

MATERIAL FOR THERMO-ELEKTRO-GENERATOR

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ABSTRACT

By the method of the vertical directed crystallization layered systems ("sandwiches") have been received on the basis of $\text{Bi}_2\text{Te}_3\text{-Cu}$, $\text{Bi}_2\text{Te}_3\text{-B}$, $\text{Bi}_2\text{Te}_3\text{-Ni}$. In these structures there is an alternation of the following structural blocks:

1. $\text{Bi}_2\text{Te}_3\text{-Cu}$ ($\text{Bi+Te}^{(1)}\text{-Cu-Te}^{(1)}$)
2. $\text{Bi}_2\text{Te}_3\text{-B}$ ($\text{Bi+Te}^{(1)}\text{-B-Te}^{(1)}$)
3. $\text{Bi}_2\text{Te}_3\text{-Ni}$ ($\text{Bi+Te}^{(1)}\text{-Ni-Te}^{(1)}$)

Structures, $\text{Te}^{(1)}\text{-Cu-Te}^{(1)}$, $\text{Te}^{(1)}\text{-B-Te}^{(1)}$ and $\text{Te}^{(1)}\text{-Ni-Te}^{(1)}$ are not connected among themselves by strong chemical links and they are the components of typical super-molecular ensemble where skeleton Bi_2Te_3 represents itself as the owner for atoms - visitors (Cu, Ni and B). Skeleton Bi_2Te_3 can also accept in its inter-layer spaces the excessive over-stoichiometric components (and also others easily-diffused impurities: Ag, Au, Li, Nb, Al and so on). Most likely, layered structure Bi_2Te_3 can be transformed in clatrate forming system with nanostructural elements, having new electronic properties.

Keywords: skeleton, impurities, nanostructural, electronic, layered, electric, films, bi-dimensional, links, misfit, chalcogenide

I. INTRODUCTION

Layered compounds have sharply anisotropic electric, mechanical, optical and other characteristics. Sometimes layered crystals are classified on the basis of the links nature. They contain some types of links, differing on force, and the same links "are constructed" on various planes, the weakness of links between layers and occurrence between them impurity films allows to realize and find out the physical phenomena of bi-dimensional (or quasi-bi-dimensional) type. Most frequently strong covalent or it ionic – covalent links are realized along the plane of cohesion (planar "longitudinal" links) and weak molecular (Van der Waals hydrogen type) for inter-plane cross-section links. A circle of layered (or quasi-layered) crystal formations is wide - from mononuclear up to multi-component crystals. The greatest attention from them attract chalcogenide (Se, Te, S). Such strong and refractory compounds as corundums, borides, some nitrides, which lamination it is caused by strong propensity of these materials to polytypicism are also referred to the layered.

Significant interest is drawn by misfit compounds. These mixed chalcogenide with common formula where $(\text{MX})_{1+x}$ $(\text{TX}_2)_m$, where $\text{M}=\text{Sn, Pb, Bi, Ln}$; $\text{T}=\text{Ti, V, Nb, Ta, Cr}$; $\text{x}=\text{S, Se}$; ($\text{x}=0,08-0,28$; $\tau=1,2,\dots$). We shall particularly note, that the

basis of these compounds consist of two layered substructures - MX and TX_2 , having disproportion in one crystallographic direction. Consecutive alternation of layers of substructures results in formation of united three-dimensional substructure. For such type of structures unusual physical and chemical properties and morphology of crystals, non-additivity of physical characteristics, multistage phase transitions [1-3] are marked. The Authors [2] mark, that properties misfit compounds are defined by a competition of the forces responsible for preservation of rigidity of disproportionate substructures (bi- chalcogenide matrixes TX_2 , cubic structure of visitor MX) and the forces responsible for preservation united supra-structure.

In this connection especially it is necessary to take into consideration the results of generalizations of the data on chemical methods of stratifying di-chalcogenide transitive metals in the liquid environment with formation of mono-layered dispersions containing quasi-bi-dimensional layers of these compounds [4].

II. MAIN TEXT

As an example we shall take also the layered compounds of inclusion in graphite with alkaline metals. Sometimes for families with bi-dimensional (layered clatrates) and "zero"-dimensional (molecular clatrate) structures of the owner the notion "clatrate" is used [5]. As far as it is possible to recognize it the future researches will show. The term "clatrates", designate compounds with three-dimensional frame structure (owner) in which isolated motives from molecules are made, atoms or the ions (visitors) not forming covalent links with a skeleton. The crystal lattice of the owner cannot exist in absence of the visitor. For stabilization of a skeleton filling is required, at least, some minimal part of cavities, therefore, the clatrates are received by joint crystallization of the owner and the visitor. The particles made in a three-dimensional matrix, as a rule, cannot leave it without destruction of the whole "ensemble" [5].

