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A Topological Structure Model and Nonlinear Formation Model of ZnO Tetrapods

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Abstract. The work proposes a ZnO tetrapod formation model based on a topological representation of the octahedral nanoscale clusters growth space transformation during the polymorphic transition from *B*3 to *B*4 at the nanoscale. The iterated system function system method is used to model the precrystallisation stage of the hierarchical tetrapod crystal structure formation in the highly non-equilibrium dynamic chaos synthesis conditions.

Keywords: topological space, crystal polymorphism, hierarchy, dynamic chaos, self-assembly, IFS, fractal, affine transformations.

INTRODUCTION

Geometry modification at the nanoscale is a tool to control properties of materials [1]. The unique physico-chemical characteristics of the ZnO tetrapod nanoform (t-ZnO) (Fig. 1) [2] is related to its hierarchical structure of connected *B*4 crystals. The non-equlibrium conditions of the high-temperature vapour-transport synthesis reactor where t-ZnO is formed [3, 4] may cause predictable polymorphic transitions between the metastable *B*3 and stable *B*4 phases [5, 6].

T-ZnO is highly favourable for various technological applications [7–11]. While its crystal structuring is well studied [12, 13], there is no clear understanding and model of its formation mechanism in dynamic chaos conditions.

The aim of this work is to develop a ZnO tetrapod morphology model based on the description of the polymorphic transition from a *B*3 octahedral nucleus to four *B*4 rod crystals as a topological space transformation at the nanoscale.

OBJECT DESCRIPTION

Hierarchy in structural organisation is determined by the compound nature of higher structural levels in relation to lower levels. Thus, t-ZnO is a hierarchical system as of two levels of structural organization:

1. *B*4 monocrystal.
2. The t-ZnO nanoform consisting of a union of separate *B*4 monocrystals.

The structuring of the t-ZnO nanoform is tightly connected to the crystal properties of the *B*4 monocrystals, yet cannot be described solely by the laws that govern their formation.

In our previous work [15] among the theoretically studied polyhedral clusters only two were found to be thermodynamically stable in the conditions of t-ZnO synthesis – the $Zn_{85}O_{80}$ and $Zn_{146}O_{140}$ *B*3 octahedra. This provides additional proof to the octahedral nucleus t-ZnO formation model [8]. Thus during the initial stage of formation the morphological properties of the nucleus are the ordering parameters controlling the relative arrangement of the priority [0001] growth directions in the four first generation rod crys-

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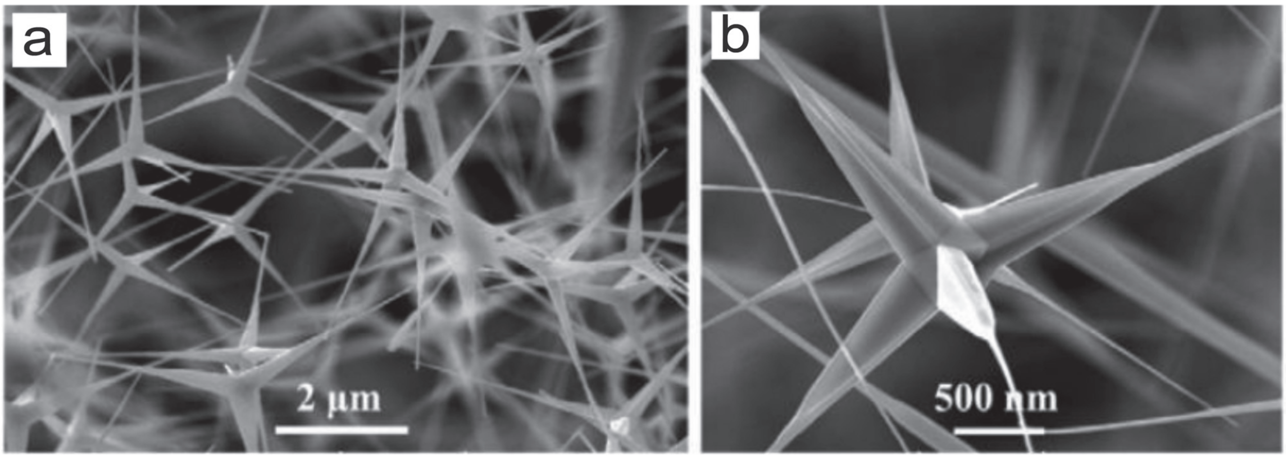


Fig. 1. ZnO tetrapods. *a*, *b* – different magnifications [2]

tals of the tetrapod hierarchical nanostructure (Fig. 2). The crystals can be easily separated due to the existence of stacking faults occurring because of mismatches of crystal planes [16].

