

Kinetic analysis of the crystallization processes in the protonated potassium polytitanates

© Alexander V. Gorokhovskiy^a✉, Svetlana I. Saunina^b, Dmitriy A. Zakharyevich^b,
Lilia A. Maximova^a, Elena V. Tretyachenko^a, Natalia O. Morozova^a

^a Yuri Gagarin State Technical University of Saratov, 77, Polytekhnicheskaya St., Saratov, 410054, Russian Federation,

^b Chelyabinsk State Technical University, 129, Brat'ev Kashirnykh St., Chelyabinsk, 454001, Russian Federation

✉ algo54@mail.ru

Abstract: The kinetics of the TiO₂ crystalline phase formation in the powdered samples of protonated potassium polytitanate (PPPT) having an amorphous layered structure was studied by differential scanning calorimetry (DSC). The theoretical analysis was carried out using the THINKS free software, based on the methods of Kissinger, Friedman and Vyazovkin, as well as the method of combined kinetic analysis, and the methods of linear and non-linear regression. The obtained results have shown that the formation of the crystalline TiO₂ (anatase) in the investigated system occurs in two stages. The theoretical results were analyzed taking into account their correspondence to the kinetic models of crystallization process including: two independent flexible one-step stages; two sequentially flowing flexible single-step stages; two parallel flowing (competing) flexible single-step stages. The main kinetic parameters of the crystallization process are determined using the best satisfaction to the Bayesian fit criterion (BIC). Based on the results obtained, the mechanism of two sequentially flowing stages is proposed. The first stage of crystallization, involves the diffusion of surface-active components (H₂O, H₃O⁺, K⁺) in the interlayer space to the surface of PPT particles and following desorption of water and transformation of the layered amorphous PPPT structural polyanions into the distorted crystalline anatase-like structure. At the second stage of the process, the distorted anatase structure is transformed into the traditional crystalline form, and, finally, the process of crystallization of protonated PPT is completed by the formation of small crystals of potassium hexatitanate onto the surface of particles with the participation of potassium ions previously diffused from the bulk.

Keywords: potassium polytitanate; thermal analysis; crystallization; isoconversional kinetic analysis; kinetic parameters; mechanism.

For citation: Gorokhovskiy AV, Saunina SI, Zakharyevich DA, Maximova LA, Tretyachenko EV, Morozova NO. Kinetic analysis of the crystallization processes in the protonated potassium polytitanates. *Journal of Advanced Materials and Technologies*. 2023;8(1):030-040. DOI:10.17277/jamt.2023.01.pp.030-040

Кинетический анализ процессов кристаллизации в протонированных полтитанатах калия

© А. В. Гороховский^a✉, С. В. Саунина^b, Д. А. Захарьевич^b,
Л. А. Максимова^a, Е. В. Третьяченко^a, Н. О. Морозова^a

^a Саратовский государственный технический университет имени Гагарина Ю.А.,
ул. Политехническая, 77, Саратов, 410054, Российская Федерация,

^b Челябинский государственный университет,
ул. Братьев Кашириных, 129, Челябинск, 454001, Российская Федерация

✉ algo54@mail.ru

Аннотация: Методом дифференциальной сканирующей калориметрии (ДСК) исследована кинетика формирования кристаллической фазы TiO₂ в образцах протонированного полтитаната калия (ПТК), имеющего аморфную слоистую структуру. С использованием свободного обеспечения THINKS на основе методов

Киссинджера, Фридмана, метода комбинированного кинетического анализа, с применением методов линейной и нелинейной регрессии проведен анализ соответствия полученных экспериментальных кривых ДСК различным кинетическим моделям процесса кристаллизации, включая: два независимых гибких одноступенчатых шага; два последовательно протекающих гибких одноступенчатых шага; два параллельно протекающих (конкурирующих) гибких одноступенчатых шага. Определены основные кинетические параметры процесса, в наибольшей степени удовлетворяющие экспериментальным данным по критерию соответствия Байеса (BIC). Результаты исследования показали, что образование кристаллической фазы анатаза в данной системе идет в два этапа. На основании полученных результатов предложен механизм двухстадийного процесса кристаллизации протонированных ПТК, предусматривающий на первом этапе диффузию поверхностно-активных компонентов (H_2O , H_3O^+ , K^+) в межслойном пространстве к поверхности частиц ПТК, с дальнейшей десорбцией воды и преобразованием слоистой аморфной структуры полианионов ПТК в искаженную структуру анатаза. На втором этапе процесса происходит трансформация искаженной структуры анатаза к ее традиционной кристаллической форме, и завершается процесс кристаллизации протонированных ПТК образованием мелких кристаллов гексатитаната калия на поверхности кристаллических частиц TiO_2 с участием остаточных ионов калия, ранее продиффундировавших из внутренних слоев частиц ПТК к поверхности.

Ключевые слова: полтитанаткалия; термический анализ; кристаллизация; изоконверсионный кинетический анализ; кинетические параметры; механизм.

Для цитирования: Gorokhovskiy AV, Saunina SI, Zakharyevich DA, Maximova LA, Tretyachenko EV, Morozova NO. Kinetic analysis of the crystallization processes in the protonated potassium polytitanates. *Journal of Advanced Materials and Technologies*. 2023;8(1):030-040. DOI:10.17277/jamt.2023.01.pp.030-040

1. Introduction

The understanding of the mechanism and description of the kinetics of reactions in solid-phase systems is of great importance in the development of methods for the synthesis of so-called high-tech composite materials. In recent years, intensive research has been carried out in the field of obtaining intermediate products intended for use in the synthesis of complex oxides in the form of various titanates, zirconates, bismuthates, niobates, which are functional materials for various purposes [1–3].

An example of the implementation of this approach is the synthesis of intermediates based on quasi-amorphous potassium polytitanates (PPT) subjected to modification under various chemical and thermal effects [4–6]. The obtained materials exhibit a high thermal reflectance, a low coefficient of friction, and a high dielectric constant [3–7].

Potassium polytitanate (PPT) synthesized in hydroxide-nitrate melts [7] is an ideal intermediate, which, due to its layered structure, can be easily modified by any compounds by intercalation or decoration.

