# On the modelling of solid state reactions. Synthesis of YAG

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There is a model of yttrium aluminium garnet (YAG) synthesis presented in this article. The developed model is based on nonlinear reaction–diffusion partial differential equations. The solution was carried out numerically using finite difference techniques. We got dependability curves for diffusion and reaction rates and offered possible method to localize values of diffusion and reaction rate constants precisely enough.

**KEY WORDS:** yttrium aluminium garnet, reaction–diffusion model, finite difference schemes

**AMS subject classification:** 35K57, 65M06

## 1. Introduction

The composition $3Y_2O_3:5Al_2O_3$ commonly called as yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG), adopts the cubic garnet structure and when doped with a transition metal or lanthanide element, YAG is an important solid state laser material widely used in luminescence systems and window materials for a variety of lamps [1–6]. In view of the high-temperature chemical stability and an extremely high creep resistance, YAG is a promising fibre material for the preparation of ceramic composites [7–16]. The electrical conductivity of YAG is also

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reported to be lower than any other polycrystalline oxide [17]. Owing to such wide and diverse application potential of YAG-based ceramics, new routes for the synthesis of pure and homogeneously doped yttrium aluminium garnet are highly desirable.

The solid state synthesis of YAG ceramic from $Al_2O_3$ and $Y_2O_3$ powders usually requires extensive mechanical mixing and lengthy heat treatments above $1600\,°C$ [18,19]. These processing conditions do not allow facile control over micro-structure, grain size and grain size distribution in the resulting powders or shapes. Several wet-chemical techniques such as polymerized complex route [20], metal-organic preceramic processing [18], coprecipitation methods [21,22] or yttrium carboxylate–alumoxane route [3] have been used to produce YAG phases. Most of these methods suffer from the complex and time consuming (long refluxing times, gelation periods of several days, etc.) procedures and/or mismatch in the solution behaviour of the constituents. As a consequence of the different isoelectric points, gross inhomogeneities may be present in the obtained ceramic, for example significant amounts of $Y_2O_3$, $Al_2O_3$, $YAlO_3$ and $Y_2Al_4O_9$ phases are present, even above $1650\,°C$, in the $Y_3Al_5O_{12}$ phase synthesized by above mentioned "soft chemistry" methods.

Recently, for the preparation of nanocrystalline YAG we have developed a new sol–gel process using mixtures of inorganic salts of the respective elements [23,24]. This study have demonstrated the versatility of the sol–gel method to yield monophasic YAG samples at lower sintering temperature $1000\,°C$ when compared to the temperature required for the solid state synthesis ($>1600\,°C$). The successful synthesis of crystalline YAG phase at $1000\,°C$) is the one of the lowest reported temperature for the crystallisation of this material. The sol–gel method of preparation of YAG in aqueous media is inexpensive and thus appropriate for the large scale production of YAG ceramics. Also, lanthanide-doped YAG ceramics could be successfully obtained by sol–gel method.

Therefore, it has been well demonstrated that the sol–gel process offers considerable advantages of good mixing of the starting materials and excellent chemical homogeneity of the product. Moreover, the molecular level mixing and the tendency of partially hydrolyzed species to form extended networks facilitate the structure evolution thereby lowering the crystallization temperature. The reactivity of the precursor makes the preparation of particular phases possible at ambient and gentle conditions while starting from a solid state precursor either high temperatures or high pressure or the use of a catalyst is needed.

Thus, it is clear that the conditions for the formation of monophasic YAG are dependent largely on the synthesis method used. By changing solid state method to the sol–gel chemistry approach, the YAG formation temperature decreases from $1600\,°C$ upto $1000\,°C$. However, the important question concerning the reasons for the observed changes in the preparation temperature by changing synthesis method remains to be answered. Such a situation has initiated the present work, motivating us to elucidate the reasons responsible for the

low-temperature formation of $Y_3Al_5O_{12}$ using sol–gel technique. The optimization of synthesis parameters of sol–gel processes have been determined mostly in an experimental way, i.e., according to the desired properties of the final ceramic material. To overcome these difficulties, the pathway of chemical reactions should be performed according to the possible computational modelling. However, no model has yet been constructed that provides quantitative agreement of the reaction mechanisms with the experimental data of process parameters and desired structural, morphological and physical properties of the final ceramic material.

