

## THE LAYERED SUPRASTRUCTURES ON THE BASE OF SEMICONDUCTOR SYSTEMS: Bi<sub>2</sub>Te<sub>3</sub>-METAL AND PbTe(PbS)-NiSb

S.Sh. KAKHRAMANOV

*Scientific-industrial unity "Selen" of National Academy of Sciences of Azerbaijan Republic, Baku*

E.M. DERUN, M.G. PISHKIN

*Yildiz Technical University, Department of Chemical Engineering, Istanbul, Turkey*

The considered review and clathratus analysis of misfit eutectic compounds PbTe(PbS)-NiSb, layered chalcogenides allows to consider the inorganic systems in the capacity of molecular construction fragments for the directed design of nano-dimension order layered supramolecular compounds.

The layered systems ("sandwiches") on the base of Bi<sub>2</sub>Te<sub>3</sub>-Cu, Bi<sub>2</sub>Te<sub>3</sub>-B, Bi<sub>2</sub>Te<sub>3</sub>-Ni, Bi<sub>2</sub>Te<sub>3</sub>-Nb, Bi<sub>2</sub>Te<sub>3</sub>-Sn, Bi<sub>2</sub>Te<sub>3</sub>-S are obtained by the method of vertical directed crystallization. The alternation of following structural blocks takes place in these structures:

(Bi-Te<sup>(1)</sup>-Cu-Te<sup>(1)</sup>...), (Bi-Te<sup>(1)</sup>-B-Te<sup>(1)</sup>...), (Bi-Te<sup>(1)</sup>-Ni-Te<sup>(1)</sup>...), (Bi-Te<sup>(1)</sup>-Nb-Te<sup>(1)</sup>...), (Bi-Te<sup>(1)</sup>-Sn-Te<sup>(1)</sup>...), (Bi-Te<sup>(1)</sup>-S-Te<sup>(1)</sup>...).

These structures can be related to the compound parts of supramolecular ensemble, where Bi<sub>2</sub>Te<sub>3</sub> frame is in the capacity of master for the fascinated atoms-guests (Cu, Ni, Sn, S, Nb and B). Probably, the layered structure Bi<sub>2</sub>Te<sub>3</sub> can be formed in clathratuforming system with nano-structural fragments.

### Introduction

The modern statements on the directed design of supramolecular systems on the base: layered misfit compounds, clathratustructures and silicates with frame structures, layered structures with variable dimension of structural planes, layered compounds with variable dimension of structural planes with "guests" of different dimension in the "master" lattice, matrix crystals are considered in [1-3].

The analysis shows, that the dimensions and forms of matrix and "guest" (cluster) molecules play the main role in organization of the regularities of suprastructural layered misfit compounds, clathratus and silicates with frame structures, different intercalated layered compounds.

In the ref [1] it is emphasized, that intercalates, clathratustructures and structures of "guest-master" type exist only in solid state. These structures aren't discreet supramolecules, and are related to solid supramolecular ensembles. The "guests" ensembles in the "longitudinal" master structures and discreet supramolecules are emphasized. The one-, two- or three-dimensional continuous or half-continuous crystal formations with ion or covalent connection character are meant under the conception "longitudinal" structures. Nowadays, the circle of these objects is drawn approximately. However, the some object classification of supramolecular inorganic chemistry takes place. They are related to [2]: intercalates with "guests" of different dimensions in "master" lattice, clathratustructures, silicates with frame structures. The study of the given objects, and also many-phased and other complex layered objects can give the information about new mechanisms of their creation.

The principle of complementary geometry and topology can be broken at the formation of inorganic supramolecular ensembles. The systems "guest-master" in the layered intercalates (for example, in the layered dichalcogenide matrix, graphite, clay) are especially emphasized in the ref [2]. The layers in the "master" lattice are connected because of the Van der Waalse interactions in them; the layers are opened at the "guest" introduction, and the change of interlayer distance is the test of the intercalate formation [3]. The value of this change depends on "guest" dimensions and

can exceed in 3-5 times the initial crystallographic parameter of "master" lattice.

It is known, that so-called "matrix crystals" are supramolecular ensembles of synthetic opal with blank spaces of the definite dimension, forming the regular cubic sublattice. The ("guest") forms the quazi-lattice with enormous big parameters at the filling of the blank spaces. The geometric disproportion of lattices is compensated by the deformation of the one of them ("guest").

Another example of "master" and "guest" disproportion is the intercalate variety in layered dichalcogenide matrix, which are misfit compounds. They also can be related to the objects of supramolecular chemistry.

Further, let's consider the some nano-chemistry objects, having the aim of the formation of closed and half-closed nano- and micro-reactors. The molecular constructions, which are able to reversibly "take prisoner" the "guest" molecules and set them at liberty, are formed. All these structures belong to the class of molecular containers, which are able to take prisoner the given molecules and set them at liberty at the condition changes [4].

From the one hand, the nano-chemistry produces the own objects which are nano-particles, nano-reactors, nano-containers, and from the other hand it uses the nano-particles' advantages, their unusual and pliable variable properties for the own needs. The two key conceptions: nano-particle and nano-reactor are defined. The nano-particle characterizes the dimension parameter. The nano-reactor defines the nano-particle function. The "empty" tube silicon fibers, which are one-dimension nano-reactors, have been created. The quazi-two-dimensional nano-reactors, which are hard graphite-like planes, connected by the bridges from carbonic chains, have been synthesized. The distances between graphite-like planes in such reactors can be varied [5].

The description of fundamentally new organization of chemical substance up-to-date, when the correspondence of dimensions and form of the one type molecules "guests" to the carcass cavities, constructed by other molecules "masters" has the significant meaning at the formation of the different materials, deserves attention. Such principle of compound formation allows us to join them in coordinating

form, i.e. saturated molecules are more stable thermodynamically, than impurity of the initial components [6].

