

TWO-DIMENSIONAL NANO-REACTORS ON THE BASE OF BISMUTH AND STIBIUM CHALCOGENIDES

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The electron-microscopic images and roentgen-diffractometer fotos in Bi_2Te_3 and Sb_2Te_3 layered systems show, that $\text{Te}^{(1)}\text{-Te}^{(1)}$ gap plays nano-reactor role. The origination, self-organization and formation of quazi-two-dimensional layers with nano-islands, nano-rods and nano-crystals take place in such nano-reactors. These structural blank spaces – nano-reactors – are filled by compounds, the following modification of which leads to nano-crystal formation, for example, in $\text{Bi}_2\text{Te}_3\text{<Cu>}$: CuTe , Cu_2Te , Cu_{64}O , $\text{Cu}_{0,647}\text{Te}_{0,353}$; in $\text{Sb}_2\text{Te}_3\text{}$: B_2O , BiBO_3 , $\text{Bi}_2\text{B}_8\text{O}_{15}$.

Introduction

The present paper is dedicated to problems of nano-particle introduction in space between layers of layered crystals with weak Van der Waals bond. Essentially the layered compounds themselves are able to "take prisoner" of "guest" molecules in synthesis process, and also at intercalation. The class of intercalated compounds doesn't practically limited, i.e. the big atom number exists (especially easily-diffusing ones with small ion radiuses), which can be introduced in different layered crystals (graphite, GaSe, InSe, Bi_2Se_3 , Bi_2Te_3 , Sb_2Te_3 and etc.). The combination on microscopic level of metallic layers with semiconductor ones can be lead to obtaining of crystals with new electron properties. Now the possibility to investigate the set of new physical phenomena has already existed. That layered compounds, in which the anisotropy is strong and essentially leads to almost two-dimensional electron motion in crystal attract the most interest in this meaning. Moreover, the structural transitions with formation of wave of charge density have been revealed in layered compounds [1]. Earlier transitions of such type had been found in quazi-one-dimensional crystals. In this connection the intercalated layered systems of bismuth and stibium chalcogenides and such changes of electron properties, which are observed after intercalation, are interested [2].

However, first of all it is necessary to make the technological processes more exact, in result of which it is possible to create metallic (or others) nano-layers between layers in semiconductors. Indeed, the layers in nano-crystals can be considered as one type of nano-reactors of atom scale. The set of "forced" reactions can take place in such nano-reactors, similar to simplest nano-reactors (in which reagents are spatially organized, - Van der Waals molecules and partners are fixed by intermolecular non-valency interactions). This is new science region about "nano-world". Nano-chemistry is described in many articles, the view of which is given in [3]. The molecular dynamic reagents, the mechanisms and velocities of chemical transformations, local charges and their distribution, ionization energy, change in nano-reactor; the set of anomalies is revealed [3]. The new quazi-two-dimensional nano-reactors, in which the interplanar spaces can be changed because of stimulation of conformation transitions in poly-methylene chains have been

synthesized [4]. These transitions can be continuously regulated, attuning nano-reactor on given volume by the way of solvent filling [4].

The analysis shows, that nano-chemistry produces own objects - nano-particles, nano-containers, nano-reactors. The two key conceptions – nano-particle and nano-reactor have been defined. The first one characterizes the dimensional parameter, the second one defines the nano-particle function [3]. The blank nano-spaces, interlayer spaces in layered crystals can be considered by nano-reactors, when properties reagents, creating in them depend on blank space dimensions and interlayer "gaps". When these dependencies disappear, the blank nano-spaces become only nano-dimensional containers, in which presoner particles behave themselves by the same way, if they would be in unlimited volume [4].