The main goal of this study is to construct a mathematical model which allows the effective computer simulation of YAG synthesis. Developing the model, we assume, that the mass transport by diffusion, and reaction are the limited stages of YAG synthesis. We predict, that the temperature regime is high enough to consider the reaction space as liquid media. So in general the developed model is based on non-stationary diffusion equations containing a non-linear term related to kinetic of reaction (see section 2). Further, we offered models for the reaction space and pick out one-, two- and three-dimensional cases. (In this article we consider one- and two-dimensional cases.) The numerical solution of the derived PDE was carried out using finite difference techniques (see section 3).

Solving the model, we encountered the difficulties to determine the values of the diffusion and reaction rate constants of the reaction components. So in this article we decided to investigate the appeared problem. We offered possible solution to the problem. More particularly, we got dependability curves for diffusion and reaction rates (see figures 4–7). Further, we defined *domination* term (see Definition in section 4) and, proceeding from this definition, we set the domination areas for diffusion and reaction. Thereby we localized the values of constants precisely enough (see section 4).

In closing we emphasize that the similiar solid state reactions could be investigating analogously.

## 2. Mathematical model

At preparatory stage of YAG synthesis all components were powdered and mixed thoroughly in some cubic volume $V \subset \mathbb{R}^3$ (see figure 1). Mixture was heated enough. Then we considered the run of the reaction in obtained homogenous solution. Now, allow us to remind reader some well known theoretical facts of chemical kinetics.

Reaction space of our model is a time-independent quantity, so reaction (e.g., $aA + bB \rightarrow cC$) rate $w_i$ for the $i$th component is defined by

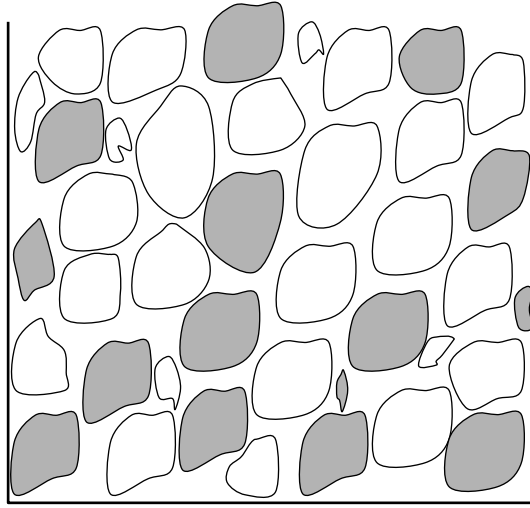$$w_i = \frac{\partial c_i}{\partial t},\tag{1}$$

Figure 1. Reaction space.

where $c_i = c_i(x, t)$ is the concentration of the $i$th component at a point $x = (x_1, x_2, x_3)$ of the region $V$ at time $t$. Reaction rate $w$ is defined by

$$w = \frac{1}{-a}w_1 = \frac{1}{-b}w_2 = \frac{1}{c}w_3, \tag{2}$$

where $a, b, c > 0$. Further, the main law of the chemical kinetics states that
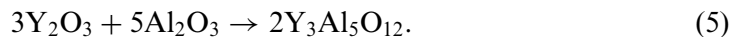
$$w = kc_1^{n_1}c_2^{n_2}, \tag{3}$$

where $n_i > 0$ is the order of reaction for $i$th component, $k$ is the reaction rate constant.

solid state reaction rate depends on diffusion process. According to the second Fick's law

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^{3} D_i \frac{\partial^2 c_i}{\partial x_j^2}, \tag{4}$$

where $D_i$ is the diffusion coefficient of the $i$th component.

In this study, we consider fixed solid state reaction – synthesis of YAG

$$3Y_2O_3 + 5Al_2O_3 \rightarrow 2Y_3Al_5O_{12}. \tag{5}$$

Let $c_1$, $c_2$, and $c_3$ be the concentrations of the reaction components, and set $n_i = 1$ (see [3]). Then (see [1–4]) solid state reaction [5] mechanism can be

described by the reaction–diffusion system

$$\frac{\partial c_1}{\partial t} = \sum_{j=1}^{3} D_1 \frac{\partial^2 c_1}{\partial x_j^2} - 3kc_1c_2,$$

$$\frac{\partial c_2}{\partial t} = \sum_{j=1}^{3} D_2 \frac{\partial^2 c_2}{\partial x_j^2} - 5kc_1c_2, \quad x \in V, \ t > 0, \tag{6}$$

$$\frac{\partial c_3}{\partial t} = \sum_{j=1}^{3} D_3 \frac{\partial^2 c_3}{\partial x_j^2} + 2kc_1c_2.$$

