# METAL INTERLAYER NANO-PARTICLES IN BISMUTH TELLURIDE

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The interlayer nano-aggregates, forming between $T_e^{(1)} - T_e^{(1)}$ layers in $Bi_2Te_3$ are the new class of fractal nano-objects. Their aggregation takes place at atom agglutination on the same mechanisms as the known solid-state fractal structures formed on free faces of crystal in unlimited volumes, have.

The analysis of nano-fragment fractality characters is carried out on the basis of AFM-images and X-ray-diffractometer photos in $Bi_2Te_3$<metal> layered systems.

## Introduction

The article is dedicated to nano-particle formation problems in crystals of $A_2^V B_3^{VI}$ type the Van der Waals bond of which is weak one. Indeed, the layered compound themselves are capable to "captivate" the guest molecules in the crystal growth process and also at intercalation. The class of intercalated compounds is practically unlimited on, i.e. there is big number of metals (especially easily-diffusing 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 others). The combination of metal layers with semiconductor ones on microscopic level can lead to crystal obtaining with new electron properties. Such nano-objects with the position of high technology can be the subject of special investigations. The filling of nano-tubes by metals (Cu, Ni, Fe, Ag) with the goal of nano-wire obtaining covered by carbonic "wear" is mentioned in work [1].

The analysis shows that nano-chemistry produces the own nano-particle objects, nano-containers, nano-reactors. The two key conceptions: nano-particles and nano-reactor have been determined. The first one characterizes dimensional parameter; the second one defines the nano-particle function [1].

It is necessary to note the one more article [2] in which the approaches to the synthesis of nano-composites on the basis of zero-, one- and two-dimensional solid-state nano-reactors formed by zeolite cavities or interlayer empty spaces of layered compounds have been considered. The work on obtaining of active nano- fibers $Bi_2Te_3$ in matrix of porous aluminum oxide is known [3]. However, the fractal particles of nano-meter dimension [4] form in $Bi_2Te_3$ itself as a result of crystallization in interlayers.

The fractal structures obtained in [4] are analyzed with the position of physics of fractal clusters (FC). They form in the crystal growth processes at agglutination of solid particles [5-6].

The study of $Bi_2Te_3$<metal> surface morphology and their comparison with multi-fractals of complex signals, the consideration of interlayer fractal aggregates with observable nano-layer assemblies [7-9] require the clearance in the perception of self-organized nano-particles on the basis of cuprum, nickel and argentums between $T_e^{(1)} - T_e^{(1)}$ $Bi_2Te_3$.

In this connection the new experimental data on the study of (0001) $Bi_2Te_3$ surface morphology by doped metals are required.

Taking into consideration the above mentioned it's possible to formulate the following tasks: firstly, how Van der Waals crack $T_e^{(1)} - T_e^{(1)}$ in $Bi_2Te_3$ can be considered as nano-reactor for metal (Cu, Ni and Ag) impurities and secondly, what are the fractality characters of forming interlayer nano-fragments.

## Investigation technique

$Bi_2Te_3$ compound is obtained by thermal synthesis at 900-950$^0$K which usually is carried out in quartz ampoules where Bi, Te and impurities (Ni or Cu, Ag) are put in necessary relation. After alloy synthesis they are put in graphitized ampoules (by diameter 9 mm), melted again and then the single crystalline ingots are obtained by vertical directed crystallization at temperature gradient $\Delta T$=100grad/cm and solidification rate 1cm/h. The impurity nano-particle morphology in such crystals after chipping along (0001) $Bi_2Te_3$ plane is investigated. Such samples $Bi_2Te_3$-Me can be considered as intercalation ones from the structural point of view, because the layers of matrix-master and matrix-guest (Cu, Ni and Ag) can be emphasized. Here the increase of interlayer distance at metal atom penetration into interlayer empty spaces is character because of weak chemical bond between $T_e^{(1)} - T_e^{(1)}$.

The diffusion intercalation of Cu, Ni and Ag atoms is carried out at 500$^0$K. For this purpose the metals are sprayed perpendicular to basis plane (0001) by thermal method on clean surface. Later the introduction (intercalation) process along (0001) layers is carried out at temperature gradient $\Delta T$=30grad/cm, the sprayed sample part is hot side. Note that coefficients of diffusion for all impurities are strongly anisotropic one, and for Cu, Ni and Ag along (0001) basis surface they are too big ones that promotes to their easy diffusion into $T_e^{(1)} - T_e^{(1)}$ space during several hours. The (0001) surfaces have been investigated on the samples obtained by such method and the electron-microscopic images and X-ray-diffractometer pictures have been analyzed.