In this case, the structure of PPT particles can be defined as quasi-amorphous. It is based on double polyanionic layers formed by titanium-oxygen octahedra with a highly ordered structure of individual polyhedra; on X-ray diffraction patterns, the reflection at angle 2θ of about 48.1° has a rather high intensity and a small half-width, which is typical for all crystalline titanates [8]. However, other reflections associated with the mutual orientation of titanium-oxygen octahedra are weakly expressed, and sometimes they are completely absent. Some $[\text{TiO}_{6/2}]$

octahedra contain vacancies, from 5 to 20 % of the octahedra are formed by titanium with the Ti^{3+} valence state, their shape is distorted, which leads to the formation of a deformed layered structure with an interlayer distance varying over a wide range (from 0.2 to 1.1 nm). H_3O^+ and K^+ cations, which compensate the excess negative charge of titanate polyanions, as well as molecules of water located in the interlayer space of PPT particles [6, 8].

During the heat treatment, potassium polytitanates, regardless the molar ratio of $n = \text{TiO}_2/\text{K}_2\text{O}$, which can vary over a very wide range from 2 to 6 [4, 7], crystallize with the formation of $\text{K}_2\text{Ti}_4\text{O}_9$, $\text{K}_2\text{Ti}_6\text{O}_{13}$ and TiO_2 . At the same time, the ratio of components in the final product, as well as the temperature of the beginning of their crystallization (450–600 °C), vary depending on a value of n .

The protonated forms of potassium polytitanate ($n = [\text{TiO}_2]/[\text{K}_2\text{O}] > 8$), obtained during the treatment of the parent (commercial) PPT in the aqueous solutions at $\text{pH} < 7$, are used to produce various functional ceramics by sintering [4–7]. However, their thermal behavior is not investigated yet in details. In addition, recently, it was found that anatase crystals, prepared by hydrothermal treatment of layered low alkali lepidocrocite-type titanates at 140 °C, preferentially exposed their (010) planes at the crystal surface and show high photocatalytic activity in dye-sensitized solar cells [9]. In this regard, it is very important to investigate the thermal behavior of the protonated forms of the lepidocrocite-like potassium polytitanates.

In connection with the foregoing, the aim of this research is to study the kinetic regularities of the process taking place during crystallization of the partially protonated forms of the potassium polytitanate (PPPT). To achieve this goal, the following purposes are considered: 1) identification of the kinetic model that best describes crystallization of the anatase phase during the thermal treatment of PPPT intermediate; 2) recognition of the topotactic phase transformation mechanism supporting obtaining the product (TiO₂, anatase) characterized with a specific structure; 3) determination of the main kinetic parameters of the crystallization process, such as activation energy and pre-exponential factor, as a function of the PPPT conversion using the data of differential scanning calorimetry (DSC).

Such information could help in preparing new ceramic materials by this approach using varied regimes of the thermal treatment of PPPT based intermediates.

2. Materials and Methods

2.1. Materials

Commercial quasi-amorphous potassium polytitanate (PPT-4 trade mark, Nanocomposite Ltd., Saratov, Russia) synthesized in the hydroxide-nitrate melt by processing the TiO₂ powder at 500 °C in accordance with [7] was used as a raw material. The parent PPT-4, characterized with the chemical composition of K₂O·4TiO₂, was treated with distilled water until a pH value of the dispersion equal to 7. This value corresponds to the partial dealcalization of the parent product (PPT-4) used to obtain intermediates for the synthesis of functional ceramics having the hollandite-like structure [4, 6]. The resulting powder was filtered using a Whatman paper filter No. 40 and dried at 50 °C in an oven SNOL 67/350.

According to the data of X-ray fluorescence analysis (Spectroscan MAX-GV, Spectron, Russia), the studied protonated PPT powder had the following chemical composition (wt. %): K₂O (1.9 ± 0.1), TiO₂ (98.1 ± 0.1).

2.2. Characterization

The phase composition of the intermediates and their crystallization products was studied using a D8 Advance X-ray diffractometer (Bruker, Germany), CuK_α radiation. The obtained results were processed using the EVA software and PDF-2 file cabinet. The structural features of the PPPT particles obtained after the thermal treatment were investigated by

transmission electron microscope (TEM) (JEOL JEM 1011, Jeol, Japan) at accelerating voltage of 80 kV.

Thermal analysis of the PPT powder was carried out on an STA 449 FS Jupiter synchronous thermal analyzer (NETZSCH, Germany) in a non-isothermal mode. Experimental differential scanning calorimetry (DSC) curves were obtained in the temperature range from 30 to 800 °C at the heating rates of 5, 10, 15, and 20 K·min⁻¹. The weight of the powdered specimens was ~30 mg.

Further, the obtained results of thermal analysis were used in theoretical studies.

2.3. Theoretical methods

The formal kinetic analysis of solid-state reactions based on experimental thermo-analytical data obtained under non-isothermal conditions was carried out in accordance with the methods presented in the well-known works of Kissinger, Friedman and Carroll, Coats and Redfern.

The kinetics of solid-state reactions is usually described by two functions: $f(T)$ is a temperature dependence, $f(\alpha)$ is a function, degree of transformation (conversion). The function $f(T)$ is expressed by Arrhenius-type kinetic equations, and the function $f(\alpha)$ is associated with a physical model describing the kinetics of a solid-state reaction:

$$\frac{d\alpha}{dt} = A e^{\frac{-E}{RT(t)f(\infty)}}, \quad (1)$$

where α is the degree of conversion of the reagent into products (the degree of conversion), $f(\alpha)$ is a function determined by the chosen reaction model, t is time, T is temperature, A is a pre-exponential factor, E is the activation energy, R is a universal gas constant [10].

The parameters A , E , $f(\alpha)$ are often called the kinetic trinity. The task of kinetic analysis is to determine the values of these parameters, provided that they retain their physical meaning. Such parameters make it possible to describe the processes of solid-phase interaction depending on temperature changes, heating rates, etc.