The initial conditions ($t = 0$) for $c_i$ are

$$c_i(x, 0) = c_i^0, \quad i = 1, 2, 3, \quad x \in \overline{V} = V \cup \partial V \tag{7}$$

and the boundary conditions at $\partial V$ are

$$\frac{\partial c_i}{\partial x_j}\bigg|_{x \in \partial V} = 0, \quad i, j = 1, 2, 3, \ t \geqslant 0. \tag{8}$$

The structure depicted in figure 1 is chaotic – exact initial position of little particles of the reaction components in $V$ is unknown. So, it is quite reasonable to impose some conditions on $V$.

Let all particles are of same shape and its volume is small enough. More particularly, let particles are of cube shape and the edge of the cube is $1\,\mu$m. (Guiding by experimental data, volume of these particles must be approximately $1\,\mu$m$^3$.) Further, let these particles recurring periodically in $V$ in $x_1, x_2, x_3$ directions (see figure 2(a)).
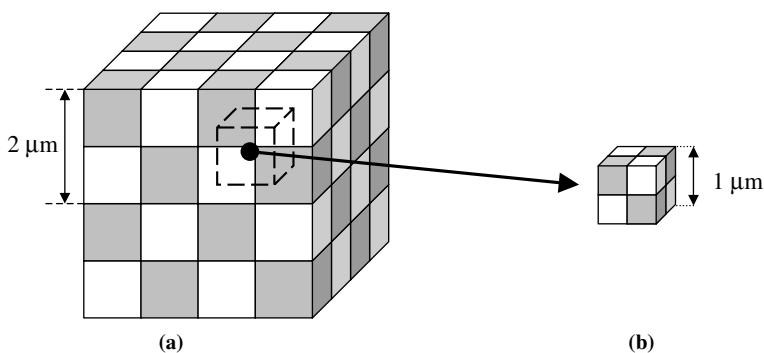


Figure 2. Model of the reaction space $V$ in common three-dimensional case. (a) Assumed shape and position of particles in $V$. (b) Definition of the less recurring element in $V$.

*Remark.* In our numerical experiments half-time $t_{1/2}$ was considered – the time required for half of the initial components to disappear

$$\int_V (c_1(x, t_{1/2}) + c_2(x, t_{1/2}))\mathrm{d}x = \frac{1}{2} \int_V (c_1(x, 0) + c_2(x, 0))\mathrm{d}x. \qquad (9)$$

So, it is easy to see, that for our periodic structure, reaction can be considered not in complete space, but in $V' = (0, 1) \times (0, 1) \times (0, 1) \subset \mathbb{R}^3$ (see figure 2(b)).

Solution of [6–8] system in common three-dimensional case is complicated enough. Also, as we mentioned in section 1, we encountered the difficulties to determine some parameters of the model. So, in this article, simpler cases are considered.

Consider the cases when particles recur periodically in $V$: (a) in one direction (e.g., $x_1$), and (b) in two directions (e.g., $x_1$ and $x_2$). As previously, the less recurring element in $V$ is defined (see figure 3). It is obvious, that in cases (a) and (b) second-order derivations $\partial^2 c_i/\partial x_2^2 = 0$, $\partial^2 c_i/\partial x_3^2 = 0$, and $\partial^2 c_i/\partial x_3^2 = 0$, respectively. Therefore, in case (a) three-dimensional problem [6–8] is equivalent to one-dimensional problem, i.e., $x = x_1$, and in case (b) – to two-dimensional, i.e., $x = (x_1, x_2)$. (In the future, we use "(a)" and "(b)" to denote one- and two-dimensional case, respectively.)

Laboratory experiments were performed for several temperature regimes. We fixed results for 1000 and 1600 °C. It was found, that synthesis time (and so half-time) was equal for both regimes if particles were smaller (guiding by experimental data, approximately 10 times in all directions) at lower temperature. Therefore, for $T = 1000$ °C we assumed

(a) $V' = \{x : 0 \leqslant x \leqslant 1\}$,
(b) $V' = \{(x_1, x_2) : 0 \leqslant x_1 \leqslant 1, \ 0 \leqslant x_2 \leqslant 1\}$

and for $T = 1600$ °C:

(a) $V' = \{x : 0 \leqslant x \leqslant 10\}$,
(b) $V' = \{(x_1, x_2) : 0 \leqslant x_1 \leqslant 10, \ 0 \leqslant x_2 \leqslant 10\}$.