From a mathematical point of view the t-ZnO structure unites four independent spaces of *B*4 growth, hence a topological description is applicable.

TOPOLOGICAL MODEL OF THE ZnO TETRAPOD STRUCTURE

A tetrapod isolated from the tetrapod array is formed in $\mathbb{R}^3$ space with a usual topology. However according to diffractometry and electron microscopy studies [17], each of the *B*4 crystals grows in its own crystal growth space.

Thus, at the first growth stage the octahedral nucleus is formed in the topological space (TS) of *B*3 crystal growth X_{B3}, where positions of atoms are defined by the separation of X_{B3} into elementary cells of the ZnO *B*3 crystal lattice. A $Zn_{146}O_{140}$ octahedron is considered the stable nucleus form. A non-optimised arrangement of atoms in such a nucleus is equivalent to a closed subset $Z_{B3} \subset X_{B3}$ (Fig. 3*a*).

At the second growth stage the growth space transforms around Z_{B3} and four *B*4 crystal growth regions $X_{B4|i}$, $i = 1,\ldots,4$ appear. Here and further the "|" symbol is used to separate indexes.

In the context of graph theory, a structure that contains the octahedral ZnO nucleus and four crystals growing from its four unpassivated (111) faces is an oriented noncyclic graph (Fig. 3*b*). The growth space on this stage is a disjunctive sum $Z_{B3} \cup X_{B4|1} \cup X_{B4|2} \cup X_{B4|3} \cup X_{B4|4}$ where $\{X_{B4|i}, i = 1,\ldots,4\}$ are non-overlaping TSs of *B*4 crystal growth. Each $X_{B4|i}$ space is separated into subsets $X_{B4|i|\mathrm{Zn}}$ and $X_{B4|i|\mathrm{O}}$ according to positions of Zn and O atoms in the *B*4 crystal lattice, respectively.

Since the number of atoms in the octahedral core in comparison to the number of atoms in the *B*4 crystals of the t-ZnO structure both diagnosed experimentally and theoretically is insignificantly small, $|Z_{B3}| \div |X_{B4|i}| \approx 10^{-9}$ or it may be absent entirely, it may be neglected when modelling the t-ZnO structure. This will have an effect on the structure of the graph (Fig. 3*c*). Then to form a t-ZnO structure atoms will take positions according to the TS

$$X_{\text{t-pod}} = \bigcup_{i=1}^{4} X_{B4|i}. \qquad (1)$$

Each space $X_{B4|i}$ is homeomorphic to a compact TS of a *B*4 crystal's growth $X_{B4|0}$ and can be defined by a system of continuous mappings

$$F_{\text{t-pod}} = \{f_1,\ldots,f_i\} : X_{B4|0} \to X_{\text{t-pod}}\ , \qquad (2)$$

which by mapping $X_{B4|0}$ arrange the four spaces constituting (1) in accordance with the symmetry of the unpassivated facets of Z_{B3} (Fig. 4).

Having defined a finite-size *B*4 crystal $X_{B4|0}$ centered at the origin (0,0,0) and oriented so $\mathbf{r}_{[0001]} \parallel \mathbf{r}_z$, where $\mathbf{r}_{[0001]}$ is the [0001] crystallographic direction in $X_{B4|0}$ and $\mathbf{r}_z$ is the direction of the *z* axis, each f_i function can be defined by a sequence of translation and rotation.

In the thermodynamic conditions of synthesis the [0001] direction in each of the *B*4 crystals of the t-ZnO structure is the priority growth direction and each crystal grows "stretched" in the direction from the t-ZnO center and "compressed" in the lateral directions. Then with the addition of a preliminary mapping of contracting scaling the functions will include all affine transformations:

$$\forall f_{aff|i} = [f_{rot|i} \circ f_{tr|i} \circ f_{sc|i}] : X_R \to X_{aff|i}\ , \qquad (3)$$

where $f_{sc|i}$, $f_{tr|i}$ и $f_{rot|i}$ are scaling, translation and rotation mappings, respectively and $X_R \subset \mathbb{R}^3$. In the optimised matrix form designed to model the t-ZnO structure