The main conceptions of clathrate chemistry give the beginning of the deliberate search of submolecular formations. The clathrate investigation [7-9] helped to understand, why the molecules of initial components are able to join into thermodynamically stable phase at the entire absence of valency chemical connections between them.

It is need to consider the organization of chemical substance in the correspondence with dimensions and forms of molecules of matrix "guests" and "masters" [10-11].

The layered structures with variable dimension of structural cavities are needed to advisably use in the capacity of the two-dimensional nano-reactors. The layered structure accelerates the diffusion of the different substances in the interlayer space and thus, eases the chemical modification of the layered compounds. In this relation the works, dedicated to the synthesis of nano-composites with the use of layered matrixes are interest.

### **The supramolecular structures on the eutectic base**

The eutectics can be considered as supramolecular layered ensembles. In the ref. [12] the main statements of eutectic theories are analyzed and the review of more significant results, obtained at the investigation of eutectic melts of inorganic substances is given. The evidences in the proof of the supramolecular eutectic conception, taking into the consideration the interaction of disproportional structures and opening the formation mechanisms of supramolecular eutectic ensembles in the boundary layers ("on-line bases") are present. The numerous direct experimental confirmations of "interacting phases" conception exist [13-14].

The theoretic analysis proves the possibility of the self-organization of suprastructures from the structures, which are disproportional ones in the one crystallographic direction. The consideration of the eutectic compositions, which are at least disproportional ones on all three crystallographic directions in terms of the supramolecular chemistry allows to receive the answers on many questions and avoid the vaguenesses, mentioned at the discussion of the existing eutectic conceptions [12-14]. The supposed supramolecular conception in eutectic theory [12] doesn't reject the classic statements [12]. It differs from them only the fact, that abstract thermodynamic criterias, such as the surface energy or interfacial tension, are replaced by real parameters of interacting substructures: disproportion, hardness, interaction potential.

The presented experimental data can prove in the proof of supramolecular eutectic conception. The special properties of eutectic melts, dependence of their structures on synthesis conditions (temperature, cooling rate, mechanical interactions) are defined by quantity of on-line phase and degree of its organization [12].

It can be supposed, that eutectic is the system, characterizing by unified energy electron spectrum. The analysis of literature data allows us to conclude, that some chemical interaction takes place in eutectics on the inter-phase boundaries. However, the electron structure of eutectic and the reasons of its formation haven't cleared yet.

That's why we here pay attention to study of peculiarities of microstructure morphology, physico-chemical

properties of eutectic melts with the aim of the revealing of the nature of interphase interaction, proving in the proof of the supramolecular conception.

The aim of the present paper is the analysis and revealing of the usual laws in layered structures with "guest" elements in inorganic suprastructures such as: clathrate, eutectics, misfit compounds and layered systems with intercalates and impurities of different dimension in "master" lattice.

### **The investigation technique of eutectics and multi-layer structures**

The eutectic melts of the following systems: PbS(PbTe)-Sb, PbS(PbTe)-NiSb have been grown up by Bridgman method at the velocity  $v=3$  mm/h and temperature gradient  $\Delta T=100^\circ$  between heaters. The purity of the initial materials: Sb, Pb, S, Te was not less 99,999%.

Some microstructures were investigated on microscope MIM-7, on bitmapped electron microscope (REM) JSM-50A with device for local X-ray analysis and on electron microscope JSM-2000 in beams of secondary electron emission, in beams of transmitted electrons, X-ray images in beams: Te, S, Ni, Sb.

The multilayer structures of chalcogenide crystals of bismuth and stibium were grown up by method of vertical crystallization (at  $T\approx 700\pm 5^\circ\text{C}$  and velocity  $V=0,5\text{cm/h}$ ). The chalcogenide crystals Bi and Sb were obtained by the same way as clathrates by joint crystallization of "master" (Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>Se<sub>3</sub>) and "guest" (impurities). The electron microscope of type - JSM5410LV was used for study of surface morphology (0001) of layered crystals. The X-ray investigations of base chip surface (0001) of Bi<sub>2</sub>Te<sub>3</sub> and its solid solutions with Sb<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> were carried out on the X-ray diffractometer Philips Panalytical XRD (X-ray diffractometer). We don't present the X-ray diffractograms, however they prove about presence between layers Te<sup>(1)</sup> - Te<sup>(1)</sup> of nano-fragments from the introduced impurities (cuprum, nickel, niobium, tin, sulfur and bore).

### **Discussion of results.**

#### **The supra-structures in eutectics PbS(PbTe)-NiSb**

The regular order microstructures are character to eutectic melts (fig. 1(a,b) and 2(1-8)).

The previous investigations show, that structure in PbTe-NiSb, SnTe-NiSb, PbS-Ni systems is similar. Firstly let's consider the crystallization in PbTe-NiSb and PbS-NiSb systems. The PbTe-NiSb eutectic (fig. 1(b)) has fibrous structure, PbS-NiSb eutectic has plate structure (fig.2 (1-4)). The eutectics of (PbS-Sb) PbTeSb systems can be referred to the anomalous ones, limited by rod structure with paddle one of rods and planes. The investigated eutectic PbS-NiSb (fig. 2) can be referred to normal ones, i.e. to "regular" ones on form and phase distribution. Each structure grows with unified strictly delineated crystallization front, clearly revealing the contact surface of sub-blocks. The definite crystal-graphical relations, which are character for the given systems, that doesn't observed in anomalous eutectics, exist between phases in normal microstructures, investigated by us. The atom interaction of eutectic supra-structures is that direct physical reason, which causes the crystal coalescence of these phases on definite, more energetically profitable directions, and provides the high stability of interphase boundary.