To establish the kinetic parameters using the DSC method, isoconversion methods of Friedman, Ozawa-Flynn-Wall, Kissinger, Vyazovkin are usually used [10]. These methods make it possible to determine the A and E values without any consideration of the mechanism of the investigated process. At the same time, to determine a type of the $f(\alpha)$ dependence, a model approach is used. Theoretically, several theoretical models can be

Table 1. Mathematical models describing the kinetics of crystallization processes occurring in solid-phase systems according to various mechanisms [11–14]

Mechanism	Symbol	Function type $f(\alpha)$	m	n
Phase boundary controlled reaction (contracting area)	R2	$2(1 - \alpha)^{1/2}$	0	0.5
Phase boundary controlled reaction (contracting volume)	R3	$3(1 - \alpha)^{2/3}$	0	0.66
Random nucleation and nuclear growth	A2	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	0.50 0.54	0.77 0.83
Random nucleation and nuclear growth	A3	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	0.66 0.72	0.70 0.76
Random nucleation followed by an instantaneous growth of nuclei. (Avrami-Erofeev eqn. $n = 1$)	F1	$(1 - \alpha)$	0	1.0
Random Scission of polymer chain	L2	$2(\alpha^{1/2} - \alpha)$	0.4	~ 1.0
Two-dimensional diffusion	D2	$[- \ln(1 - \alpha)]^{-1}$		
Three-dimensional diffusion (Jander equation)	D3	$3/2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$		
Process is controlled by nucleation followed by the linear growth of nuclei			$m < 1$	$n > 1$

considered that satisfactorily describe the experimental data.

To determine the $f(\alpha)$ dependence, a number of models, based on various physical models of the occurrence of solid-state transformations, are proposed [11–14] taking into account the geometric characteristics and driving forces of solid-state processes (Table 1).

A formal kinetic analysis of the structural transformations and crystallization of TiO_2 (anatase) during the non-isothermal annealing of protonated PPT powder was carried out using the DSC data.

Kinetic calculations were performed using the THINKS software [15] by the methods of Kissinger [16], Friedman [17], Vyazovkin [18], as well as the method of combined kinetic analysis (CKA) [19] altogether with the methods of linear and nonlinear regression.

The choice of a model for the crystallization process (independent parallel, competing and sequential stages of the reaction) was carried out using a flexible extended Prout–Tomkins correspondence formula (ePT model)

$$W = \frac{d\alpha}{dt} = k(1 - \alpha)^n (1 - q(1 - \alpha))^m, \quad (2)$$

where W is the rate of the reaction, k is a effective rate constant, α is the degree of conversion, q is a numerical integration factor with a non-zero rate of

the process in the absence of an explicit reaction of its initiation, which can be optimized to ensure compliance with any given set of experimental data [12], n, m are exponent parameters.

According to [12], at $q = 0.9999$, equation (2) has the following form

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \alpha^m. \quad (3)$$

A choice of the theoretical model with the best description of the experimental data was carried out according to a value of the Bayesian information criterion (BIC) [20, 21].

3. Results and Discussion

The DSC data obtained at different heating rates (the DSC cover at $\beta = 10 \text{ K} \cdot \text{min}^{-1}$ is reported as a sample in Fig. 1) shows that, when the PPT-4 intermediate powder is heated, after removal of physically adsorbed water (endothermic peak at 100–120 °C) the crystallization process takes place (exothermic peak at 472 °C).

X-ray diffraction patterns of the parent partially protonated PPT powder and the products obtained after the thermal treatment at the temperatures of 450 and 800 °C, are shown in Fig. 2. In accordance with the data of X-ray phase analysis, the isothermal

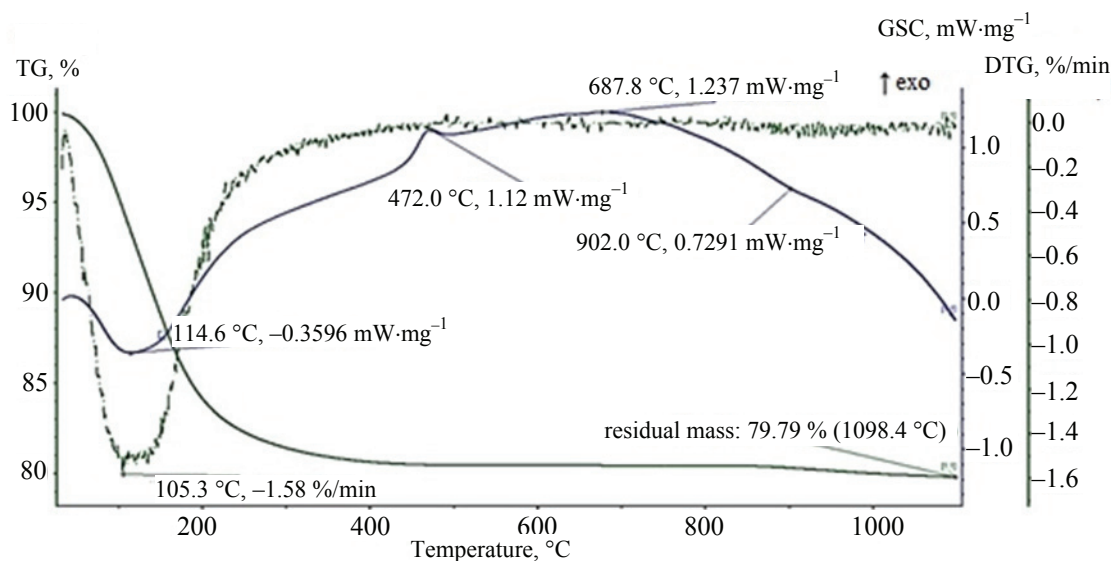


Fig. 1. DSC curves of PPT-4 powder at $\beta = 10 \text{ K} \cdot \text{min}^{-1}$