It is need to clarify how the impurity nano-particles behave themselves in interlayer space $\text{Te}^{(1)}\text{-Te}^{(1)}$ in layered crystals Bi_2Te_3 , Sb_2Te_3 and their solid solutions, what influence they do on physic properties in whole. Here it is need to realize two sides of dimension effect, as pure scale, spatial one, so physic-chemical phenomena, when properties of obtained quazi-two-dimensional systems in wide temperature interval depend on introduced atom dimensions. It is possible to formulate the following tasks in the light of above mentioned: firstly, so far as Van der Waals gap $\text{Te}^{(1)}\text{-Te}^{(1)}$ in Bi_2Te_3 and Sb_2Te_3 can be considered as nano-reactor for impurities and secondly, what sort of morphology of impurity centers, creating on surface (0001) in Bi_2Te_3 and Sb_2Te_3 and which changes in crystal properties the nano-particles introduce in nano-reactor.

The experimental investigation

The investigations had been carried out on doped samples Bi_2Te_3 after ingot synthesis at alloy temperature 1050°K towards impurity. The crystal growth was carried out in graphitized ampoules at band-directed crystallization, the band traverse speed was $v=0,5$ cm/h with temperature gradient ($200\text{-}210$ K/cm) at temperature 1050°K .

The electron-microscopic images were obtained on microscope by mark JSM 5410LV on SPM-9500j3 and on atomic-power microscope (ACM); device braking ability was 20 nm in lateral direction and 0,1 nm in vertical one. The new-pricked planes (0001) (Bi_2Te_3) and (Sb_2Te_3) were

investigating, the etching wasn't carried out. The knives from solid metallic alloys were used for chip. The chip took place on cleavage plane (0001) and gave general mirror smooth surface.

The obtained results and their discussion

We will consider such nano-objects, which have been created at filling of $Te^{(1)}-Te^{(1)}$ space by such substances, as Cu, Nb, B in Bi_2Te_3 and Te, Sb, B in Sb_2Te_3 .

The filling takes place as in synthesis process, crystallization one (at definite gradient temperatures), so in intercalation. The filling of interlayer gap, at which the nano-

islands and micro- and macro-wires, presents the special interest. Let's consider the presented the electron-microscopic (EM) images (fixed on microscope JEOL-JSM 5410LV) of pricked surface (0001) of Bi_2Te_3 , doped by cuprum, are presented on fig.1 (a,b) - ($Bi_2Te_3<Cu>$). Conglomerations of nano-rods and nano-islands are seen in left side of fig.1(a) The big clots of islands (in center of fig.1(a)) have diameter dimensions less than 500 nm, and nano-particles of different nano-dimensions ($\approx 5-10$ nm) are situated round them. The images of two islands by order 500 nm in more enlarged scale are given (fig.1(b)).

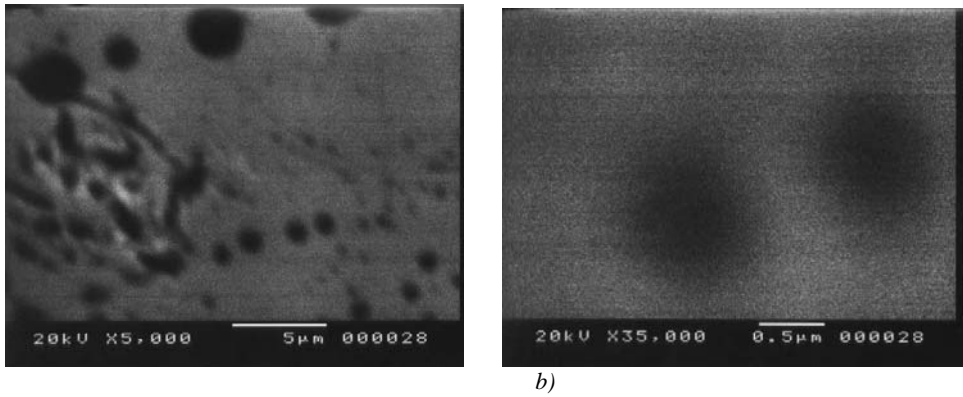


Fig.1.(a,b) – The electron-microscopic images of nano-rods and islands on $Bi_2Te_3<Cu>$ (0001) surface - (a), EM-images of separate islands (in enlarged scale) – (b).