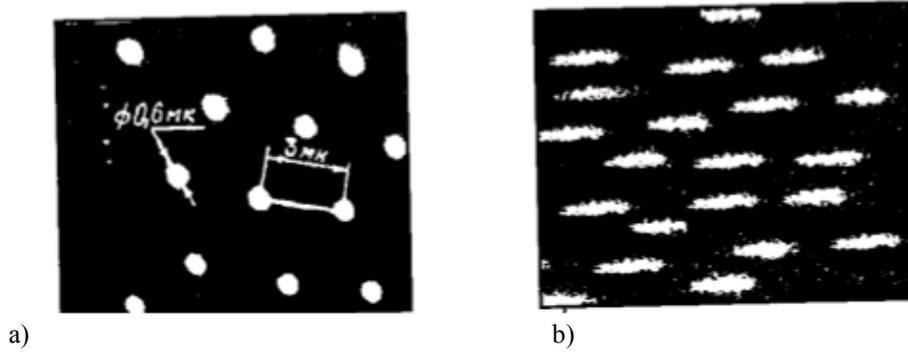


Fig.1. The transversal polished microsection of eutectic surface PbTe-NiSb (a); longitudinal polished section (b).

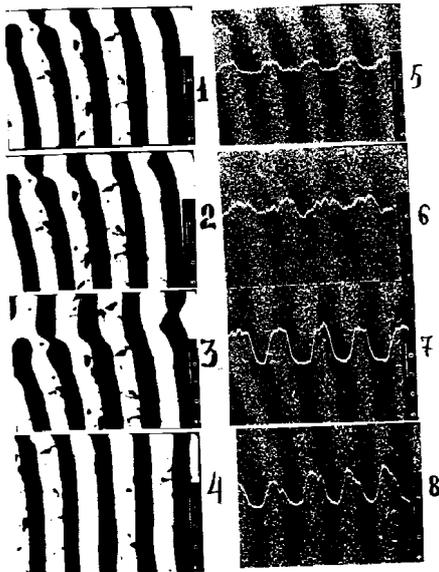


Fig.2. The longitudinal section of PbS-NiSb eutectic in mode (Sotro - (contrast from the composition) – (1-4); the longitudinal section in characteristic beams (5-8). The clearer elements are hard ones, for example PbTe(PbS) parts on the NiSb phase are looked like in photo clear ones in mode “Sotro”.

The investigation of possible oriented relations in system eutectics of  $A^{IV}B^{VI}$ -NiSb type, carried out on the samples of directly grown up in eutectic of PbS-NiSb system showed, that plane (111) PbS intergrows with plane (0001) NiSb by such way, that monoatomic layer of stibium is under monoatomic sulfur layer on interphase boundary.

The microstructure regularity should influence on the periodic potential change of all structural eutectic elements totally, and just: periodic potential of one lattice should change by periodic potential of another lattice with some period being constant for given eutectic and bigger value than lattice constant of each phase. The assumption about the fact, that disagreement compensation of elementary cell parameters on boundary of phase conjugation should be carried out not only by the way of creation of dislocation arrays on this boundary, but by some lattice extension of one phase and compression by another one, that is proved experimentally. The elastic lattice deformation is maximum on the boundary and exponentially decreases in phase depth. The connection desay between the atoms in near boundary region inside phases should cause decrease of order in the given region. That's why the potential periodicity inside supra-molecular formations in eutectic in respect of that

which takes place in crystal of initial component, will be significantly change.

The crystallization peculiarity and eutectic electron structure causes the fast inter-phase connection, which reveals in such properties of eutectic melts as high values of mechanical strength, plasticity, and also stability of microstructure to long heat influences.

Thus, crystallized eutectic is supra-molecular system, in which the redistribution of electron density in the comparison with initial components takes place, in the result of which the connection appears between atoms of different blocks on boundary, coming to electron generalization, and connection becomes weak between atoms inside each sub-block in near boundary region.

The oriented crystal eutectic melts can be considered as solid supra-structures, in which periodic potential of phase alternation collides on periodic potentials of crystal lattices of each phase, that causes the unit energy structure for electrons of total crystal.

### The supra-molecular structures on the base bismuth-metal telluride

And now let's consider the electron-microscopic photos of bismuth telluride surface (0001), doped by cuprum, nickel, bore, niobium, tin and sulfur. The photos of chip surface  $Bi_2Te_3<Cu>$  are given on the fig. 3.

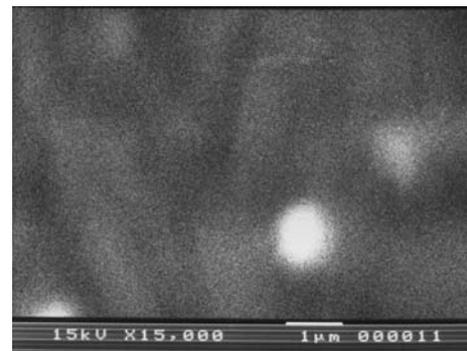


Fig.3. The electron-microscopic photo of basis surface  $Bi_2Te_3$  (0001), doped by cuprum.

The  $Bi_2Te_3<Ni>$  photos are given on the fig. 4(a,b);  $Bi_2Te_3<B>$  photos are given on fig.5 and 6; the samples, doped by tin (fig.7 and 8) and niobium are presented on the fig. 6-9. The doped solid solutions ( $Bi_2Te_3-Bi_2Se_3$ ) of n-type with sulfur are given on the fig.10, and solid solution of p-type on the ( $Sb_2Te_3-Bi_2Se_3$ ) base with also sulfur impurity is presented on the fig.11.