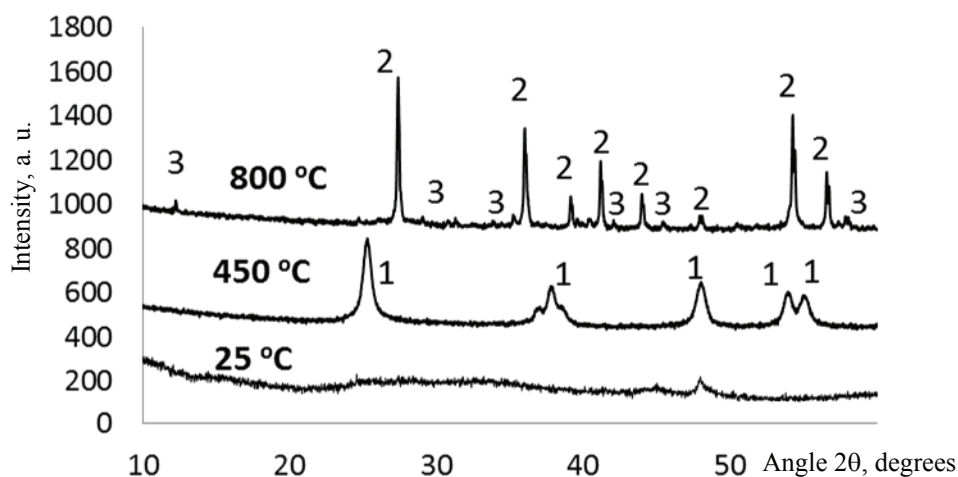


Fig. 2. X-ray diffraction patterns of a sample of protonated PPT (pH = 4):
1 – anatase; 2 – rutile; 3 – $\text{K}_2\text{Ti}_6\text{O}_{13}$

thermal treatment of the parent powdered sample at 450 °C leads to the crystallization of TiO_2 in the form of anatase. Increasing the treatment temperature up to 800 °C promotes the transformation of the TiO_2 crystal structure into the rutile form and, in addition, a presence of a certain amount of K_2O in the composition of PPT powder contributes to obtaining a certain quantity of potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$).

The following research theoretical analysis of the kinetic data was carried out taking into account the obtained experimental results.

The isoconversion method was used to determine the initial kinetic parameters of the anatase structure formation, however, realizing that this process can have multistage nature indicated by

the asymmetry of the first exothermic peak at 435–500 °C.

The isoconversion analysis data on a dependence of activation energy (E_a) vs degree of conversion (α) were obtained using the methods: Friedman, Vyazovkin and Kissinger (Fig. 3).

The application of the Kissinger method, which is usually used to estimate the kinetic parameters of the dominant reaction near the maximum of the exothermic peak [22], shows that the activation energy only at the initial stages of the process coincides with the data obtained by the Friedman and Vyazovkin methods. This fact indicates a complicated mechanism of TiO_2 (anatase) crystallization process, may be similar to the case described in [23].

However, in the first approximation, the method of linear regression analysis was used taking into account a possibility of approximating the crystallization process with one-stage model of the process. The results of the theoretical modeling, carried out using the method of linear regression analysis, are shown in Fig. 4.

According to the data of the combined kinetic analysis, at $\alpha = 0.10\text{--}0.96$, the following values of the kinetic parameters were obtained $E_{a1} = (179.6 \pm 2.6)$ $\text{kJ}\cdot\text{mol}^{-1}$, $\ln(A_1, \text{s}^{-1}) = (25 \pm 0.4) \text{s}^{-1}$, $n_1 = 1.20 \pm 0.02$, $m_1 = 0.08 \pm 0.02$. The best approximation to the experimental DSC curves is given by the results described by the first order reaction model (F1) (see Table 1). The model F1 assumes instantaneous nucleation and further two-dimensional growth of nuclei. This process should be considered as dominant.

The kinetic results obtained for the parent PPPT powder by the isoconversion method and the linear

regression method can be very conditionally correlated with real ones, since these methods give reliable results in the case of a one-stage process or with the dominance of one stage.

To carry out more detailed analysis, the capabilities of the THINKS program were used to simulate the kinetics of two-stage crystallization processes considering different order of the stages described with the Prout-Tomkins formula (ePT model, equation (2)):

- 1) ePT(1) + ePT(2) – two independent flexible one-stage steps;
- 2) ePT(1) \rightarrow ePT(2) – two sequentially flowing flexible single-stage steps;
- 3) ePT(1) || ePT(2) – two parallel (competing and mutually influencing) flexible one-stage steps.

The results of simulation obtained taking into account the kinetic parameters obtained by the isoconversion method and linear regression analysis, are presented in Fig. 5 and Table 2.

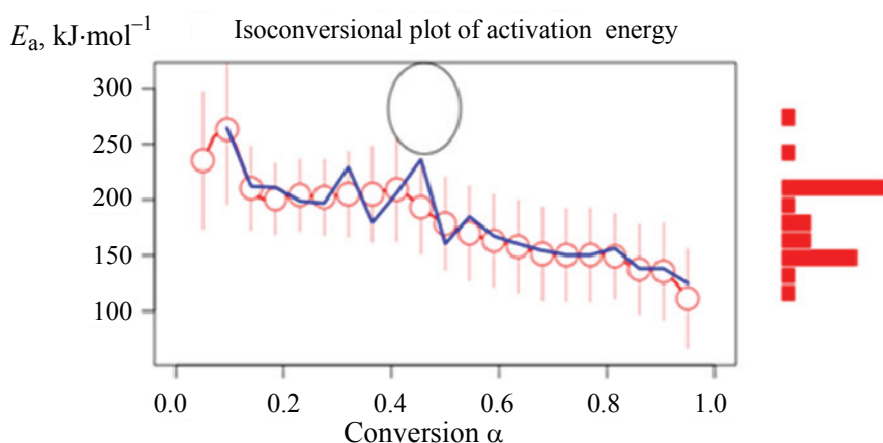


Fig. 3. Apparent activation energy of the TiO_2 (anatase) crystallization process for a PPT sample, calculated by the isoconversion methods of Friedman (points), Vyazovkin (line) and Kissinger (ellipse, takes into account the error of the calculated data)