The electron-microscopic images are obtained at atom-force microscope (AFM) of NC-AFM trend. X-ray-diffractometer investigations are carried on the installation of *Philips Panalytical* trend. The preparation of atomically clean surface by the way of chip by special instruments is carried out along (0001) basis plane in the air before experiments.

AFM-images in 2D scale, nano-particle distribution functions with similar dimensions (Fourier-spectrums), nano-fractal density of distribution on (0001) surface on height (Z) (histograms) have been investigated for all doped samples besides AFM-images of (0001) $Bi_2Te_3$ in 3D scale. However, we don't show them in the connection with limitation of number of figures.

**The experimental results and their discussion**

The discussion subject is of fractal character revealing between $T^{(1)}$-$T^{(1)}$ layers in $Bi_2Te_3$<Cu>, $Bi_2Te_3$<Ni> and $Bi_2Te_3$<Ag> nano-aggregates in the comparison of their morphology with fractal systems forming on free surface of solid bodies in unlimited volume.

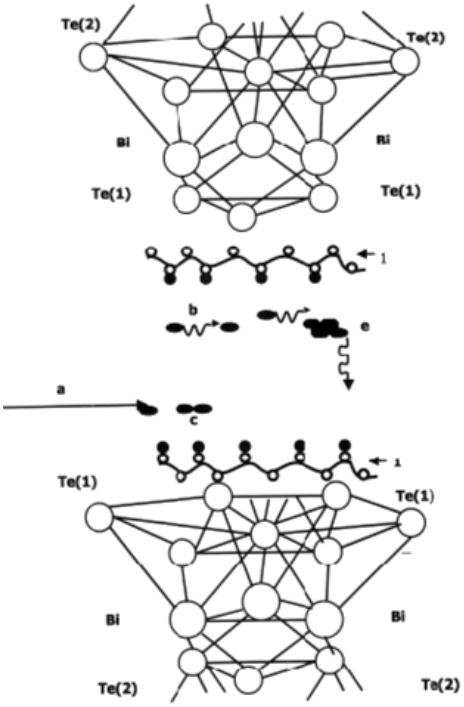


*Fig.1.* The scheme of atom distribution of bismuth and telluride atoms in $Bi_2Te_3$ structure and diffusion ways at intercalation of easily-diffused impurities in interlayers:
a is atom penetration along (0001) plane;
b is formation of new island;
c is particle diffusion;
d is aggregation;
e is island diffusion.
f is particle aggregation between $T_e^{(1)} - T_e^{(1)}$.

The guest atoms (Cu, Ni, Ag…) localize in bismuth telluride in Van der Waals empty spaces formed by atoms of neighbor layers of telluride quintets. Each quintet consists of five simple layers. The atoms of separate layer are similar and form the hexagonal lattice. The atoms of each following layer are posited under the triangle centers formed by the atoms of the previous layer. $T_e^{(1)}$ atoms have on three atoms (six Bi atoms) from each adjacent layer in the capacity of near-neighbors. $T_e^{(1)}$ connects with three *Bi* atoms from the one side, and with three $T_e^{(1)}$ atoms from the another one, i.e. there are two essentially different places for *Te* atoms in the lattice. The scheme of atom positions in $Bi_2Te_3$ crystal lattice and diffusion ways (marked by the arrow (a)) and particle aggregations between telluride quintets (b, e, c) leading to nano-layer formation (1) are given on the fig.1. The distance between quintets is comparably big, i.e. $T_e^{(1)} - T_e^{(1)}$ bond is very weak one. The vacancies after Te, complexes of "dislocations – impurity atom" type, boundaries of blocks and grains, micro-cracks, concentration heterogeneities and micro-segregations [7] can be the most probable places of accumulation and nano-fragment formation on the Cu, Ag, Ni basis.

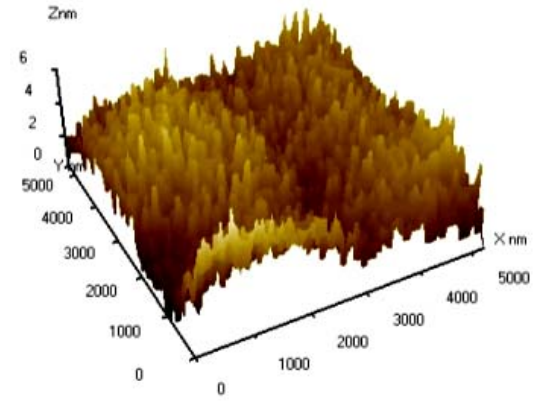


*Fig.2.* AFM- image of (0001) surface of bismuth telluride intercalated by Cu in 3D scale.