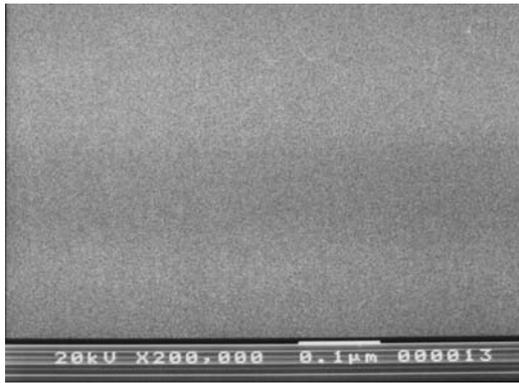


Fig.4. The electron-microscopic surface  $\text{Bi}_2\text{Te}_3\langle\text{Ni}\rangle$  (0001).

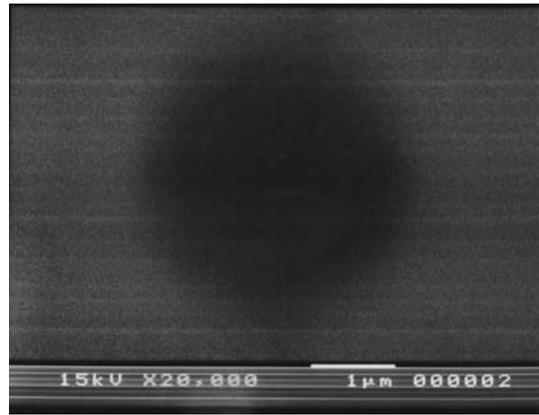


Fig.7. The tin island between  $\text{Te}^{(1)} - \text{Te}^{(1)}$  five-bit bytes of bismuth telluride.

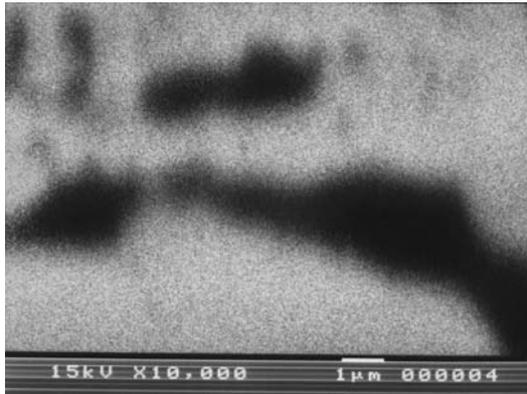


Fig.5. The surface (0001) of bismuth telluride  $\text{Bi}_2\text{Te}_3\langle\text{B}\rangle$ , doped by bore.

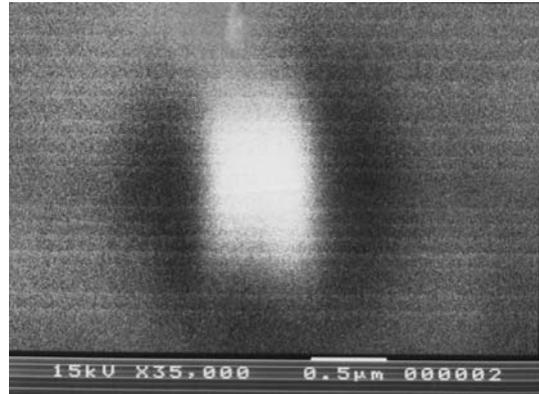


Fig.8. The  $\text{Bi}_2\text{Te}_3\langle\text{Sn}\rangle$  (0001) surface.

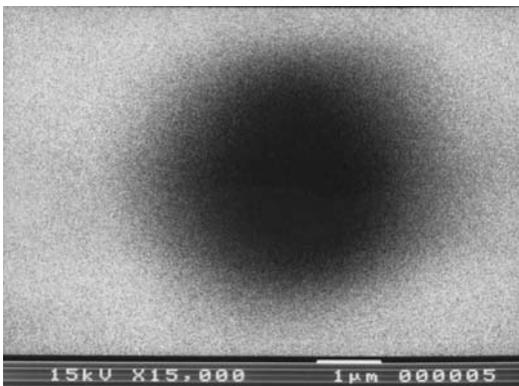


Fig.6. The bore island on  $\text{Bi}_2\text{Te}_3\langle\text{B}\rangle$  (0001) surface.

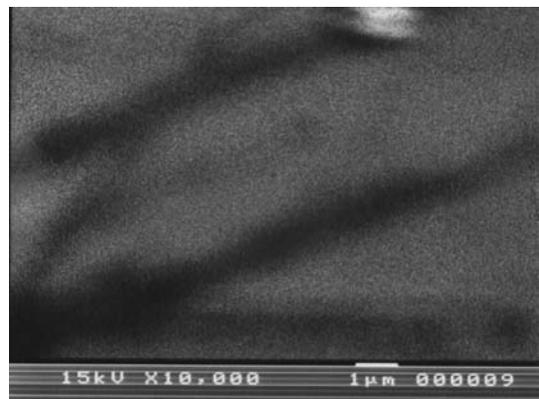


Fig.9. The linear stripes in  $\text{Bi}_2\text{Te}_3$ , doped by niobium.

The surface morphology (0001) of doped crystals has the set of communities:

- the nano-fragments of different forms and dimensions are situated between  $\text{Te}^{(1)} - \text{Te}^{(1)}$  layers,
- the concentration tendency of small particles into big ones in the form of island and stripe of nano-streaky structure) takes place;
- the formations of round islands on solid layered bands are character for all impurity layers;
- the easily diffused impurities Nb, Cu, B form stripes, often by wavy striation
- the layered nano-fragments, containing the disordered cluster formations (aggregations) and discharges of cuprum, niobium and bore atoms take place,
- diffused processes play the main role in nano-particle formation in two-dimensional nano-reactor in interlayer  $\text{Te}^{(1)} - \text{Te}^{(1)}$  bismuth telluride.