Determining significance for formation of clatrate structure, has a ratio of the sizes of cavities in a skeleton of the owner and molecules or atoms of the visitor, and the chemical nature of introduced particles, plays not so big role.

Whether there are layered compounds similar to the layered structures considered above and clatrate-

similar with three-dimensional and with bi-dimensional structures of the owner. In our opinion such classical layered crystals can be chalcogenide of bismuth and antimony. What pulls them together, and what distinguishes various layered crystals from clatrate compounds? How in layered compounds Bi_2Te_3 , Sb_2Te_3 and in their firm solutions to create « constructive block clatrate-similar » structures?

The present report is devoted to these problems. Performance of a problem was accompanied with easy introduction of impurities (as own Bi, Sb, Te, Se and introduced, for example: easily diffused – Ag, Au, Li, Cu, Na, Ni, B, Nd and etc.) to Van der Waals cracks. Studying of morphology of a surface (0001) and X-ray diffraction pictures would show, that " almost a bonded area " in inter-layer space could not be free.

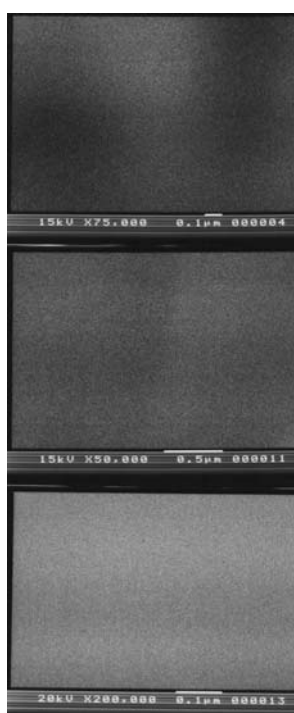


Fig. Electronic-microscopic pictures of morphology of a visitors surface (Cu, Ni and B) in a skeleton of telluride of bismuth

Methodology of the experiments. Multilayered structures of crystals were raised by method of vertical crystallization (at $E \approx 700 \pm 5^\circ\text{C}$, and speeds $V = 0,5 \text{ cm/hour}$). Crystals of chalcogenide Bi and Sb were received as the clatrates, by joint crystallization of the owner (Bi_2Te_3 , Sb_2Te_3 , Bi_2Te_3) and the visitor (Impurities).

For studying the morphology of surface they used electronic-microscopic microscope of model – JSM5410LV. X-Ray structural researches base chipped surface (0001) Bi_2Te_3 and its firm solutions with Sb_2Te_3 and Bi_2Te_3 were carried out on Philips Analytical XRD (X-ray diffractometer). In figure are given morphology of superficial layers (0001) in $\text{Bi}_2\text{Te}_3 < \text{Ni} >$ (a), (Bi_2Te_3 -96 mol% - Bi_2Te_3) $< \text{Cu} >$ (δ, β) and (Sb_2Te_3 75mol % - $\text{Bi}_2\text{Te}_3 < \text{B} >$) (2). X-Ray diffractograms is

not brought, however they have confirmed presence of $\text{Te}^{(1)}\text{-Te}^{(1)}$ film the entered impurity (copper, nickel and boron) between the layers.

III. CONCLUSION

Reception nano-particles (Cu, Ni, B) in bi-dimensional nano-reactor (Bi_2Te_3) failed. In such compounds (Bi_2Te_3) as we shall describe below the layers are connected among themselves weak Van der Waals forces what has allowed to change easily the size of inter-layered spaces. Besides that, the layered structure has allowed to speed up considerably the diffusion of atoms, in inter-layered space ($\text{Te}^{(1)}\text{-Te}^{(1)}$) and by that to facilitate chemical updating of layered compounds.

As a result of easy chipping (at room temperature) along a basic plane (0001) of crystals of telluride of bismuth, are revealed self-formed layers of impurity during crystallization. For understanding and finding-out of the mechanism of formation of the layered structure with new impurity complexes we shall consider nuclear layers in telluride of bismuth.

Crystals Bi_2Te_3 will consist of nuclear layers, perpendicular axes C and alternating in sequence $\text{Te}^{(1)}\text{-Bi-Te}^{(2)}\text{-Bi-Te}^{(1)}\text{-Te}^{(1)}\text{-Bi-Te}^{(2)}\text{-Bi-Te}^{(1)}$.