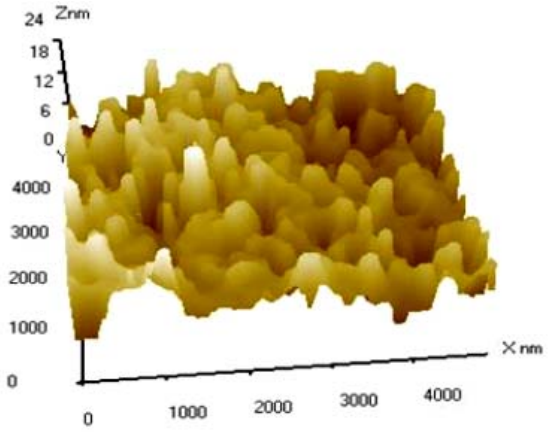


*Fig.3.* AFM-image of (0001) surface of self-intercalated $Bi_2Te_3$<Cu> (in 3D scale).

Let's give the experimental data by the example of $Bi_2Te_3$<Cu, Ni and Ag> system. From fig. 2-3 it is seen what nano-crystalline formations appear on (0001) surface at cuprum intercalation and at synthesis of bismuth telluride towards with Cu with following crystallization. The cuprum penetrates into layers as in nano-container not interacting with super-stoichiometric components of $Bi_2Te_3$: tellurium or bismuth at intercalation at temperature $500^0$K. X-ray-diffraction peaks from cuprum nano-particles (they aren't

given here) evidence about it. X-ray-diffractograms (fig.4) of $Bi_2Te_3$<Cu non-intercalated samples (obtained in the crystal growth process) show the peaks mainly from nano-particles CuTe, Cu and $Cu_{0,647}Te_{0,353}$. Here $T_e^{(1)} - T_e^{(1)}$ $Bi_2Te_3$ plays not only nano-reactor role (as it was mentioned in [1-2]), in which Ni, CuTe and $Cu_{0,647}Te_{0,353}$ form, but the role of nano-container for cuprum (fig.4).

The morphology of (0001) $Bi_2Te_3$ surface in three-dimensional scale (3D) at Ni intercalation is presented on the fig.5; here the fractal nano-structures mainly consist of Ni.

The supposed diffusion ways of particles and their aggregation with following formation of fractal aggregates (fig.1) are probably connected with filling impurity process of places round dislocation pits and vacancies after Te on (0001) $Bi_2Te_3$ surface. The beginning of nano-cell formation takes place in impurity diffusion processes along basis surface (0001) and with nano-fractal growth from surface on Te vacancies on the same telluride quintets. The gradually growing "towers"-benches (FC) form as a result of nano-fragment dimension increase from the surface. The surfaces on (0001) basis plane because of interacting and contacting between each other that is visually reflected on their topography. The coagulation process achieves its peak at which the parallel "mountain hills" form unique nano-fractal surface which we observe on the fig.6 for $Bi_2Te_3$<Ni> system. Here the boundary separating the fractal surface (left one) with right part (which is similar and close one to single fractals) is clearly seen.