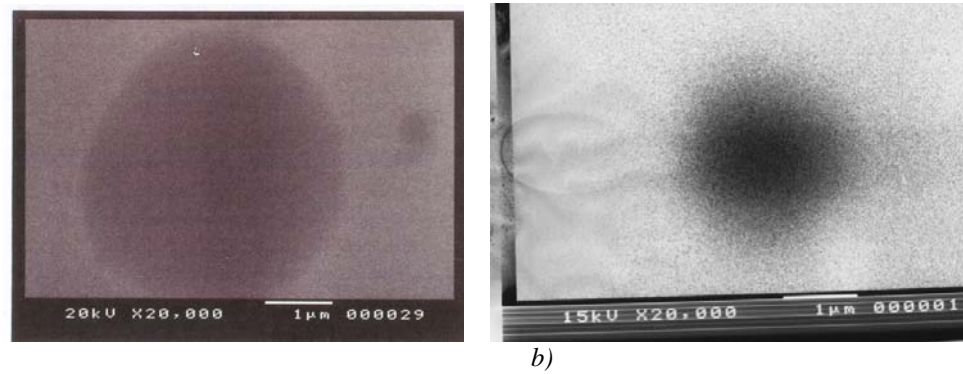


Fig.2.(a,b) – EM photos of (0001) surface in $Bi_2Te_3<Cu>$ - (a) and island in $Sb_2Te_3<Sb>$ - (b).

The islands of different dimensions are also seen in presented electron-microscopic photos on fig.2(a,b), so one big island ($Bi_2Te_3<Cu>$) is given on fig.2 (a); the island in $Te^{(1)}-Te^{(1)}$ gap of $Sb_2Te_3<Sb>$ system is given on the fig.2(b), very small stibium nano-particles are outstanding round this island.

The islands of different dimensions on surface (0001) Bi_2Te_3 , doped by boron are shown on fig.3 (a,b). The nano-fragments from nano-rods Bi_2Te_3, $Sb_2Te_3<Sb>$ and $Bi_2Te_3<Nb>$, having nano-dimensions only on height (they are presented on fig.4 (a,b,c) are formed in nano-reactors. The nano-rods in $Bi_2Te_3<Nb>$ being nano-wire analogues are presented on the fig.4 (b) [3], they are more obvious and consist in rod, as photos from $NdTe_4$ show. Such particles (nano-rods) are called nano-structures [3].

The visible islands, as special objects in nano-reactors, demand more detail investigation: it is need to study their morphology in more fine-line microscope. These

investigations would allow to reveal more detail the nano-dimension particle structure (these are islands or nano-particles by dimension less than 10 nm). The given photos, obtained on microscope by SPM-9500j3 mark revealed the nano-island microstructures (fig.5 (a,b,c,d)). As it is seen they consist in longitudinal nano-rods by width less than 10nm.

From which phases did the nano-fragments in nano-reactor – between $Te^{(1)}-Te^{(1)}$ in $Bi_2Te_3<Cu>$, Bi_2Te_3, $Bi_2Te_3<Nb>$ form? It is impossible to judge about them only by EM photos. We resorted to study of roentgen-diffractometer photos of surface (0001) in doped $Bi_2Te_3<Cu>$ and Sb_2Te_3 crystals (fig. 6 (a,b,c,d)). Such photos for alloys of p-type are presented on the fig: $Sb_2Te_3 <Sb>$ - fig. 7(a); solid solution $Bi_{0,5}Sb_{1,5}Te_3<Te>$ -fig.7(b);for alloy composition $Bi_{1,20}Sb_{4,80}Te_9(Te)$ - fig. 7(c); $Bi_2Te_3(B)$ - fig. 8(a) and $Bi_2Te_3(Nb)$ - fig. 8(b).