Moreover, the general island quantity decreases in the result of easy shift of easily diffused islands in all studied systems that naturally leads to coalescence. Temperature mode in migration process (see fig.5-8) plays the main role. Even small temperatures increase the mobility not of very small nano-clusters, but of islands of big sizes, that leads to earlier coalescence. The island aggregations of introduced impurities in all photos are seen; the process of island coalescence, wavy “bridges” on which their growth and pinch into more big islands and stripe-like aggregations takes place, are seen (fig. 6-10). Moreover, the island concentration takes place as in the result of the movement of many particles with formation of unified island (fig. 6-8) in intermediate state, so in the result of migration of one of the coalescent islands to

another one. The island migration mobility is very uniform. And its direction doesn't depend on sublattice crystal-graphical orientation. The density distribution of bore particles in island and round it (fig.6) is considerably less, than density distribution of tin (fig.7) in island and in entire layer. Here very small ion radiuses of introduced impurities, their high diffusion coefficient along (0001)  $\text{Bi}_2\text{Te}_3$  surface and distance between  $\text{Te}^{(1)}$  -  $\text{Te}^{(1)}$  layers, which is equal to  $2,6\text{\AA}$  play significant role.

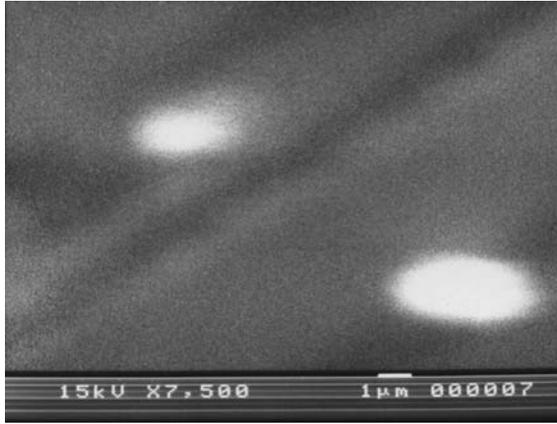


Fig.10. The linear stripes of sulfur and blank spaces on the surface (0001) of solid solution  $(\text{Bi}_2\text{Te}_3 - \text{Bi}_2\text{Se}_3)\langle\text{S}\rangle$ .

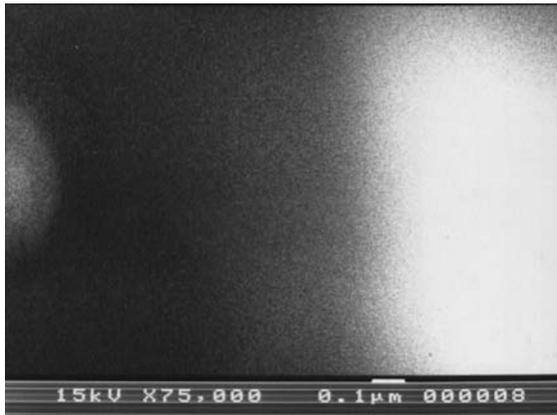


Fig.11. The electron-microscopic photo in surface (0001) of solid solution  $(\text{Sb}_2\text{Te}_3 - \text{Bi}_2\text{Te}_3)$ , doped by sulfur.

The common nature of self-regulation of impurity nano-layers in layered crystal  $\text{Bi}_2\text{Te}_3$  takes place in many electron processes, in particular on the extremal behavior of temperature dependence of Hall coefficient [15-16].

### The creation of substructure parts in bismuth telluride

The alternation of the following structure blocks:  $(\text{Bi}-\text{Te}^{(1)}-\text{Cu}-\text{Te}^{(1)}\dots)$ ,  $(\text{Bi}-\text{Te}^{(1)}-\text{B}-\text{Te}^{(1)}\dots)$ ,  $(\text{Bi}-\text{Te}^{(1)}-\text{Ni}-\text{Te}^{(1)}\dots)$ ,  $(\text{Bi}-\text{Te}^{(1)}-\text{Nb}-\text{Te}^{(1)}\dots)$ ,  $(\text{Bi}-\text{Te}^{(1)}-\text{Sn}-\text{Te}^{(1)}\dots)$ ,  $(\text{Bi}-\text{Te}^{(1)}-\text{S}-\text{Te}^{(1)}\dots)$  is carried out in the obtained "sandwiches" on the base of bismuth telluride. These structures don't connect with each other by strong chemical bonds and are component of typical supra-molecular ensemble, where  $\text{Bi}_2\text{Te}_3$  carcass is in the capacity of "master" for "guest" atoms. The  $\text{Bi}_2\text{Te}_3$  carcass can accept the super-stoichiometric components (and also easy diffused impurities: Ag, Au, Li, Al and others) in own

interlayer spaces. Probably, the layered structure  $\text{Bi}_2\text{Te}_3$  can transform in clathratus-like system with nano-structural fragments, having new electron properties.

The compounds with three-dimensional carcass structure (master), in which the isolated motives from molecules, atoms or ions ("guest"), not creating covalent bonds with carcass are concluded, are mentioned by "clathratus" terms. The "master" crystal lattice can't exist in "guest" presence. The infill of some minimal part of cracks is needed for the carcass stabilization also as in bismuth telluride-metal, that's why clathratases are obtained by the joint crystallization of "master" and "guest" [17].

The ratio of cavity dimensions in carcass of "master", molecules or "guest" atoms has the defining meaning for the formation of clathratus structure, and chemical nature of introduced particles plays insignificant role. The carcass and "guest" atoms have opposite charges in semiconductor clathratases. Moreover, "guests" are always monoatomic ones in semiconductor clathratases. The compounds, containing the molecules or polyatomic ions in the capacity of the "guest", haven't obtained yet [17].

Whether the layered compounds, like above considered layered structures and clathratus-like with "master" three-dimensional and two-dimensional structures exist? By our opinion, the bismuth and stibium chalcogenides can be such classic layered crystals. What make them closer and what discriminates the different layered crystals from clathratus compounds? How to form "constructive block clathratus-like" structures in layered compounds  $\text{Bi}_2\text{Te}_3$ ,  $\text{Sb}_2\text{Te}_3$  and their solid solutions?

