m)$ (a) and on the cation to anion ratio $\text{cat}/\text{an} = (n+2m)/(n+3m)$ (b) in $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$.

of $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$. An analysis of the crystal structures of $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$ shows that the cation to anion ratio $\text{cat}/\text{an} = (n+2m)/(n+3m)$ plays a key role in their formation [18]. For the binary compounds Bi_2Te_3 and $\alpha\text{-GeTe}$, the ratio is $2/3$ and 1 , respectively. For ternary layered compounds, the ratio is between $2/3$ and 1 . Figure 3b presents the dependence of c/N on the cation/anion ratio in the structures of $n\text{GeTe} \cdot m\text{Bi}_2\text{Te}_3$. The dependence $c/N = f(\text{cat}/\text{an})$ is nearly linear, in agreement with the basic principle underlying the structure formation of the given layered compounds.

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