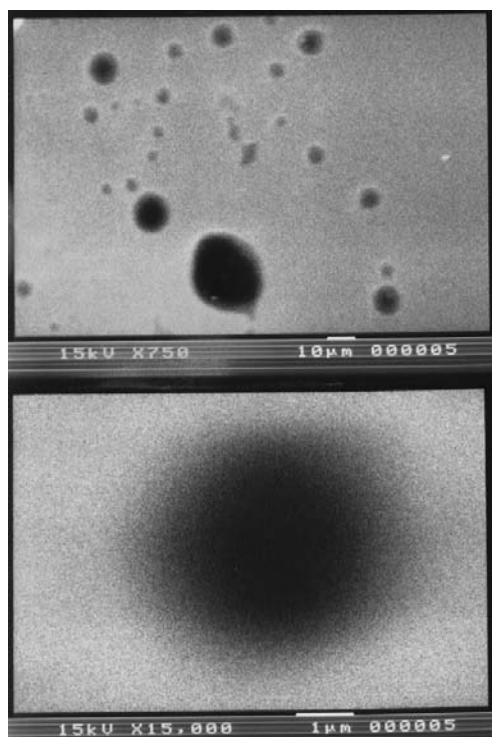


Fig.3.(a,b) – EM images of island surface (0001) $\text{Bi}_2\text{Te}_3\langle\text{B}\rangle$ – (fig.3,a) and photo of the same surface of one island – (fig.3,b).

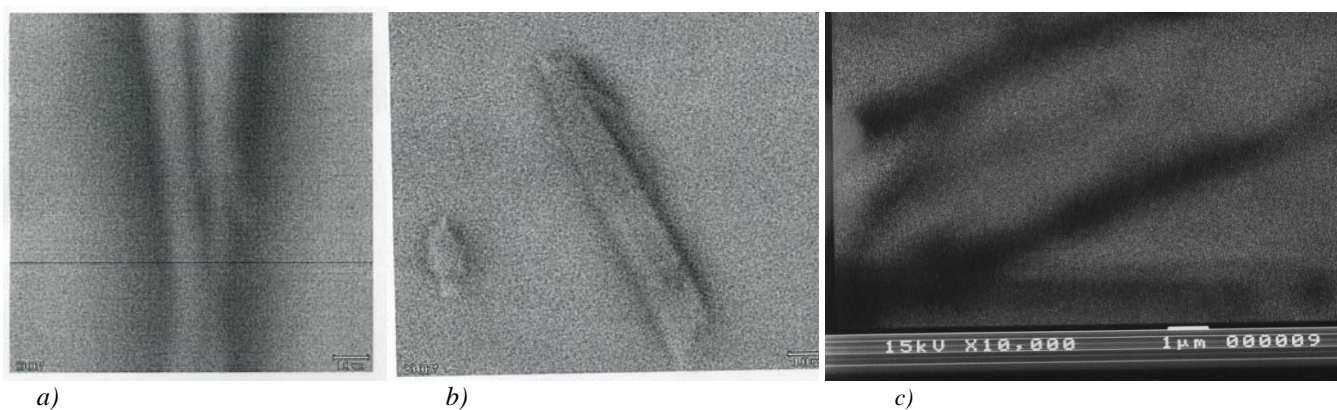
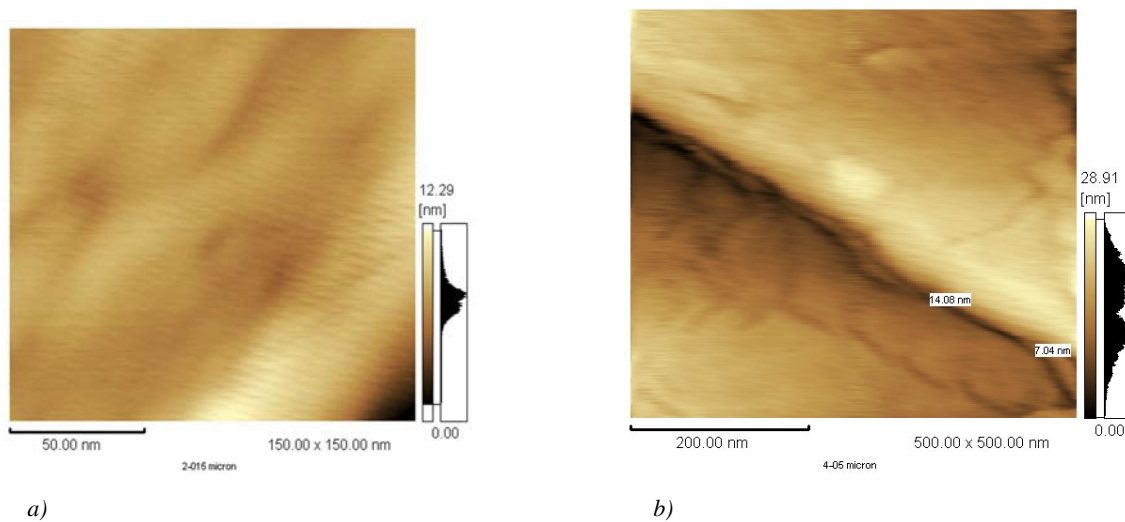