The study of surface morphology (0001) and X-ray diffraction photos show that impurities of different types can be introduced into Van der Waals "band"  $\text{Te}^{(1)} - \text{Te}^{(1)}$ .

The obtaining of (Cu, Ni, B, Nb, Sn) nano-particles in two-dimensional nano-reactor, i.e. in  $\text{Te}^{(1)} - \text{Te}^{(1)}$  ( $\text{Bi}_2\text{Te}_3$ ) is justified. The layered structure allows to significantly accelerate of atom diffusion in interlayer space  $\text{Te}^{(1)} - \text{Te}^{(1)}$  and thus to simplify the modification of layered compounds.

The self-generated nano-fragments from impurities are revealed in crystallization process in the result of easy chipping (at room temperature) along basal plane (0001) of bismuth telluride crystals. Let's consider the atom layers in bismuth telluride for the clearing of formation mechanism of layered structure with new impurity complexes. The  $\text{Bi}_2\text{Te}_3$  crystals consist of atom layers, perpendicular to  $C$  axis and alternating in consistency  $\text{Te}^{(1)} - \text{Bi} - \text{Te}^{(2)} - \text{Bi} - \text{Te}^{(1)} - \text{Te}^{(1)} - \text{Bi} - \text{Te}^{(2)} - \text{Bi} - \text{Te}^{(1)}$ .

The dimensions of elementary cell:  $C=30$ ,  $487\pm 0,001$ ,  $a=4,3835\pm 0,0005$  for hexagonal cell and  $a=10,478$ ,  $\alpha=24^\circ 32'$  for rhombic one [18]. The tellurium of central layer of double-double package is considered as anion; the external layers of telluride connect with bismuth covalently. They are analyzed as the double layers  $\text{Te}^{(1)} - \text{Bi}$ . The connections between Te and Bi atoms ( $3,22\text{\AA}$ ) are mainly covalent ones, and less distance  $\text{Bi}-\text{Te}^{(1)}$  ( $3,12\text{\AA}$ ) says about more strong connection in view of ion contribution. The planes, containing atoms of one sort, are parallel ones (0001). The complexes – associates  $\text{Bi}-\text{Te}$  and  $\text{Te}-\text{Te}$  play important role at the  $\text{Bi}_2\text{Te}_3$  crystallization [18]. Moreover, the coordinating polyhedrons, defining the connection of bismuth and telluride atoms in double sublayer of double-double package are considered.

Incidentally, here it is desirable to give some data on study of bismuth surface by method of scanning alleyway microscopy [19]. The carrying out of such investigations is simplified by the fact, that layered crystals (Bi, Sb and their chalcogenide compounds) easily split on basal plane because their natural fragility. Moreover, the atom-pure surface opens on which the density of extrinsic atoms is of 1 mcm<sup>-2</sup> order. The main peculiarity of bismuth is in the fact, that conduction electrons have small concentration of 10<sup>-5</sup> order atom<sup>-1</sup>, their wave length and Debye screening radius are more big than atomic spacing and achieves the values in hundreds Angstrom units. The total reconstruction of entire conduction electron system should be carried out on distances of such order. Starting from this it can be expected the radical reconstruction of electron spectrum near Bi surface, including Bi-Te<sup>(1)</sup> and Bi-Te<sup>(2)</sup> layers in Bi<sub>2</sub>Te<sub>3</sub>. The typical electron-microscopic chip images show, that bismuth surface consist of atom-plane terraces with definite drop of levels between them. The decomposition is always carried out between two farther planes from each other [19]. The terrace boundaries are often close to straight line, following along directions of atom sets on the surface. The terraces with strongly arched boundaries and round islands (cavities) of nano-meter dimensions take place. There are two systems of terrace boundaries: atom-direct terraces and diffused by heat motion ones. These pictures are seemed qualitatively different in the dependence on crystal imperfections. The 1-3 atom-smooth terraces with direct boundaries, going on directions of atom sets are distributed at the chipping of weakly-defective bismuth crystals on total picture (1×1 mcm). The terraces, having form of passing stripes of two-atom height and different width are observed. The surface form is seemed more different for defective crystals. For example, the terraces of different forms, their boundaries also coincide with direction of atom sets are observed. However, the boundaries of all three equivalent orientations are presented equally; the isolated nano-islands, which are analogical to ones between layers in Te<sup>(1)</sup> - Te<sup>(1)</sup> in Bi<sub>2</sub>Te<sub>3</sub>-metal in islands, observed by us are often appeared. The dislocations, the output on the surface of which is revealed as the place of new terrace creation take place in picture limits and twinning cases are possible. However, the tractability of described results requires the special analysis. Such defects of crystal structure, connected with dislocation loops are investigated in Bi<sub>2</sub>Te<sub>3</sub> and in its solid solutions [20]. It is established, that the dislocations, situated in basal plane (0001) is the dominant type of defects in the given monocrystals. As it is seen, the necessity of the perfection estimation of inter-layer crystal structure not only perfect monocrystals, but doped crystals, having the nano-dimensional defects, exist. The doped surfaces (0001), obtained (terraces, blank spaces, wave-like stripes, atom aggregations) in closed crack of Te<sup>(1)</sup> - Te<sup>(1)</sup> bismuth telluride, given by us were example.

The crystal complexes, having these configurations, insignificantly deform, imbedding into lattice of bismuth telluride. Tellurium atoms substitute bismuth atoms, that leads to formation of anti-structure defects in Bi-Te placement. Tellurium atoms, substituting bismuth, give the carriers of electron type. In total, the clathratus formation is considered as the reason, in the result of which the impurity atom loses its doping activity.