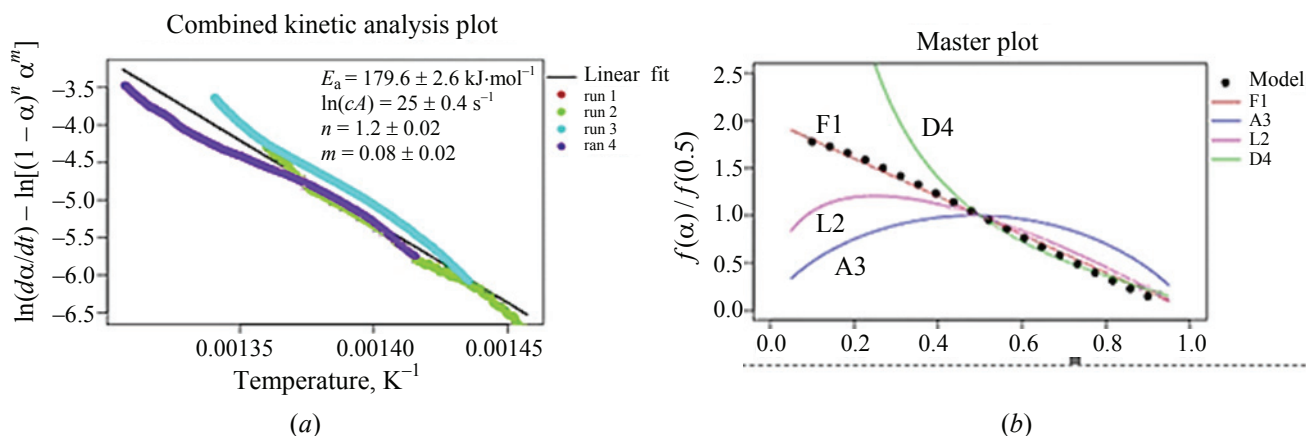


Fig. 4. Calculated data of linear regression analysis:
(a) combined kinetic analysis; (b) comparison of functions $f(\alpha)$ normalized at $\alpha = 0.5$ $\{f(\alpha)/f(0.5)\}$ for the corresponding kinetic models

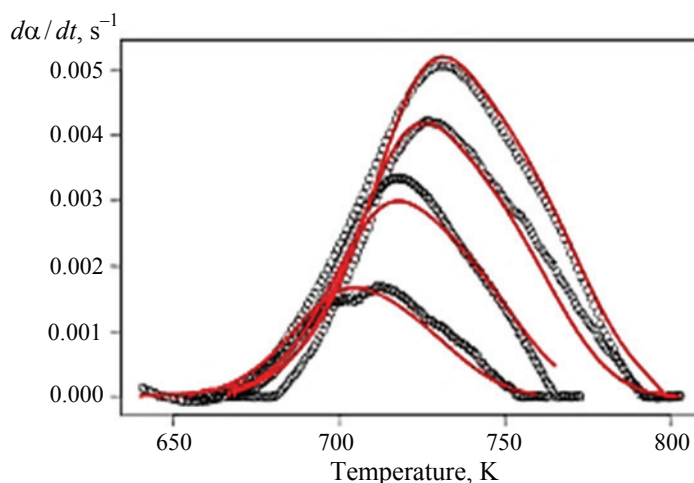


Fig. 5. Results of modeling the TiO_2 (anatase) formation during the crystallization of the PPPT, obtained by the method of nonlinear regression analysis for different heating rates: the points are experimental values, the lines are results of the theoretical regression analysis (\diamond – experiment; — – regression result)

Table 2. Kinetic parameters obtained in a two-stage simulation of the formation of the crystalline phase of anatase in a PPT sample at various stages of the process

Kinetic parameters	Nonlinear regression		
	Kinetic scheme		
	ePT \rightarrow ePT	ePT + ePT	ePT \parallel ePT
E_{a1} , kJ mol^{-1}	210*	210*	210*
$\ln(A_1, \text{s}^{-1})$	31.2 ± 0.0	30.9 ± 0.0	30.5 ± 0.0
n_1	1.17 ± 0.04	1.68 ± 0.06	1.73 ± 0.0
m_1	0.31 ± 0.01	0.36 ± 0.01	0.23 ± 0.01
E_{a2} , kJ mol^{-1}	155*	155*	155*
$\ln(A_2, \text{s}^{-1})$	20.6 ± 0.0	20.3 ± 0.0	$(5.0 \pm 1.24) \cdot 10^5$
n_2	1*	1*	1*
m_2	0*	0*	0*
BIC	–49336	–48039	–47611
Contribution of the first stage to the total activation energy (cd_1)	0.45	0.62	–

* Preset parameter values.

The data of simulation shows that in our case the anatase crystalline phase formation is most accurately described by a sequential two-stage model ePT(1) \rightarrow ePT(2). The minimum value of the BIC matching criterion (Bayesian information criterion, Bayesian coefficient), $\text{BIC} = -49336$, is achieved with the contribution of the first step to the total activation energy of 45 % ($cd_1 = 0.45$). In this case, the first stage of the crystallization process is limited

by nucleation with further linear growth of nuclei and branching over the surface, whereas, the second stage is described by the F1 model corresponding to instantaneous nucleation with further two-dimensional growth [23].

For the chosen ePT(1) \rightarrow ePT(2) scheme of the PPPT powder crystallization, the best agreement with the experimental DSC data was achieved with the kinetic parameters given in calculation 1 (Table 3).

Table 3. Flexible single-stepping (ePT) kinetic parameters of the extended Prout-Tompkins model obtained by non-linear regression for anatase crystalline phase formation. The transformations proceed for varied values of n and m according to the scheme ePT \rightarrow ePT

Kinetic parameters	Calculation number		
	1	2	3
E_{a1} , kJ mol ⁻¹	257	257*	257*
$\ln(A_1, s^{-1})$	39.2 ± 0.0	39.5 ± 0.0	38.0 ± 0.0
n_1	1.28 ± 0.03	1.37 ± 0.04	1.85 ± 0.02
m_1	0.20 ± 0.01	0.24 ± 0.01	0.21 ± 0.01
E_{a2} , kJ mol ⁻¹	141	141*	141*
$\ln(A_2, s^{-1})$	18.3 ± 0.0	18.0 ± 0.0	$5.0 \pm 1.24 \cdot 10^5$
n_2	1*	0.86 ± 0.02	0.5*
m_2	0*	-0.38 ± 0.05	0*
BIC	-49581	-49635	-49002
Contribution of the first stage to the total activation energy (cd_1)	0.40	0.33	0.73

* Preset parameter values.