Fig.4.(a,b,c) – EM photos of rods in nano-reactors $\text{Bi}_2\text{Te}_3\langle\text{B}\rangle$ – (a), $\text{Sb}_2\text{Te}_3\langle\text{Sb}\rangle$ – (b) and $\text{Bi}_2\text{Te}_3\langle\text{Nb}\rangle$ – (c).



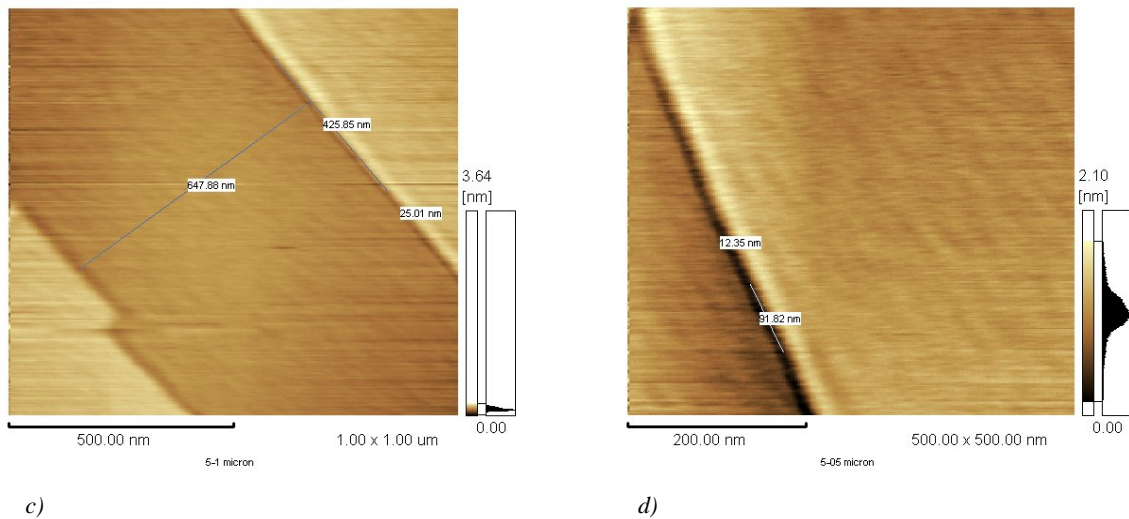


Fig.5.(a,b,c,d) – EM images (om SPM-9500j3 microscope) of nano-rods in nano-reactors from $\text{Bi}_2\text{Te}_3\langle\text{B}\rangle$ – (a), from $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3\langle\text{Te}\rangle$ – (b), from $\text{Bi}_2\text{Te}_3\langle\text{B}\rangle$ – (c) and from fragment part of $\text{Bi}_2\text{Te}_3\langle\text{B}\rangle$ – (d).

From these roentgen-diffractograms it is seen, that blank spaces are gaps and they are filled by nano-particles of different dimensions and different nano-crystals in Bi_2Te_3 and Sb_2Te_3 . The type of nano-fragments, which have been formed in this space, depends on introduced impurity. The following nano-fragments: CuTe , $-\text{Cu}_{0.647}\text{Te}_{0.353}$ have been self formed in $\text{Bi}_2\text{Te}_3\langle\text{Cu}\rangle$ compound on base of superstoichiometric Te and introduced Cu (till (0,2-0,3) weight %). Besides of the main Bi_2Te_3 peaks the small (51°) Bi_2Te_3 peaks and also Cu atoms are outstanding (fig.6). It was impossible to clarify the peak “fate”, corresponded to 9° . The other diffractograms $\text{Bi}_2\text{Te}_3\langle\text{Cu}\rangle$, in which not quite refined bismuth is used, is presented on the fig. 6(c). Probably, here the oxygen remnants formed Cu_6O in Bi.