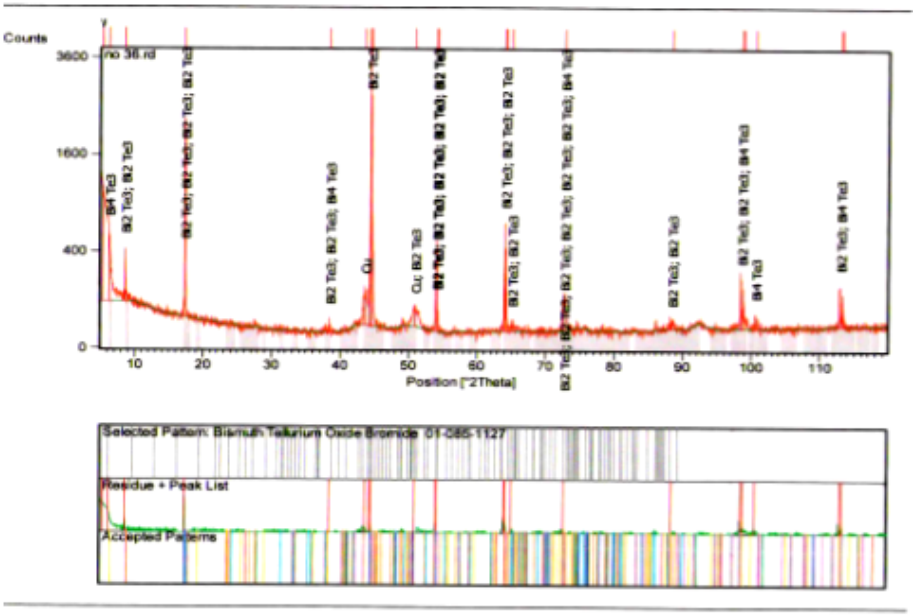


*Fig. 4.* X-ray-diffractometer photo of $Bi_2Te_3$ doped by Cu.

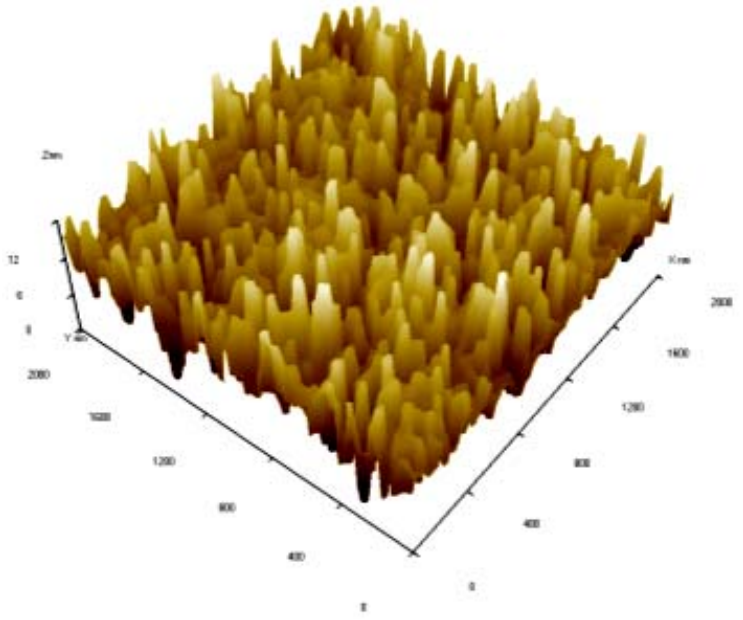

*Fig. 5.* AFM-image of (0001) surface $Bi_2Te_3$<Cu> (in 3D scale).

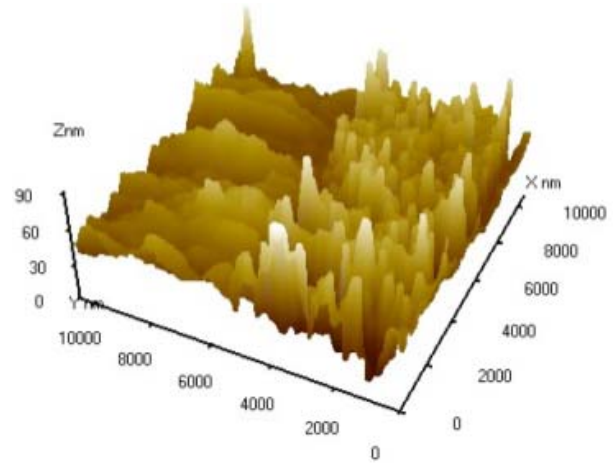


*Fig. 6.* AFM-image of fractal surfaces in $Bi_2Te_3$<Ni> system.

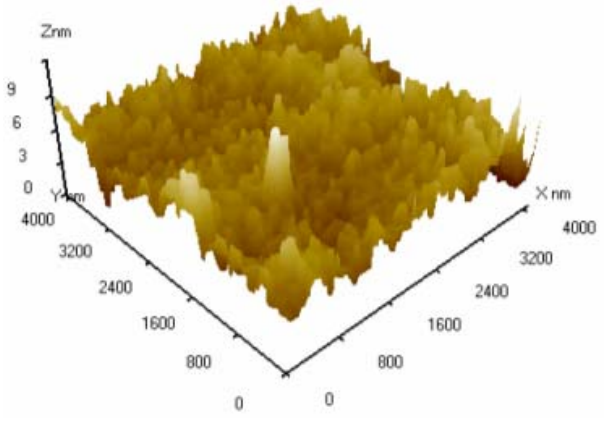


*Fig. 7.* (0001) surface in solid solution ($Bi_2Se_3$ 4mol% - $Bi_2Te_3$ 96mol%) doped by argentums (AFM-photo in 3D scale).