$$\forall f_{aff|i}(\mathbf{r}) = \left[\mathbf{r} \times \begin{bmatrix} s_x \\ s_x \\ s_z \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ (a \cdot s_z)/2 \end{bmatrix}\right] \times \qquad (4)$$
$$\times \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\psi_i & -\sin\psi_i \\ 0 & \sin\psi_i & \cos\psi_i \end{bmatrix} \times \begin{bmatrix} \cos\varphi_i & \sin\varphi_i & 0 \\ -\sin\varphi_i & \cos\varphi_i & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

where ψ_i and φ_i are rotation parameters around the x and z axes, s_x и s_z are scaling parameters along the x and z axes respectively, a is the size of the initial crystal and $(a \cdot s_z)/2$ is the translation parameter that aligns the image's border with the x–y plane.

The full set of parameters for the mappings from the system

$$F_{aff} = \{f_1, \ldots, f_i\} : X_R \to X_{aff}\ ,$$

that provide the tetrapod configuration is given in Table 1. The result of mapping a TS $X_{R|0}$ of the size a with functions (4) and the parameters from Table 1 is shown in Fig. 5*a*.

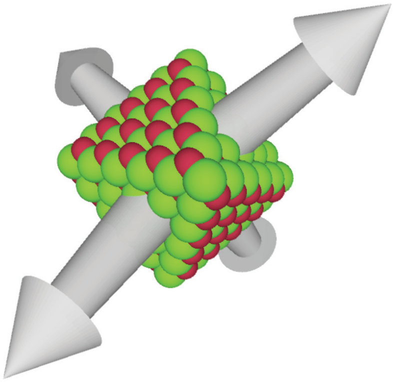


Fig. 2. [0001] crystal growth directions in four *B*4 crystals forming on the *B*3 octahedral $Zn_{146}O_{140}$ nucleus. Bright atoms – Zn, dark atoms – O

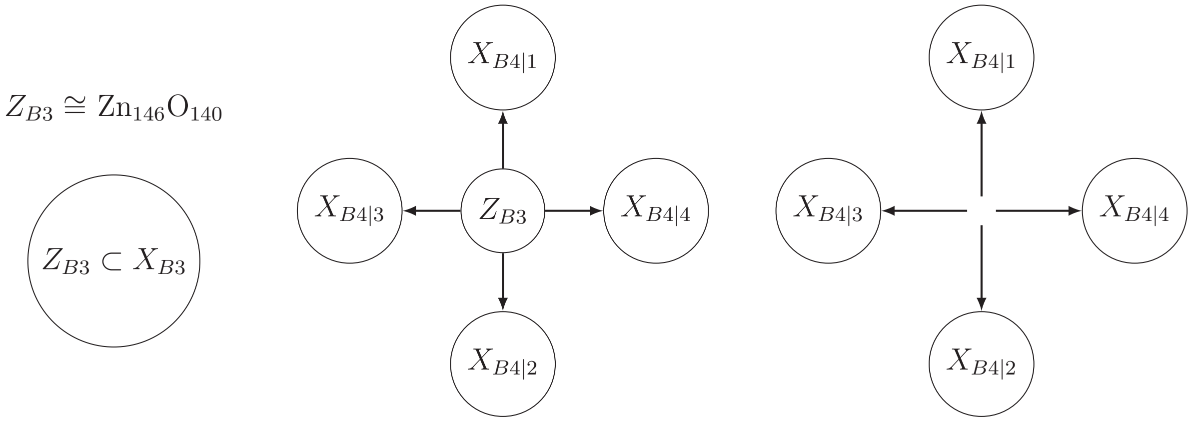
By limiting $X_{\text{t-pod}}$ to

$$X_{\text{t-ZnO}} = \bigcup_{i=1}^{4} (f_{aff|i}(X_{R|0}) \cap X_{B4|i})$$

the *B*4 lattice structuring from the respective $X_{B4|i}$ is preserved yet the anisotropy of the growth speed is reflected in the t-ZnO structure model. The maps of a hexagonal prism crystal generated using parameters from Table 1 (s_x increased to 0.54) are shown in Fig. 5*b*.