Here the nano-particle peaks from Bi_2Te_3 and CuTe also are outstanding. The numerous investigation of diffractograms (more 10) show, that the physicochemical conditions in $\text{Te}^{(1)}\text{-Te}^{(1)}$ nano-reactor, leading to formation of CuTe , Cu_2Te , $\text{Cu}_{0.647}\text{Te}_{0.353}$ islands and bismuth telluride itself appear in Bi_2Te_3 -cuprum system. These nano-fragments have found their reflection on diffractograms, presented on fig.6 (a,b,c,d).

The CuTe appearance (having more high melting point) and other nano-particles in Bi_2Te_3 and Sb_2Te_3 nano-reactors (with significant low melting point -585°C and 630°C) shows on the fact, that nano-particles in nano-reactors form at significant low temperatures.

EM images reveal nano-object variety, which crystallize in nano-reactors in Bi_2Te_3 - and Sb_2Te_3 -Van der Waals gaps. We will consider only such nano-objects, which appear in nano-reactor just as this takes place in nano-tubes. These are “restricted” nano-fragments: islands, nano-wires or nano-wires inside nano-tube, and also complex nano-particles.

It is obtained, that part of surface energy increases with decrease of nano-particle dimensions (in nano-reactors) and therefore, melting point of formed crystals decrease. Such changes (melting point decrease) earlier were observed for different “free” nano-particles [3].

The analogous transformations, revealing in given nano-reactors, can lead to new origin results. The melting point decrease of formed particles in nano-reactor, changes dynamic of their transition and leads to formation of plane

one-layer nano-fragments of different orientation. The islands (fig.1), rods (fig.4) of different densities and closed complex figures, inside which the same islands and nano-rods (fig.9) are emphasized at crystal growth. The formed nano-particles strongly differ each from other on construction, but nevertheless they locate on quasi-two-dimensional impurity layers between $\text{Te}^{(1)}\text{-Te}^{(1)}$ chalcogenides of bismuth and stibium.

The nano-island formation in $\text{Te}^{(1)}\text{-Te}^{(1)}$ gap is connected with effect of nano-layer self-organization in given systems. Van der Waals gap is original two-dimensional space-limited nano-reactor (surface, limited by basis planes (0001), where the origination and final formation of nano-objects and nano-crystals take place.

Firstly, the appearance of mono-layers and the diffusion increase of their number, further the appearance and island enlargement prove the transition from two-dimensional-layer to three-dimensional one in layer crystallization process on telluride surface of bismuth and stibium.

The cuprum and baron atoms in dependence on their quantity (not more 0,5 weight %), can increase the period of repeat of structure five-layered packs (d), and also decrease the concentration of hole carriers, totally compensating the donor effect in investigated crystals, transiting in neutral position between $\text{Te}^{(1)}\text{-Te}^{(1)}$ layers and taking ($\text{Te}^{(1)}\text{-Bi-Sb}$), ($\text{Bi-Sb-Te}^{(1)}$) layers, which are less on dimensions.

The so-called crystal reconstruction takes place in process of crystal growth with its interlayer formation. In these nano-reactors either the definite crystal structure, differing from rest Bi_2Te_3 structure part appears, or superstructures form in its cell, locating between layers.

The formation mechanism of given space to some extent remembers the filling of internal cavities of nano-tubes (NT) [4-5]. As in [5], so at Bi_2Te_3 and Sb_2Te_3 growing up the impurity filling takes place at synthesis directly. The task-oriented growing up in $\text{Te}^{(1)}\text{-Te}^{(1)}$ membrane can be carried out already after addition agent introduction. The task-directed crystallization of $\text{Bi}_2\text{Te}_3\langle\text{impurity}\rangle$ and $\text{Sb}_2\text{Te}_3\langle\text{impurity}\rangle$ by different methods, including intercalation by diffusion method (fig. 6,d) finally leads to formation of quasi-two-dimensional layers with islands and nano-rods.