It is note, that tellurium introduction in the capacity of the complexes into bismuth telluride decreases the

concentration of current carriers. The analogical picture, connected with concentration decrease of hole carriers, are observed in Bi<sub>2</sub>Te<sub>3</sub><Sn, B>.

As we see the layers of bore, cuprum, tin, niobium, sulfur and nickel create the nano-fragments, consisting of the nano-clusters, locating between Te<sup>(1)</sup> - Te<sup>(1)</sup> layers (fig.3-11).

It is need to note, that nano-particle has the complex form and structure, and linear dimension is characteristic, which can significantly increase 100 nm and dimension of structural element. (Cu - Te<sup>(1)</sup> - Bi - Te<sup>(2)</sup> - Bi - Te<sup>(1)</sup>) - Ni, (B, Sn, Nb, S) - Te<sup>(1)</sup> - Bi - Te<sup>(2)</sup> - Bi - Te<sup>(1)</sup> ) are such structural elements in the “sandwiches”, investigated by us.

### Conclusion

The particles (of cuprum, nickel, niobium, tin and bore), located between Te<sup>(1)</sup> - Te<sup>(1)</sup> layers can be called the nano-structural fragments, having minimal sizes on the height by order 0,3 nm. They are also divided on one-, two- and three-dimensional ones in dependence on the anisotropy of geometric elements. The location of introduced two-dimensional layers of cuprum [21], nickel, niobium, tin and bore is well demonstrated by all figures (3-11). The electron-microscopic photos of morphology of “guests” surface (Cu, Ni and B) in carcass of bismuth telluride show (fig.1):

- the combination of nano-clusters in nano-system in interlayer space Te<sup>(1)</sup> - Te<sup>(1)</sup> creates the different nano-fragments;

- the formation of unified structure in limit system, which is similar to clathratus systems, is carried out at combined crystallization of “guests” and “carcass”;

- moreover, crystal lattice of “master” Bi<sub>2</sub>Te<sub>3</sub> saves, however, the motives of two-dimensional “guests” have already included in Te<sup>(1)</sup> - Te<sup>(1)</sup> cavities, not creating the covalent bonds with three-dimensional carcass;

- the small dimensions of monoatomic “guests” (Cu, Ni and B) play the significant meaning for the formation of clathratus structure in Bi<sub>2</sub>Te<sub>3</sub> in given case.

The interlayer distance can be increased in the case of big dimensions of impurity layers such as tin. Thus, the complex layered compounds on the base of bismuth telluride and its solid solutions (Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>), in which the alternation of two- three-dimensional sub-blocks is carried out, are synthesized and characterized. These two constituent structures are components of typical supra-molecular ensemble, where Bi<sub>2</sub>Te<sub>3</sub> carcass takes place in the capacity of “master” for “guest” atoms. The Bi<sub>2</sub>Te<sub>3</sub> carcass accepts the other own excess components (super-stoichiometric), and also nano-fragments of different types in own interlayer space. In total, we can suppose, that carcass of layered Bi<sub>2</sub>Te<sub>3</sub> is the clathratusforming structural element. Such formations of Bi<sub>2</sub>Te<sub>3</sub> with nano-structural “guests” have oscillating character of Hall coefficient, magnetoresistance and other kinetic parameters in wide temperature interval (4°K and 77 - 300°K) [16]. All these effects have connected with direct formation of nano-structures in matrix volume Bi<sub>2</sub>Te<sub>3</sub> in process of its chemical modification.

The considered view and analysis of eutectic clathratases, misfit compositions and dichalcogenides allow to consider the layered inorganic systems in the capacity of molecular constructive fragments for the directed construction of nano-dimensional ordered supra-molecular compounds. The introduction of different “guests”, and also clusters into cavity of one carcass leads to the interaction

between them and it becomes the motive force of formation of supra-molecular compound.

The eutectics can be related to supra-molecular systems. The redistribution of electron density is carried out in them in the comparison with initial components. In the result the connection, leading to the electron generalization appears between atoms of different blocks on the boundary and the connection decreases between atoms inside each sub-block in the near boundary region.

The morphology peculiarities of  $\text{Te}^{(1)} - \text{Te}^{(1)}$  interlayers in  $\text{Bi}_2\text{Te}_3$ -metal, connected with formation of cavities and interlayer blank spaces have been considered. The structural blocks in layered chalcogenides, and also in  $\text{PbTe(PbS)-NiSb}$  eutectics have been created by the intercalation, combined synthesis of melts with impurities and following crystal growth.