By setting the activation energy calculated for the initial and final stages of the crystallization (Fig. 3) $E_{a1} = 257$ kJ·mol⁻¹ ($\alpha = 0$) and $E_{a2} = 141$ kJ·mol⁻¹ ($\alpha = 0.9$) and by varying the n and m values, in the calculation 2, it was recognized that more accurate approximation to the experimental DSC curves (BIC = -49635) could be obtained with the 33 % contribution of the first stage of the process in the energy expenditure necessary to form anatase (TiO₂) ($cd_1 = 0.33$ Table 3, column 2).

In the second version of the calculation, the first stage of the process also corresponds to the instantaneous nucleation and further two-dimensional growth of nuclei ($n_1 = 1.37 \pm 0.04$, $m_1 = 0.24 \pm 0.01$), however, in this version, the optimal values of the kinetic parameters for the second stage ($n_2 = 0.86 \pm 0.02$, $m_2 = -0.38 \pm 0.05$) do not allow interpretation of the mechanism of this stage in accordance with previously published data [14]. At the same time, it should be noted that a negative value of $m_2 = -0.38 \pm 0.05$ indicates that a slowdown in the crystallization process is observed at the second stage.

In order to describe the experimental DSC curves, taking into account the slowdown of crystallization at the second stage, the model of a compressing plane surface [8] was applied. As a result, in the third calculation it was found that using

the preset values of $n_2 \approx 0.5$ and $m_2 \approx 0$, corresponding to this model (Table 3, column 3), we obtained less adequate value of BIC parameter (BIC = -49002), in comparison with the data of calculation No. 2, however, the physical meaning of the first step was retained and, at some change in the numerical values of the kinetic parameters, the contribution of the first stage in the energetics of the crystallization process increased up to 73 % ($cd_1 = 0.73$), whereas the second stage of the process successfully described the slowdown of the crystallization process.

Thus, taking into account the data of theoretical analysis, it can be assumed that the formation process of the crystalline phase of anatase in our case can be represented in two stages. The initial stage could be described as a process of self-organization of nanoparticles in the layered structure of the protonated potassium polytitanate due to van der Waals forces supporting the ordering of the PPPT structure in areas smaller than 10 nm. This stage was not reflected in the considered model and can be attributed to the temperature range of 150–400 °C after desorption of physically adsorbed and structural (located in the interlayer space of PPPT particles) water (see Fig. 1). This structural change can be recognized in the TEM images of the parent PPPT powder isothermally treated at 400 °C (Fig. 6).

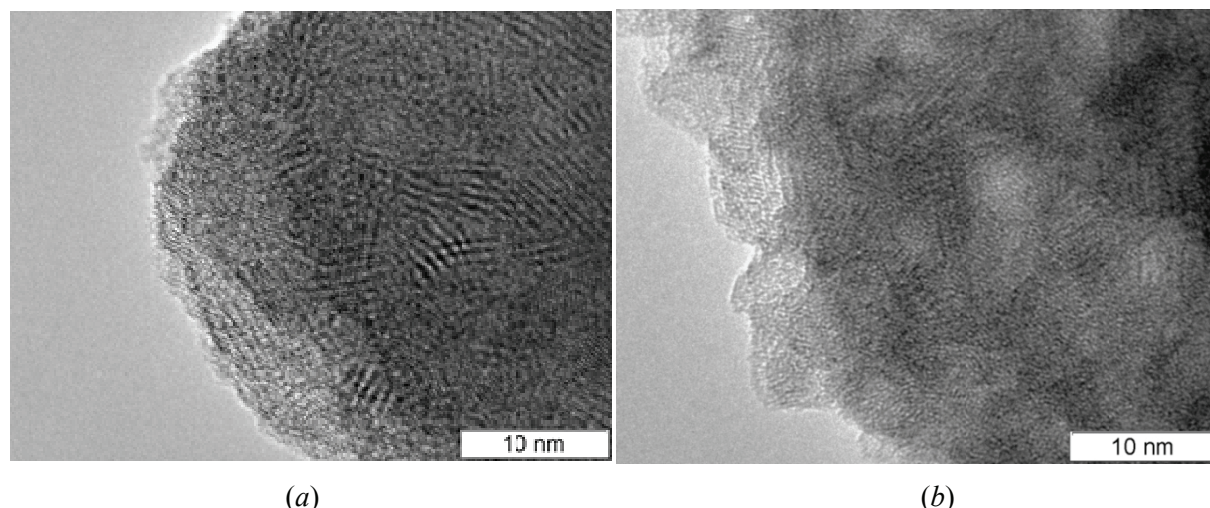


Fig. 6. TEM images of the parent PPPT particle (a) and the PPPT particle thermally treated at 400 °C (b)

Most of the external surface of grains could be identified as (010) surface plane both in the initial and in the treated at 400 °C PPPT particles similar to the data on lepidocrocite-like low alkali titanate described in [9]. However, in the initial state the interlayer distance varied in a wide range (Fig. 6a), whereas after the thermal treatment this distance reduces and becomes more regular (Fig. 6b). According to our previously published data [7], in this temperature range, the transition of structurally bound water occurs in the interlayer space of PPT, the diffusion of its molecules to the particle surface, and subsequent desorption. However, it should be borne in mind that in the interlayer space of PPT, along with water molecules, there are K^+ and H_3O^+ ions, which compensate the excess spatially distributed charge of quasi-two-dimensional polyanions formed by titanium-oxygen octahedra. Since potassium and hydronium cations, as well as water molecules, are surface-active components in the oxide structures [24], it can be assumed that their diffusion to the surface of particles inside the interlayer space (deintercalation) is accompanied by the approach of polyanions, followed by the interaction of layers due to Van der Waals forces. [26].

The above mentioned processes lead to topotactic transformations of the PPPT layered structure, $TiO_{6/2}$ octahedra of the layered structure, free of K^+ and H_3O^+ cations, are uniformly shifted to the positions, which are close to the characteristic of distorted anatase structure, and, step by step, form the structure of crystalline anatase [9, 26].

The considered mechanism of crystallization of quasi-amorphous protonated potassium polytitanate corresponds to the kinetic model of the process proceeding according to the two-stage scheme $ePT(1) \rightarrow ePT(2)$: the first step is the formation of a distorted anatase structure; the second step is the

transformation of the distorted anatase structure into the normal crystalline one. This process is well described by the theoretical data obtained using the simulation based on the first-order model F1 (random nucleation followed by instantaneous growth).