FORMATION MODEL OF ZnO TETRAPODS

The spontaneous formation of t-ZnO hierarchical structures indicates the existence of an evolutionary process that includes the transition of initial Zn samples to the gas phase and



a *b* *c*

Fig. 3. Graphs reflecting the t-ZnO structure evolution. *a* – formation of the Z_{B3} octahedral nucleus; *b* – formation of the *B*4 crystal growth topological spaces $\{X_{B4|i}, i = 1, \ldots, 4\}$ on the facets of the $Zn_{146}O_{140}$ nucleus; *c* – dissolution of the nucleus and preservation of the configuration of four [0001] *B*4 crystal growth directions in $\{X_{B4|i}, i = 1, \ldots, 4\}$

its exit from the gas phase as t-ZnO. The external ordering parameters – the open system of the vapor transport synthesis reactor and the continuous inflow of reagents – together with the inherent ZnO crystal structuring properties create conditions that sustain the functioning of a t-ZnO generation system as a morphogenesis program aiming to reach a final ideal, similar to homeostasis. Such a final ideal is defined by the mutual influences of components in the tetrapod generation system among each other. For systems that dissipate energy and information, such as the t-ZnO generation system, this ideal state is described by an attractor – a set of a dimension smaller than the dimension of the dissipative system, to which the neighbouring states of the dissipative system are drawn to with time [14].

Translational methods used for describing crystal structures and quantum-chemical modelling methods which regard the attractor of a dissipative systems as a uniquely defined state unrelated to the surrounding medium are incapable of effectively describing the formation process of t-ZnO hierarchical structures, which is dependent on the reactor temperature, the reaction time and the causal relationships between the stages of t-ZnO elements formation.

The interacting octahedral clusters in the t-ZnO reactor medium can be considered islands forming a precrystallisation percolation system in the 3-D Folmer-Weber mechanism of thin film crystallization [6]. Then the process of t-ZnO generation is a technological cycle with the following stages:

1. ZnO synthesis in the gas phase.
2. Formation of octahedral nanocrystalline *B*3 nuclei.
3. Formation of dynamic self-assembled precrystallisation percolation structures of octahedral nuclei.
4. Crystallisation of the percolation structures into t-ZnO hierarchical structures.
5. Formation of a discrete array of similar ZnO tetrapods.

Despite the difference in formation energy of the *B*3 and *B*4 polymorphic modifications [20], in the extreme non-equlibrium ZnO synthesis condition primary nanoforms may nucleate as both *B*3 and *B*4, *B*3 being preferable. The short reaction times and the spontaneous character of interactions require the formation model to handle time parametrisation in a nonclassical way.

The structure of the gaseous system of octahedral nuclei and ZnO clusters in the approximation of an infinite number of infinitely small particles is a structureless array of chaotically moving dots. The X_R TS of such a system of dots moving in $\mathbb{R}^3$ with in the approximation of an infinitely large reactor is path-connected [21]. Then the dynamic percolation system state reflects a transitional state between X_R and the disconnected $X_{\text{t-ZnO}}$ TS:

$$X_R \to X_{\text{t-ZnO}}.$$

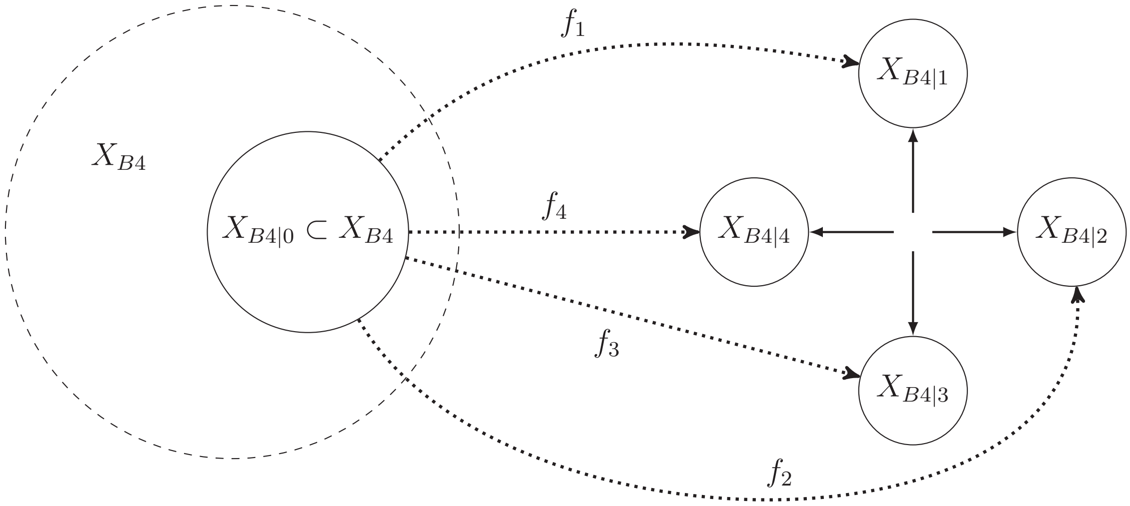


Fig. 4. Defining the topological space $\{X_{B4|i}, i = 1, \dots, 4\}$ as maps of an initial $X_{B4|0}$ *B*4 crystal growth topological space

This transitional state unites the properties of both systems and is characterised by kinetic instability.