The unique fractal surfaces between $T_e^{(1)} - T_e^{(1)}$ in $Bi_2Te_3$ are obtained for all three impurities: Cu, Ag and Ni. The analogous fractal pictures obtained with the help of consistent occasional Foss additions algorithm are given in [6].

Almost all filling stages of Van der Waals band are connected with the process of rapid introduction of easily diffused impurities (Ag, Cu, Ni) in $Bi_2Te_3$ along basis plane as a result of diffusion directions (direction (a) on the fig.1).

The model of diffusion-limited aggregation (DLA) is often used for revealing of real structure formation mechanisms. Using some elements of DLA [4-6] we accept the model scheme connecting formation processes of intralayer solid-state fractal structures: penetration into layer between $T_e^{(1)} - T_e^{(1)}$ of easily-diffused atoms) Cu, Ni and Ag), diffusion on basis plane (0001) and DLA process.

We have considered the intralayer fractal aggregates (and their fractal measures) and compared them with forming FC on free surface, growing on the model of two-dimensional aggregation limited by diffusion [6,8].This means that FC grows from the germ on telluride vacancies. Making occasional hunts Cu, Ag and Ni atoms move on basis surface (0001) because of gradient diffusion. Contacting with germ of initial cluster the moving impurity atoms get close to it. Further, the another atom making occasional hunts and contacting with cluster increases its dimensions begins to move from new point in the space between $T_e^{(1)} - T_e^{(1)}$.

The dimension of interlayer space $T_e^{(1)} - T_e^{(1)}$ in *$Bi_2Te_3$*~0,3 nm, the height of nano-particles is in the limits 10-20 nm. Here it is possible the converse pressing-expansion of $T_e^{(1)} - T_e^{(1)}$ layers like "bellows". The distance $T_e^{(1)} - T_e^{(1)}$ can be regulated adjusting the investigated nano-reactor on the given volume by the way of filling (penetration) by impurities. The nano-formations on (0001) $Bi_2Te_3$ surface also reveal the characters about multi-fractal structure of interlayer fragments. Their growth dynamics accepts the quantitative and qualitative description with the help of known physics conception of solid-state multi-fractal structures in the case of their obtaining in the unlimited volume [6,9].

For establishment of obtained structure fractality we need: to check the self-similarity, define the boundaries of self-similarity, define the fractal dimensionality (D). Here the main attention is paid to the one from the system classes with fractal structure. The fractal dimensionality of such nano-objects forming in three-dimensional space at association of solid particles (on aggregation model: particle-, cluster, Brownian motion) is $D=2{,}46 \pm 0{,}05$ [5]. The qualitative characteristics of the fact how formed nano-aggregates have filled the space between $T_e^{(1)} - T_e^{(1)}$ of layered $Bi_2Te_3$. The nano-objects are formed in this space and in solid solution ($Bi_2Te_3$ - $Bi_2Se_3$)<Ag> accompanying by the association of close dimension particles (for example: $Ag_2Te$ and $Ag_2Se$) (see fig.7).

It is necessary to use also the multi-fractal theory [8-9] for description properties of self-similarity and complex scaling observable in obtained nano-structures. In the given case as it is seen from the fig.6 the investigated region is formed from two parts. Moreover, each of them has its own self-similarity property, and this factically means the multi-fractality: the multi-fractal is the union of fractal ensembles of different dimensionalities. The nano-objects presented on the fig.2 and 5 are more or less close to single fractal formations (i.e. D with some error presents itself the constant value). As it is known [8] the spectrum of multi-fractal processes can't be described as unique D indicator. Probably, the multi-fractals here form from the set of collected and single fractals pressed to each other (their can be analyzed on the basis of FC conception grown up from surface (0001) [5-6].

The obtained nano-objects on geometric dimension character have nano-dimensions on all three directions: their height doesn't exceed 15-20 nm, width and length varies in the limits less than 1oo nm; i.e. the given nano-objects on classification [2] can be related to nano-particles with unordered distribution. However, particles by ~5-10 nm (clusters) sizes are observed in (0001) surface morphology.

These nano-fractals and surfaces formed by them can be considered as the one from main factors defining the morphology of interlayer space between $T_e^{(1)} - T_e^{(1)}$.