Finally, the process of crystallization of protonated PPT is completed by the formation of small crystals of potassium hexatitanate (see Fig. 2) on the surface of TiO_2 crystalline particles with the participation of residual potassium ions, which previously diffused from the inner layers of PPT particles to the surface. This is evidenced by a weak exothermic peak on the DSC curves with a maximum at $T = 677$ °C (Fig. 1). At the same time, the transition of titanium dioxide (anatase) to the crystalline form of rutile also occurs.

4. Conclusion

Taking into account the obtained results it is possible to make the following conclusions.

1. The theoretical treatment of the DSC data obtained with various rates of heating using the Kissinger, as well as Friedman and Vyazovkin isoconversional methods, mathematical and kinetic deconvolution approaches and formal kinetic description indicates that the crystallization of partially protonated potassium polytitanate in the range of 435–500 °C includes two sequentially following stages.

2. The first stage involves diffusion of the surface-active components (H_2O , H_3O^+ , K^+) in the interlayer space to the surface of particles and transformation of the layered quasi-amorphous PPPT into the distorted crystalline anatase-like structure. In the second stage, the distorted anatase structure is transformed into the traditional crystalline form of TiO_2 (anatase).

3. A value of the activation energy (E_a) changes following the stages of the PPPT crystallization process decreasing from 257 kJ·mol⁻¹ (nucleation) to 210 kJ·mol⁻¹ in the initial stage of crystallization (formation of the disordered anatase-like structure) and to 141 kJ·mol⁻¹ in the stage of the regular anatase structure formation.

4. The following increase of temperature promotes obtaining the final crystalline structure which can be formed at $T > 800$ °C by transformation of anatase into the rutile crystalline form of TiO₂ and formation of small K₂Ti₆O₁₃ crystals onto the surface of TiO₂ particles with the participation of potassium ions previously diffused from the bulk.

5. Funding

This study did not receive external funding.

6. Conflict of interests

The authors declare no conflict of interest.

7. References

1. Setter N, Waser R. Electroceramic materials. *Acta Materialia*. 2000;48:151-178. DOI:10.1016/S1359-6454(99)00293-1
2. Cava RJ. Dielectric materials for applications in microwave communications. *Journal of Materials Chemistry*. 2001;11:54-62. DOI:10.1039/B003681L
3. Spearing SM. Materials issues in microelectromechanical systems (MEMS). *Acta Materialia*. 2000;48:179-196. DOI:10.1016/S1359-6454(99)00294-3
4. Gorokhovskiy AV, Tretyachenko EV, Goffman VG, Gorshkov NV, Fedorov FS, Sevryugin AV. Preparation and dielectric properties of ceramics based on mixed potassium titanates with the hollandite structure. *Inorganic Materials*. 2016;52:587-592. DOI:10.1134/S0020168516060042
5. Sinelshchikova OYu, Petrov SA, Besprozvannykh NV, Kuchaeva SK, Vlasov EA. Features of sol-gel synthesis of new functional materials based on complex oxides with tunnel structure. *Journal of Sol-Gel Science and Technology*. 2013;68:495-499. DOI:10.1007/s10971-013-2988-7
6. Gorokhovskiy A, Saunina S, Maximova L, Tretyachenko E, Goffman V, Escalante-Garcia JI, Vikulova M. Synthesis and electric properties of the high-k ceramic composites based on potassium polytitanate modified by manganese. *Research on Chemical Intermediates*. 2022;48:1227-1248. DOI:10.1007/s11164-022-04669-x
7. Sanchez-Monjaras T, Gorokhovskiy AV, Escalante-Garcia JI. Molten salt synthesis and characterization of polytitanate ceramic precursors with varied TiO₂/K₂O molar ratio. *Journal of the American Ceramic Society*. 2008;91:3058-3065. DOI:10.1111/j.1551-2916.2008.02574.x
8. Ponce-Peña P, Poisot M, Rodríguez-Pulido A, González-Lozano MA. Crystalline structure, synthesis, properties and applications of potassium hexatitanate: a review. *Materials*. 2019;12(24):4132. DOI:10.3390/ma12244132
9. Yuan H, Besselink R, Liao Z, ten Elshof JE. The swelling transition of lepidocrocite-type protonated layered titanates into anatase under hydrothermal treatment. *Scientific Reports*. 2014;4:4584. DOI: 10.1038/srep04584
10. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica Acta*. 2011;520:1-19. DOI:10.1016/j.tca.2011.03.034
11. Perejón A, Sánchez-Jiménez PE, Criado JM, Pérez-Maqueda L. Kinetic analysis of complex solid-state reactions. A new deconvolution procedure. *The Journal of Physical Chemistry B*. 2011;115:1780-1791. DOI:10.1021/jp110895z
12. Burnham AK, Zhou X, Broadbelt LJ. Critical Review of the Global Chemical Kinetics of Cellulose Thermal Decomposition. *Energy Fuels*. 2015;29:2906-2918. DOI:10.1021/acs.energyfuels.5b00350
13. Malek J. Kinetic analysis of crystallization processes in amorphous materials. *Thermochimica Acta*. 2000;35:239-253. DOI:10.1016/S0040-6031(00)00449-4
14. Šesták J. Rationale and fallacy of thermoanalytical kinetic patterns: How we model subject matter. *Journal of Thermal Analysis and Calorimetry*. 2012;110:5-16. DOI:10.1007/s10973-011-2089-1
15. Muravyev NV, Pivkina AN, Koga N. Critical appraisal of kinetic calculation methods applied to overlapping multistep reactions. *Molecules*. 2019;24:2298. DOI:10.3390/molecules24122298
16. Kissinger HE. Reaction kinetics in differential thermal analysis. *Analytical Chemistry*. 1957;29:1702-1706. DOI:10.1021/AC60131A045
17. Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *Journal of Polymer Science*. 2007;6(1):183-195. DOI:10.1002/polc.5070060121
18. Vyazovkin S. Modification of the integral isoconversional method to account for variation in the activation energy. *Journal of Computational Chemistry*. 2001;22:178-183. DOI:10.1002/1096-987X(20010130)22:23.O.CO;2-#
19. Pérez-Maqueda LA, Criado JM, Sánchez-Jiménez PE. Combined kinetic analysis of solid-state reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism. *The Journal of Physical Chemistry A*. 2006;110:12456-12462. DOI:10.1021/jp064792g
20. Gorn MV, Monogarov KA, Dalinger IL, Melnikov IN, Kiselev VG, Muravyev NV. Pressure DSC for energetic materials. Part 2. Switching between evaporation and thermal decomposition of 3,5-dinitropyrazole. *Thermochimica Acta*. 2020;690:178697. DOI:10.1016/j.tca.2020.178697.