Since the vapour-transport synthesis system is thermodynamically open, the number of dynamic particles and the number of their possible arrangement in space does not decrease with time as more material enters the reactor zone.

Instead of linearly searching through all possible locations in space and rotations of octahedral nuclei, calculating interatomic electrostatic forces for every moment of time during the evolution of the chaotic dynamic system of particles in the high temperature synthesis medium, which is nearly impossible with modern technology, an optimization of the t-ZnO formation model is proposed. The optimization is based on accepting the approximations that take into consideration the real conditions in the t-ZnO vapour-transport synthesis medium:

1. Constant influx of initial Zn and O_2 components into the thermodynamically open reactor.

2. High density of the reactor medium that leads to ZnO nuclei formation.

3. The most probable configuration of a nucleus is the $Zn_{146}O_{140}$ *B*3 octahedron.

4. The tetrahedral symmetry of the nuclei defines their most probable relative arrangement during the formation of a precrystallisation percolation system according to the Folmer-Weber mechanism.

5. Ubiquitous transformation of each nucleus into four *B*4 crystals.

[**Table 1.** Rotation parameters ψ_i, φ_i and scaling parameters s_x и s_z for functions of the type (4) defining $X_{\text{t-ZnO}}$]

i	ψ_i	φ_i	s_x	s_z
1	0	0	0.15	0.8
2	0	$\pi - \arcsin\frac{2\sqrt{2}}{3}$		
3	$\frac{2\pi}{3}$			
4	$-\frac{2\pi}{3}$			

6. Nuclei are attracted to each other in the dynamic system.

7. *B*4 crystals are momentarily formed around the nucleus with the priority [0001] directions perpendicular to the tetrahedrally directed unpassivated (111) facets of the octahedral *B*3 nucleus.

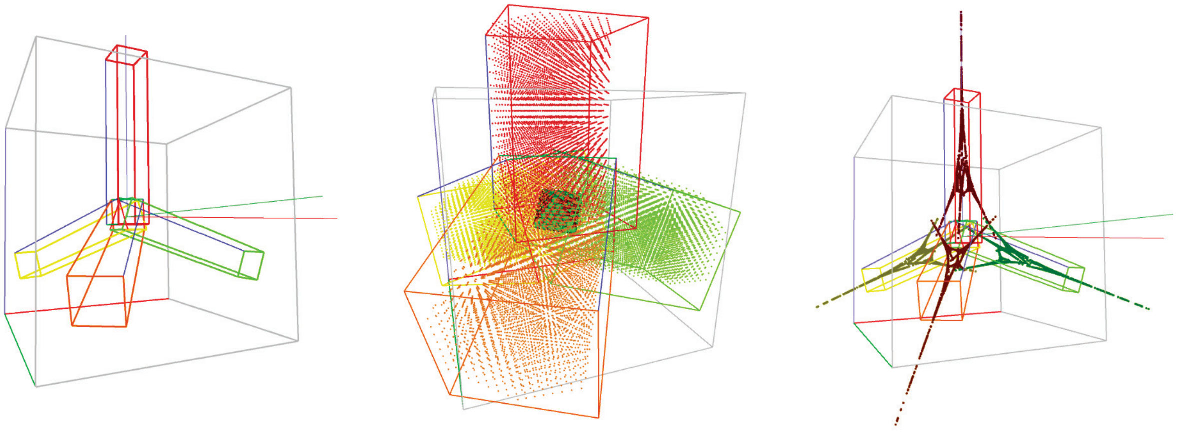
8. Only the most probable growth scenarios succeed due to the highly non-equilibrium conditions in the reactor.

9. The sizes of the nuclei and particles in the reactor medium are negligibly small and can be described as dots.

10. Each tetrapod in the generated array is formed according to a single principle.

The attraction forces between the nuclei in the dynamic system will determine the appearance of attractors – sets of positions to which stable states of the interacting system will be drawn to with time.