In other words, the transition from $T = 1000$ °C to $T = 1600$ °C could be carried out by direct transformation of variables in [6–8].
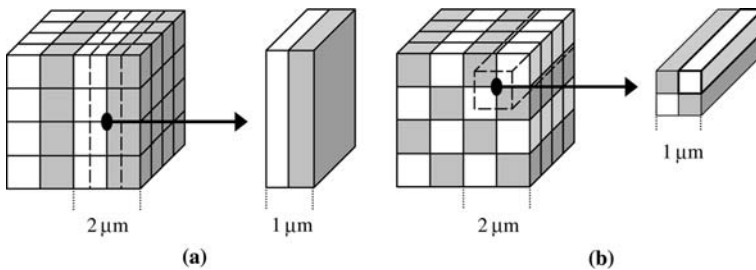


Figure 3. Model of the reaction space $V$ in (a) one- and (b) two-dimensional case.

Equations of mathematical model [6–8] were solved numerically using finite difference technique. In one-dimensional case (a), the problem was approximated by symmetric implicit scheme, and in two-dimensional case (b) – by alternating direction scheme. Both schemes were solved using stream sweeping method [25].

## 3. Numerical solution

The uniform grids were introduced in $V$

$$\omega_{h_1} = \{x_{1,i} : x_{1,i} = ih_1, \ i = 0, \dots, N_1\}, \quad N_1 h_1 = 1,$$
$$\omega_{h_2} = \{x_{2,j} : x_{2,j} = jh_2, \ j = 0, \dots, N_2\}, \quad N_2 h_2 = 1,$$
$$\omega_{\tau} = \{t^n : t^n = n\tau, \ n = 0, \dots, M\}, \quad M_{\tau} = T.$$

We use standard notation (see [25])

$$u_t = (u_i^{n+1} - u_i^n)/\tau, \quad u_{\bar{x}}^n = (u_i^n - u_{i-1}^n)/h, \quad u_x^n = (u_{i+1}^n - u_i^n)/h,$$
$$u = u(x_i, t^n), \quad \hat{u} = u(x_i, t^{n+1}), \quad \bar{u} = u(x_i, t^{n+1/2}).$$

(a) Define a discrete grid

$$\omega_{\tau,h} = \omega_{\tau} \times \omega_h = \{(t^n, x_i) : t^n = n\tau, x_i = ih, i = 0, \dots, N, n = 0, \dots, M\}.$$

Let $u_{k,i}^n = u_k(x_i, t^n)$ be the lattice function defined at $\omega_{\tau,h}$ points. We build a finite difference scheme approximating equations (6)

$$\begin{align}
u_{1,t} &= \tfrac{1}{2}(D\hat{u}_{1,\bar{x}x} + Du_{1,\bar{x}x}) - 3k\hat{u}_{1,i}u_{2,i}, \\
u_{2,t} &= \tfrac{1}{2}(D\hat{u}_{2,\bar{x}x} + Du_{2,\bar{x}x}) - 5k\hat{u}_{1,i}\hat{u}_{2,i}, \\
u_{3,t} &= \tfrac{1}{2}(D\hat{u}_{3,\bar{x}x} + Du_{3,\bar{x}x}) + 2k\hat{u}_{1,i}\hat{u}_{2,i},
\end{align} \tag{10}$$

initial conditions [7]

$$u_{k,i}^0 = c_1^0, \quad k = 1, 2, 3, \ i = 0, \dots, N, \tag{11}$$

and boundary conditions [8]

$$u_{k,0}^n = \varepsilon u_{k,1}^n, \quad u_{k,N}^n = \varepsilon u_{k,N-1}^n, \quad k = 1, 2, 3, \ n = 0, \dots, M, \tag{12}$$

where $\varepsilon = 1 - 10^{-6}$.
The initial conditions $c_i^0$ are

$$c_1^0 = \begin{cases} 3 \times 10^{-6}, \ 0 \leqslant x \leqslant 1/2, \\ 0, \quad\quad\quad 1/2 < x \leqslant 1, \end{cases} \quad c_2^0 = \begin{cases} 0, \quad\quad\quad 0 \leqslant x \leqslant 1/2, \\ 5 \times 10^{-6}, \ 1/2 < x \leqslant 1, \end{cases} \quad c_3^0 = 0.$$

Also we took $h = 0.02$ for $T = 1000°C$ and $h = 0.2$ for $T = 1600\,°C$, $r = 1$.