21. Roduit B, Hartmann M, Folly P, Sarbach A, Baltensperger R. Prediction of thermal stability of materials by modified kinetic and model selection approaches based on limited amount of experimental points. *Thermochimica Acta*. 2014;579:31-39. DOI:10.1016/j.tca.2014.01.005

22. Vyazovkin S. Kissinger method in kinetics of materials: things to beware and be aware of. *Molecules*. 2020;25:2813. DOI:10.3390/molecules25122813

23. Vyazovkin S, Burnham AK, Favregeon L, Koga N, Moukhina E, Perez-Magueda LA, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics. *Thermochimica Acta*. 2020;689:178597. DOI:10.1016/j.tca.2020.178597

24. Liu XF, Peng JH, Yang CH, Shu YY, Wu DC. The effect of surfactant and alkali on the surface tension of simulated solutions of alkali activated slag cement system. *Advanced Materials Research*. 2012;399:1246-1250. DOI:10.4028/www.scientific.net/AMR.399-401.1246

25. Zhang X, He Y, Sushko ML, Liu J, Luo L, De Yoreo JJ, Mao SX, Wang C, Rosso KM. Direction – specific van der Waals attraction rutil TiO₂ nanocrystals. *Science*. 2017;356:434-437. DOI:10.1126/science.aah6902

26. Wen P, Ishikawa Y, Itoh H, Feng Q. Topotactic transformation reaction from layered titanate nanosheets into anatase nanocrystals. *The Journal of Physical Chemistry C*. 2009;113:20275-20280. DOI:10.1021/jp908181e

Information about the authors / Информация об авторах

Alexander V. Gorokhovskiy, D. Sc. (Chem.), Professor, Head of the Department of Chemistry and Chemical Technology of Materials, Yuri Gagarin State Technical University of Saratov, Saratov, Russian Federation; ORCID 0000-0002-4210-3169; e-mail: algo54@mail.ru

Svetlana I. Saunina, Cand. Sc. (Phys.-Math.), Associate Professor, Department of Condensed Matter Physics of the Faculty of Physics, Chelyabinsk State University (CSU), Chelyabinsk, Russian Federation; ORCID 0000-0003-1274-7032; e-mail: sauninasi@mail.ru

Dmitry A. Zakharyevich, Cand. Sc. (Phys.-Math.), Associate Professor, Department of Condensed Matter Physics of the Faculty of Physics, CSU, Chelyabinsk, Russian Federation; ORCID 0000-0003-1184-9571; e-mail: dmzah@csu.ru

Lilia A. Maximova, Postgraduate, Department of Chemistry and Chemical Technology of Materials, Yuri Gagarin State Technical University of Saratov, Saratov, Russian Federation; ORCID 0000-0002-4351-5739; e-mail: liliamacsimova@mail.ru

Elena V. Tretyachenko, Cand. Sc. (Chem.), Associate Professor, Department of Chemistry and Chemical Technology of Materials, Yuri Gagarin State Technical University of Saratov, Saratov, Russian Federation; ORCID 0000-0001-9095-0920; e-mail: trev07@rambler.ru

Natalya O. Morozova, Postgraduate, Department of Chemistry and Chemical Technology of Materials, Yuri Gagarin State Technical University of Saratov, Saratov, Russian Federation; ORCID 0000-0002-1470-0011; e-mail: dlq2@yandex.ru

Гороховский Александр Владиленович, доктор химических наук, профессор, заведующий кафедрой «Химия и химическая технология материалов», ФГБОУ ВО «Саратовский государственный технический университет имени Гагарина Ю.А.», Саратов, Российская Федерация; ORCID 0000-0002-4210-3169; e-mail: algo54@mail.ru

Саунина Светлана Ивановна, кандидат физико-математических наук, доцент, кафедра физики конденсированного состояния, ФГБОУ ВО «Челябинский государственный университет» (ФГБОУ ВО «ЧелГУ»), Челябинск, Российская Федерация; ORCID 0000-0003-1274-7032; e-mail: sauninasi@mail.ru

Захарьевич Дмитрий Альбертович, кандидат физико-математических наук, доцент, кафедра физики конденсированного состояния, ФГБОУ ВО «ЧелГУ», Челябинск, Российская Федерация; ORCID 0000-0003-1184-9571; e-mail: dmzah@csu.ru

Максимова Лилия Алексеевна, аспирант, кафедра «Химия и химическая технология материалов», ФГБОУ ВО «Саратовский государственный технический университет имени Гагарина Ю.А.», Саратов, Российская Федерация; ORCID 0000-0002-4351-5739; e-mail: liliamacsimova@mail.ru

Третьяченко Елена Васильевна, кандидат химических наук, доцент, кафедра «Химия и химическая технология материалов», ФГБОУ ВО «Саратовский государственный технический университет имени Гагарина Ю.А.», Саратов, Российская Федерация; ORCID 0000-0001-9095-0920; e-mail: trev07@rambler.ru

Морозова Наталья Олеговна, аспирант, кафедра «Химия и химическая технология материалов», ФГБОУ ВО «Саратовский государственный технический университет имени Гагарина Ю.А.», Саратов, Российская Федерация; ORCID 0000-0002-1470-0011; e-mail: dlq2@yandex.ru

Received 01 March 2023; Accepted 11 April 2023; Published 26 May 2023



Copyright: © Gorokhovskiy AV, Saunina SI, Zakharyevich DA, Maximova LA, Tretyachenko EV, Morozova NO, 2023. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).