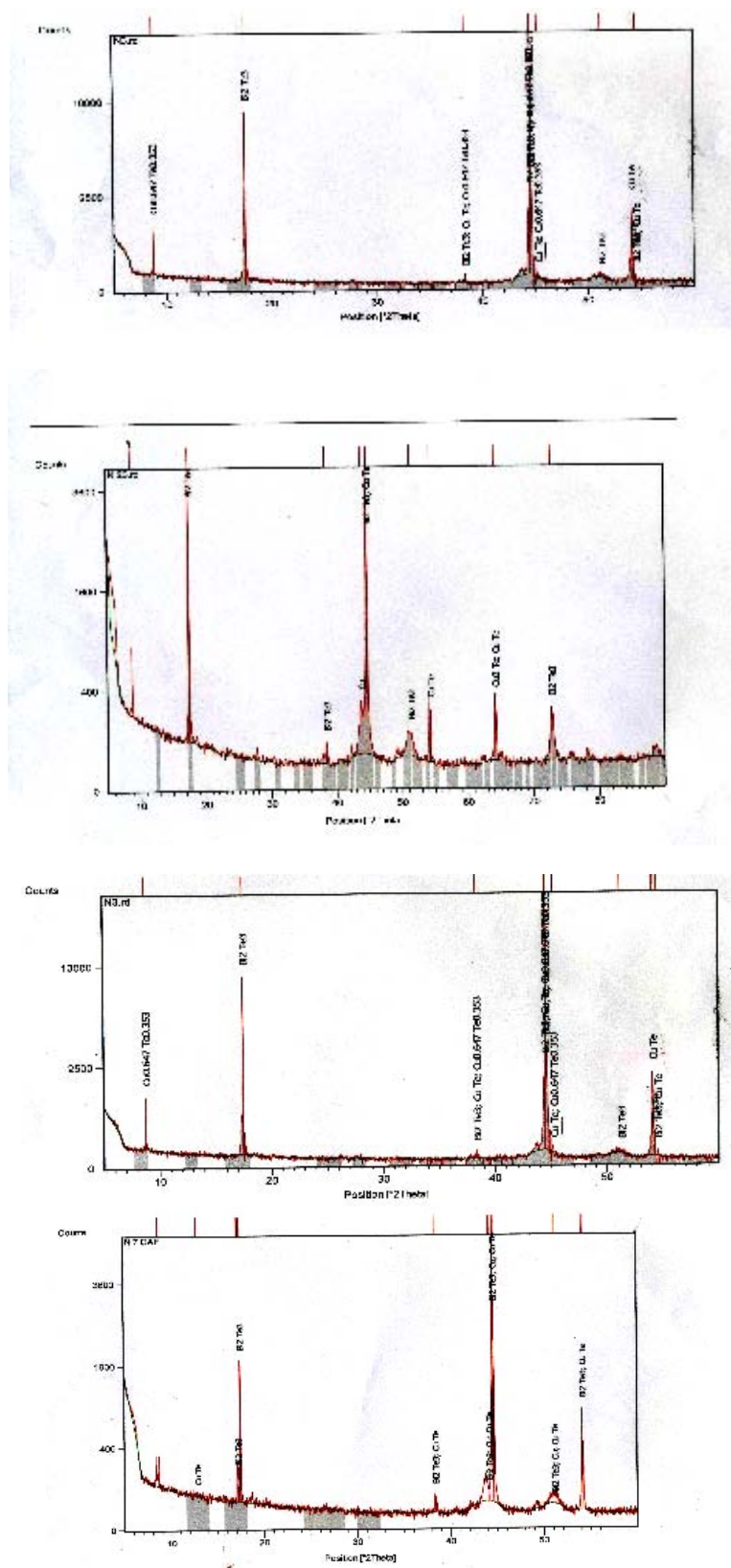


Fig.6.(a,b,c,d) - The roentgen-diffractograms of Bi₂Te₃<Cu> (0001)surface - (with nano-particles from Cu_{0.647}Te_{0.353}, CuTe, Bi₂Te₃) – (a); Bi₂Te₃<Cu> – (with nano-particles from Cu, CuTe, Cu₂Te₃ и Bi₃Te₃) - (b); Bi₂Te₃<Cu> – (with nano-particles from CuTe, Cu₆₄O) – (c), Bi₂Te₃ (intercalated by cuprum) – (with nano-particles from CuTe, Cu) – (d).