A developing dynamic system description method, supported by the fundamental theorem



a *b* *c*

[**Fig. 5.** *a* – $X_{aff|i}$ maps of the $X_{R|0}$ topological space. $X_{R|0}$ is depicted as the larger cube; *b* – $X_{\text{t-ZnO}}$ growth topological space; *c* – $A_{\text{t-ZnO}}$ attractor yielded by $\mathcal{F}_{\text{t-ZnO}}$. Dots related to different topological spaces of crystallisation are marked with different colour] of dynamic systems [26], is the iterated mappings in metric space [27]. The iterated function system (IFS) [25]:

$$\mathcal{F} = \{X, f_1, f_2, \ldots, f_N\}\ , \tag{5}$$

where $\{f_1, f_2, \ldots, f_N\}$ are continuous maps in the TS X, is a well developed method for describing attractor sets for stochastic non-linear dynamic systems. And IFS consisting of maps of the type (4) and parameters from table 1 will be denoted $\mathcal{F}_{\text{t-ZnO}}$.

Using the chaos game algorithm [26] an attractor $A_{\text{t-ZnO}}$ is yielded for the IFS $\mathcal{F}_{\text{t-ZnO}}$. $A_{\text{t-ZnO}}$ is a representation of contracting dynamic system, in every point of which occurs the formation of an octahedral nucleus and its transformation into four tetrahedrally oriented crystal formation spaces. The arrangement of the new spaces is correlated with the global symmetry of the reactor medium defined by the affine mapping parameters (Fig. 5*c*).

According to the formulated formation model approximations each dot in $A_{\text{t-ZnO}}$ will denote a singularity where the TS X_{B3} transforms into four TS of *B*4 crystal growth constituting the t-ZnO structure:

$$X_{B3} \to X_{\text{t-ZnO}}\ . \tag{6}$$

Such dots represent transitional states without a defined crystal structure or shape. The TS transformation is analogous to a polymorphic transition controlled by nanoscale symmetry and will be referred to further as *topological polyporphic nanoscale transformation*.

According to the Folmer-Weber mechanism as the concentration of particles grows the gaps in the percolation system are filled and the system crystalises. At this modelling stage the dots represent atomic clusters, atoms of which occupy nearest positions in the *B*4 crystallic lattice TSs bordering with the growing nucleus according to the separation of $X_{\text{t-ZnO}}$ into positions of Zn and O atoms. Thus the attractor $A_{\text{t-ZnO}} \subset \mathbb{R}^3$ degenerates into the subsets of discrete $X_{B4|i}$ TSs constituting $X_{\text{t-ZnO}}$, to form the t-ZnO morphology model preserving the non-linear formation dynamics effect and the hierarchical crystal structuring.

The rule of relation of a dot x_n in the attractor A of IFS $\mathcal{F}$ to the crystalisation TS $\left(X_i, i = 1, \ldots, N\right)$ in accordance with the mapping f_i that generated the dot is formulated: to define which crystalisation TS X_i is *related* to the dot x_n generated by the chaos game algorithm, x_n is associated with the mapping $\left(f_i, i = 1, \ldots, N\right)$ that generated x_n:

$$x_n \to \left(x_n, i\right)\ , \tag{7}$$

where i is the index of function $f_i \in \mathcal{F}$. The application of the *rule of relation* (7) to $A_{\text{t-ZnO}}$ is illustrated in Fig. 5*c*, where each dot *relating* to one of the four crystallisation TSs is marked with a different colour.

Despite the percolation system model does not include objects representing Zn and O atoms the formation process is controlled by the experimentally deduced and theoretically calculated characteristics of ZnO nanocrystals, their growth kinetics and polymorphic transformation properties corresponding to the thermodynamic conditions in the reactor medium. Thus, the substitution of X_{B3} by X_{B4} when using parameters from table 1 and mappings (4) to model the percolation system formation

$$X_{B3} \xrightarrow{\mathcal{F}_{\text{t-ZnO}}} X_{\text{t-ZnO}} \tag{8}$$

by yielding the attractor $A_{\text{t-ZnO}}$ is justified. The stochastic nature of the chaos game algorithm makes it similar to nature. Numerical calculation errors do not affect the model as the process of convergence to $A_{\text{t-ZnO}}$ continues with every following iterative mapping.

The rotation angles defining the tetrahedral symmetry can deviate from perfect values creating more realistic models [27].