The sizes of the elementary cell: C-30, $487 \pm 0,001$, $a = 4,3835 \pm 0,0005$ for hexagonal and $a = 10,478$, $\alpha = 24^\circ 9' 32''$ for rhombohedral cells [6]. In the flux at crystallization Bi_2Te_3 , the important role must play the complexes - associatives Bi-Te and Te-Te[6]. Thus the coordination polyhedrons determining the link of atoms of bismuth and telluride in a double sub-layer of a five-layer package are examined.

The crystal complexes having these configurations, being built in a lattice of telluride of bismuth are insignificantly deformed. In places the distribution of Bi-Te atoms of tellurium replace the atoms of bismuth what results in formation of anti-structural defects. The atoms of tellurium replacing the bismuth, give carriers of electronic type. On the whole the reason owing to which the atom of an impurity loses its alloying activity, it is necessary to count clatrate formation.

Let's note, that occurrence of tellurium as complexes in telluride of bismuth decreases the concentration of carriers of a current. The similar picture connected to downturn of concentration of the hole carriers is observed in crystals $\text{Bi}_2\text{Te}_3 < \text{Sn, B} >$.

As we see, the layers of boron, copper and nickel, settling down in inter-layers $\text{Te}^{(1)}\text{-Te}^{(1)}$ (figure) form Those structural films, consisting of very fine nano-particles.

Usually they distinguish two types of nano-particles: cluster or nano-clusters. To the first type particles of the ordered structure in the size 1,5nm, containing up to 10^3 atoms are referred, to the second – nano-particles in the size 5-100 nanometers consisting of 10^3 - 10^6 atoms. However the last definition is fair only for isotropic (spherical) nano-particles, and the threadlike and lamellar particles containing much more number of atoms and having one or two linear sizes under this definition do not get [7]. Such distinctions in the linear sizes nano-particles make expedient to subdivide them on one, two and three-

dimensional (accordingly 1D, 2D and 3D – nanoparticles). Recently they began to distinguish geometrical and physical dimension of nano-particles. It is necessary to note, that if a nano-particle has the complex form and structure then as a characteristic can be considered not its linear size which can considerably exceed 100 nanometers, but the size of structural element. As such structural elements in investigated by us "sandwiches" act: $\text{Cu-Te}^{(1)}\text{-Bi-Te}^{(2)}\text{-Bi-Te}^{(1)}\text{-Cu}$ (Ni, B)– $\text{Te}^{(1)}\text{-Bi-Te}^{(2)}\text{-Bi-Te}^{(1)}$

Such particles (copper, nickel and boron), $\text{Te}^{(1)}$ - $\text{Te}^{(1)}$ located between layers are called nano-structural. They are also subdivided into one, two and three-dimensional depending on anisotropy of geometrical elements. Electronic-microscopic pictures of morphology of a visitors surface (Cu, Ni and B) in a skeleton of telluride of bismuth (fig.) shows:

Association of nano-clusters in nano-systems in inter-layered space $\text{Te}^{(1)}\text{-Te}^{(1)}$ creates nano-cluster structure;

- Formation of united structure in the closed system similar to clatrate systems occurs at joint crystallization of "visitors" and "skeleton";

- Thus the crystal lattice of the owner is kept, however in cavities $\text{Te}^{(1)}\text{-Te}^{(1)}$ motives of bi-dimensional of the "visitors" not forming covalent links with a three-dimensional skeleton are already made;

- In this case determining significance for formation of "so called clatrate structure" had small sizes of atoms of mononuclear visitors (Cu, Ni and B).

Thus, complex layered links are synthesized and characterized on the basis of telluride of bismuth and its firm solutions (Bi_2Te_3 and Sb_2Te_3) in which alternation of two structural sub-blocks - tetradymite is carried out and (Cu, Ni and B).

These two making structures are not connected among themselves by strong chemical links and are components typical supra-molecular ensemble where skeleton

also impurity of various grades. As a whole it is possible to assume, that the skeleton of layered Bi_2Te_3 is clatrate-forming structural element. Such formations Bi_2Te_3 with nano-structural visitors possess oscillating character of Hall factor, magnetoresistance and other kinetic parameters in a wide interval of temperatures (4°K and 77 - 300°K). All these effects are connected to direct formation of nano-structure in volume of matrix (Bi_2Te_3) during its chemical updating.

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Bi_2Te_3 represents itself as the owner for atoms - visitors (Cu, Ni and B). Skeleton Bi_2Te_3 accepts in the inter-layer spaces and other excessive components (over-stoichiometric), and