from external influences. AFM-image of tellurium nano-particle in $Sb_2Te_3<Te>$ evidences about nano-dimensionless not only on width, but on diameter (less than \varnothing 10nm, see fig. 9). The nano-particles are very similar with nano-tubes could be revealed only on AFM-image of solid solution ($Sb-Bi-Te$) with Te excess till 3weight%.

So, the chemical synthesis of nano-particles can take place in Bi_2Te_3 and Sb_2Te_3 nano-reactors. The filling of such nano-reactors by metals with the aim of obtaining of metallic conductors-nano-wires, “dressed” in boron “covering” can be present the big interest. The nano-reactor not simply forms the nano-fragment (islands and rods), but protects it from oxidation and destroying action of different mediums. Such nano-objects with position of high technologies are subject of intensive study [3-5].

Conclusion

It is shown, that Van-der-Waals gap is peculiar nano-reactor, where the formation of quazi-two-dimensional layers with nano-islands, nano-rods and nano-crystals between $Te^{(1)}-Te^{(1)}$ on surface (0001) of $Bi_2Te_3<Cu,B,Nb>$ and Sb_2Te_3, $Sb_2Te_3<Te>$ take place. The nano-reactors, formed by $Te^{(1)}-Te^{(1)}$ cavities of layered crystals open the wide possibilities for nano-composite design with given thermoelectric properties. The solid-state crystal allows to avoid the aggregation of investigated nano-particles and defend them from external influences that significantly make easier their application

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BİSMUT VƏ ANTİMONUN HALKOQENİDLƏRİ ƏSASINDA İKİ ÖLÇÜLÜ NANOREAKTORLAR

Elektronmikroskopik və rentgendifraktometrik (0001) Bi_2Te_3 və Sb_2Te_3 şəkillərinə əsaslanaraq demək olar ki, $Te^{(1)}-Te^{(1)}$ aralığını nanoreaktor hesab etmək olar. Belə nanoreaktorlarda öz-özünə inkişaf edən və yaranan kvazi iki ölçülü laylar yaranır; onlar nano-adalar, nanonaqillər və nanokristallardır. $Te^{(1)}-Te^{(1)}$ - boşluqlarında-nanoreaktorlarda aşağıdakı nanokristallar əmələ gəlir: məsələn, $Bi_2Te_3<Cu>$ -da $CuTe$, Cu_2Te , $Cu_{64}O$, $Cu_{0,647}Te_{0,353}$; Sb_2Te_3 -da B_2O , $BiBO_3$, $Bi_2B_8O_{15}$.

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ДВУМЕРНЫЕ НАНОРЕАКТОРЫ НА ОСНОВЕ ХАЛЬКОГЕНИДОВ ВИСМУТА И СУРЬМЫ

Электронно-микроскопические изображения и рентгendifрактометрические снимки в слоистых системах Bi_2Te_3 и Sb_2Te_3 , показали, что щель $Te^{(1)}-Te^{(1)}$ играет роль нанореактора. В таких нанореакторах происходит зарождение, самоорганизация и формирование квазидвумерных слоев с наноструктурами, наностержнями и нанокристаллами. Эти структурные пустоты – нанореакторы – заполняются соединениями, последующая модификация которых приводит к формированию нанокристаллов, например в $Bi_2Te_3<Cu>$: $CuTe$, Cu_2Te , $Cu_{64}O$, $Cu_{0,647}Te_{0,353}$; в Sb_2Te_3: B_2O , $BiBO_3$, $Bi_2B_8O_{15}$.

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