The substitution of a multi-element mapped set by a single-element set [25] optimises the calculation and allows to generate 10^5–10^6 new dots per second.

CONCLUSION

The stochastic nature of the percolation structure formation process results from the fluctuating changes of pressure, particle concentration and temperature in the reactor medium. On the other hand the replicability of the transformation process (8) results from the optimised thermodynamic conditions that allow for the transformation process to happen only according to the topological nanoscale polymorphic transformation (6). Thus the processes of polymorphic transformations of ZnO nanostructures in the high-temperature chaos of the vapour-transport synthesis system lead to a collective synergetic process of ZnO hierarchical structures self-assembly.

The topological approach opens new possibilities in modeling more complex dendrite structures consisting of monocrystal elements, also known as oriented attachment growth structures [28] and fractal nanosystems [29, 30].

In summary, a topological model of the t-ZnO was developed, its hierarchical structure was mathematically identified as consisting of four linked TSs of *B*4 crystal growth. The TSs are arranged by affine mappings of an initial *B*4 crystal growth TS. The transition from the octahedral *B*3 nucleus growth TS to the four *B*4 crystal growth TSs are considered as a transformation of the *B*3 crystal growth TS at the nanoscale.

The chaos – nucleus – percolation system – crystal nanotechnological self-assembly cycle stages were formulated to describe the formation of the t-ZnO array. The cycle determines a topological transition from a path connected gas phase TS to the disconnected t-ZnO hierarchical crystal structure formation TS.

A hierarchical nanostructure formation modelling method was developed basing on yielding an IFS attractor. The transition from the chaotic dynamic array of particles in the gas phase to a percolation system model with a defined law of the transformation and attraction of elements is guided by the parameters of affine mappings forming the configuration of the TSs of crystal growth in the hierarchical system.

The rule of relation of a yielded attractor dot to a crystalisation TS in the hierarchical structure was formulated.

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CONFLICT OF INTEREST

The authors declare the absence of obvious and potential conflicts of interest related to the publication of this article.

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Топологическая модель структуры и нелинейная модель формирования тетраподов ZnO

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Аннотация

Цель работы. Разработка обобщенной математической модели формирования иерархических кристаллических наноформ тетраподов оксида цинка, полученных газотранспортным синтезом в условиях динамического хаоса частиц.

Методы и методология. Топологических анализ полиморфной трансформации на наномасштабе, нелинейная динамика формирования самоорганизованных структур в условиях динамического хаоса. Метод построения аттрактора аффинной системы итерированных функций, параметры для которых определены экспериментальными методиками диагностики: электронной микроскопией, дифракционными исследованиями и численными методами квантово-химических расчетов ядра иерархических структур.

Результаты. В работе установлена систематика тетраподов как иерархических структур; определен нанотехнологический цикл самоорганизации тетраподов оксида цинка хаос – ядро – перколяционная система – кристалл; произведена математическая идентификация структуры тетрапода как четырех связанных топологических пространств роста вюрцитного кристалла; разработан метод моделирования процесса формообразования тетрапода построением аттрактора системы итерированных функций; установлено правило принадлежности точки в аттракторе модельной нелинейной стохастической динамической системы топологическому пространству кристаллизации в формирующейся самоорганизованной иерархической кристаллической структуре.

Разработан теоретический подход, позволяющий создавать и модифицировать модели трехмерных пространственно-распределенных иерархических кристаллических структур с новыми, по сравнению с монокристаллом, физическими и топологическими свойствами, управлять их формой и классифицировать их по топологическим и симметрийным признакам.

Заключение. Формирование тетрапода оксида цинка происходит в четырех топологических пространствах, моделируемых непрерывными отображениями пространства роста вюрцитного кристалла *B*4. Переход от роста сфалеритного ядра к росту четырех вюрцитных кристаллов, образующих иерархическую структуру тетрапода, рассматривается как разрыв топологического пространства роста при полиморфноий трансформации на наномасштабе. Топологический подход с использованием метода аффинноий системы итерированных функцийий применим для моделирования предкристаллизационного этапа формирования мультиподов, а также дендритных кристаллических структур и фрактальных нанокомпозитов, для предсказания их морфологии, геометрических и структурных свойств.

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Ключевые слова: топологическое пространство, полиморфизм кристаллов, иерархия, динамический хаос, самоорганизация, системы итерированных функций, фрактал, аффинные отображения.

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