## Conclusions

The analysis of (0001) $Bi_2Te_3$<Cu,Ni and Ag> surface morphology shows that nano-particles (in the form of nano-

fractal formations) can form between $T_e^{(1)} - T_e^{(1)}$ layers with participation of different surface defects.

The reason of rapid growth of nano-fractal "towers" probably is that Cu (Ni, Ag) go to the initial nano-islands, draining from not only impurities of small dimensions accumulated in vacancies, but from atoms diffusing along plane (substrate), "feeding" and changing the heights of fractal formations.

The interlayer impurity nano-fragments are characterized by interaction between its elements.

What is the dimensionality of investigated structure: if we consider them as atom accumulation separately then each particle (cluster, FC) is one dimensional one; their location on the (0001) surface between $T_e^{(1)} - T_e^{(1)}$ is two-dimensional one; however, taking into consideration their fractals the dimensionality is between 2 and 3, i.e. it is fractional one.


[1] *A.L.Buchachenko.* Nanokhimiya-pryamoy put k visokim tekhnologiyam novogo veka, Uspekhi khimii, RAN, 72 (5) 2003, s.419-437.

[2] *Yu.D. Tretyakov, A.V. Lukashin, A.A. Eliseev.* Sintez funktsionalnikh nanokompozitov na osnove tverdofaznikh nanoreaktorov. Uspekhi khimii 73 (9), 2004, s. 974-998.

[3] *O. Rabin, P.R. Herz, S.B. Cronin, L .Lin, A.I. Akinwande, M.S. Dresselhaus.* Mater. Res.Soc. Symp.Proc. 637, D.4.7.1, 2001.

[4] *F.K. Aleskerov, S.Sh. Kakhramanov, E.M. Derun, M.G. Pishkin, G. Kavei.* Nekotorie osobennosti formirovaniya nanoobektov v mejsloevom prostranstve kristallov tipa $Bi_2Te_3$, J. Fizika, NAN AR, 2007, tom XII, №4, s.41-45).

[5] *B.M. Smirnov*. Fizika fraktalnikh klasterov, Moskva, «Nauka», 1991, s.134.

[6] *Jens Feder.* Fractals, Department of Physics University of Oslo Norway, 1988 Plenum Press, New York, p.250

[7] *I.V. Gasenkova, T.E. Svechnikova.* Issledovanie strukturi monokristallov tverdikh rastvorov na osnove tellurida vismuta. Dokladi VIII mejgosudarstvennogo seminara (2002) – Termoelektriki i ikh primeneniya, s. 145-150.

[8] *A.N. Pavlov, V.S. Anichenko.* Multifraktalniy analiz slojnikh signalov. Uspekhi fizicheskikh nauk, t.177, № 8, 2007, s. 859-876.

[9] *V.I. Roldugin.* Fraktalnie strukturi v dispersnikh sistemakh. Uspekhi khimii RAN, 72 (10) 2003, s. 831-859.


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## $Bi_2Te_3$-UN LAYLAR ARALIĞINDAKI METAL NANOZƏRRƏCİKLƏRİ


$Bi_2Te_3$- laylar $T_e^{(1)} - T_e^{(1)}$ arasında yaranan nanoaqreqatlar yeni tipli fractal nanoobyektlərdir. Onlar metalların $T_e^{(1)} - T_e^{(1)}$ aralığında diffuziya hərəkəti zamanı formalaşır; belə nanosistemlərin yaranma mexanizmləri isə sərbəst təbəqələrdə əmələ gələn adi fractal strukturları ilə eynidir.

Nanofraqmentlərin fraktallık analizi elektron mikroskopik (AEM) və rentgendifraktometrik şəkilləri əsasında aparılır.


**Ф.К. Алескеров, С.Ш. Кахраманов, М.А. Рамазанов**

## МЕЖСЛОЕВЫЕ НАНОЧАСТИЦЫ МЕТАЛЛОВ В ТЕЛЛУРИДЕ ВИСМУТА


Межслоевые наноагрегаты, формирующиеся между слоями $T_e^{(1)} - T_e^{(1)}$ в $Bi_2Te_3$ составляют новый класс фрактальных нанообъектов. Их агрегация происходит при слипании диффундирующих атомов по тем же механизмам, что и в известных твердотельных фрактальных структурах, сформированных на свободных гранях кристаллов в неограниченном объеме.

Анализ признаков фрактальности нанофрагментов проведен на основе АСМ-изображений и рентгенодифрактометрических снимков в слоистых системах $Bi_2Te_3$<металл>.


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