- [1] *J.M. Len.* Supramolekulyarnaya khimiya. Kontseptsiya i perspektivi. Nauka, Novosibirsk, 1998.
- [2] *F. Muller, H. Route, S. Dillinge.* Angew Chem., Int. Engl., 34, 2328 (1995).
- [3] *R. Scholhorn.* In. Inclusion Compounds, Vol. 1. (ed. J.L Atwood) Academic Press. London, 1984. p. 249.
- [4] *Yu.D. Tretyakov, A.V. Lukashin, A.A. Yeliseev.* J. Uspekhi khimii, 73 (9) 2004, s.975-998.
- [5] *A.L. Bulachenko.* J. Uspekhi khimii, 75 (5), 2003, s.419-437.
- [6] *M.P. Anisimov.* J. Uspekhi khimii 72(7)2003, s.666-703.
- [7] *K.A. Kovnir, A.V. Shevelkov.* J. Uspekhi khimii 73(9) 2004, s.999-1017.
- [8] *G.S. Nolas, G.A. Slack, S.B. Schjuman.* In Recent Trends in Thermoelectric Materials Research (Ed. T.M. Tritt) Academic Press, San Diego, 2001.
- [9] *A.V. Shevelkov.* J. Vestnik Moskovskogo universiteta, ser. 2, tom 44, №3, 2003, s.163-171.
- [10] *I.D. Mikheykin, M.Yu. Kuznetsov, E.V. Makhonina, V.S. Pervov.* Dokladi Akademii nauk, 2001, tom 376, №6, s.785-788.
- [11] *J. Rouxel, A. Meerschaut, G.A. Wiegers.* H. J. Alloys Comp. 1995, v.229, p. 144-157.
- [12] *V.S. Pervov, I.D. Mikheykin, E.V. Makhonina, V.D. Butskiy.* J.Uspekhi khimii, 72(9), 2003, S.852-862.
- [13] *K.Sh. Kakhramanov, R.M. Roshal, V.V. Didik.* Izv. AN.SSSR. Neorgan. materialy, 1983. t.10, №19, s.1613.
- [14] *K.Sh. Kakhramanov, V.V. Didik.* J. Metallofizika, I. «Naukova-dumka», (Ukraina), 1981, №2, t.3, s.31-39.
- [15] *S.Sh. Kakhramanov, E.M. Maqerramov.* J. "Khovledqe"Education" Society of Azerbaijan Republic, 2004, №2 r.29-32.
- [16] *A.G. Abdullaev, E.I. Veliyulin, S.Sh. Kakhramanov.* Vliyanie legirovaniya i interkalirovaniya na svoystva xalkogenidov vismut, Preprint №420, Instituta Fiziki NAN AR, Baku, 1991, s.3-54.
- [17] *K.A. Kovnir, A.V. Shevelkov.* J. Uspekhi khimii 73 (9) 2004, s. 1000-1015.
- [18] *T.A. Smorodina, N.N. Sheftal, A.P. Tsuranov,* Monografiya «Vkhoydenie primesnikh tsentrov v kristallicheskiy sloy poluprovodnika», Sankt-Peterburq, 1986, s. 58-110.
- [19] *V.S. Edelman.* J. Uspekhi fizicheskikh nauk, t. 175, №10, 2005, s. 1111-1115.
- [20] *I.V. Gasenkova, T.E. Svechnikova.* Neorganicheskie materialy, 2004, t.40, №6, s.663-668.
- [21] *J. Bludska, S. Karamazov, J. Navratil, I. Jakubec, J. Hora.* Solid State Ionics 171 (2004) 251-259.

S.Ş. Qəhrəmanov, E.M. Derun, M.Q. Pişkin

### YARIMKEÇİRİCİ SİSTEMLƏR ƏSASINDA $\text{Bi}_2\text{Te}_3$ - METAL VƏ $\text{PbTe(PbS)-NiSb}$ LAYLI SUPRASTRUKTURLAR

Klatratlar, misfit birləşmələr, evtektiklər, laylı dihalqogenidlər molekulyar parçaları əsasında nanoölçülü neorqanik supramolekulyar sistemlər yaratmaq olar.

Şaquli istiqamətli kristallizasiya metodu ilə aşağıdakı laylı sistemlər ("sendviçlər") alınmışdır:

$\text{Bi}_2\text{Te}_3\text{-Cu}$ ,  $\text{Bi}_2\text{Te}_3\text{-B}$ ,  $\text{Bi}_2\text{Te}_3\text{-Ni}$ ,  $\text{Bi}_2\text{Te}_3\text{-Nb}$ ,  $\text{Bi}_2\text{Te}_3\text{-Sn}$ ,  $\text{Bi}_2\text{Te}_3\text{-S}$ . Alınmış strukturlarda parçaların ardıcılığı belədir:

$(\text{Bi-Te}^{(1)}\text{-Cu-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-B-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-Ni-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-Nb-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-Sn-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-S-Te}^{(1)}\dots)$ . Supramolekulyar ansambları  $\text{Bi}_2\text{Te}_3$  karkası və  $\text{Cu, Ni, Sn, S, Nb}$  və B "aralıq" atomlar əsasında təşkil olunur.

С.Ш. Кахраманов, Е.М. Дерун, М.Г. Пишкин

### СЛОИСТЫЕ СУПРАСТРУКТУРЫ НА ОСНОВЕ ПОЛУПРОВОДНИКОВЫХ СИСТЕМ: $\text{Bi}_2\text{Te}_3$ - МЕТАЛЛ И $\text{PbTe(PbS)-NiSb}$

Рассмотренный обзор и анализ клатратов, мисфитных соединений эвтектик  $\text{PbTe(PbS)-NiSb}$ , слоистых диалкогенидов позволяют рассматривать неорганические системы в качестве молекулярных строительных фрагментов для направленного конструирования наноразмерных упорядоченных слоистых супрамoleкулярных соединений.

Методом вертикальной направленной кристаллизации получены слоистые системы («сендвичи») на основе -  $\text{Bi}_2\text{Te}_3\text{-Cu}$ ,  $\text{Bi}_2\text{Te}_3\text{-B}$ ,  $\text{Bi}_2\text{Te}_3\text{-Ni}$ ,  $\text{Bi}_2\text{Te}_3\text{-Nb}$ ,  $\text{Bi}_2\text{Te}_3\text{-Sn}$ ,  $\text{Bi}_2\text{Te}_3\text{-S}$ . В этих структурах происходит чередование следующих структурных блоков:

$(\text{Bi-Te}^{(1)}\text{-Cu-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-B-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-Ni-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-Nb-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-Sn-Te}^{(1)}\dots)$ ,  $(\text{Bi-Te}^{(1)}\text{-S-Te}^{(1)}\dots)$ .

Эти структуры можно отнести к составным частям супрамoleкулярного ансамбля, где каркас  $\text{Bi}_2\text{Te}_3$  выступает в качестве хозяина для плененных атомов-гостей ( $\text{Cu, Ni, Sn, S, Nb}$  и  $\text{B}$ ). По всей вероятности, слоистую структуру  $\text{Bi}_2\text{Te}_3$  можно превратить в клатратообразующую систему с наноструктурными фрагментами.

Received: 16.11.06