(b) Define a discrete grid

$$\omega_{\tau, h_1, h_2} = \omega_\tau \times \omega_{h_1} \times \omega_{h_2}$$

and $u^n_{k,i,j} = u_k(x_{1,i}, x_{2,j}, t^n)$ be the lattice function defined at $\omega_{\tau, h_1, h_2}$ points. Let $u^n_{k,i,j}$ also defined at $\omega_{\tau/2, h_1, h_2}$ points. We approximate equations [6] (here transition from nth to $(n+1)$th layer is executed in two stages using $\tau/2$ step)

$$
\begin{aligned}
(\bar{u}_1 - u_1)/0, 5\tau &= D_1 \bar{u}_{1, \bar{x}_1 x_1} + D_2 u_{1, \bar{x}_2 x_2} - 3k \bar{u}_{1,i} u_{2,i}, \\
(\bar{u}_2 - u_2)/0, 5\tau &= D_1 \bar{u}_{2, \bar{x}_1 x_1} + D_2 u_{2, \bar{x}_2 x_2} - 5k \bar{u}_{1,i} \bar{u}_{2,i}, \\
(\bar{u}_3 - u_3)/0, 5\tau &= D_1 \bar{u}_{3, \bar{x}_1 x_1} + D_2 u_{3, \bar{x}_2 x_2} + 2k \bar{u}_{1,i} \bar{u}_{2,i},
\end{aligned}
\tag{13}
$$

$$
\begin{aligned}
(\hat{u}_1 - \bar{u}_1)/0, 5\tau &= D_1 \bar{u}_{1, \bar{x}_1 x_1} + D_2 \hat{u}_{1, \bar{x}_2 x_2} - 3k \hat{u}_{1,i} \bar{u}_{2,i}, \\
(\hat{u}_2 - \bar{u}_2)/0, 5\tau &= D_1 \bar{u}_{2, \bar{x}_1 x_1} + D_2 \hat{u}_{2, \bar{x}_2 x_2} - 5k \hat{u}_{1,i} \hat{u}_{2,i}, \\
(\hat{u}_3 - \bar{u}_3)/0, 5\tau &= D_1 \bar{u}_{3, \bar{x}_1 x_1} + D_2 \hat{u}_{3, \bar{x}_2 x_2} + 2k \hat{u}_{1,i} \hat{u}_{2,i},
\end{aligned}
\tag{14}
$$

initial conditions [7]

$$u^0_{k,i,j} = c^0_1, \quad k = 1, 2, 3, \ i = 0, \ldots, N_1, \ j = 0, \ldots, N_2 \tag{15}$$

and boundary conditions [8]

$$
\begin{aligned}
u^n_{k,0,j} &= \epsilon u^n_{k,1,j}, \quad u^n_{k,N_1-1,j} = \epsilon u^n_{k,N_1,j}, \quad j = 1, \ldots, N_2, \\
u^n_{k,i,0} &= \epsilon u^n_{k,i,1}, \quad u^n_{k,i,N_2-1} = \epsilon u^n_{k,i,N_2}, \quad i = 1, \ldots, N_1,
\end{aligned}
\tag{16}
$$

$$k = 1, 2, 3, \quad n = 0, \ldots, 2M,$$

where $\varepsilon = 1 - 10^{-6}$.

The initial conditions $c^0_i$ are

$$
c^0_1 = \begin{cases}
3 \times 10^{-6}, & 0 \leqslant x_1 \leqslant 1/2, 0 \leqslant x_2 \leqslant 1/2, \\
3 \times 10^{-6}, & 1/2 \leqslant x_1 \leqslant 1, 1/2 \leqslant x_2 \leqslant 1, \\
0, & 0 \leqslant x_1 < 1/2, 1/2 < x_2 \leqslant 1, \\
0, & 1/2 \leqslant x_1 \leqslant 1, 0 \leqslant x_2 < 1/2,
\end{cases}
$$

$$
c^0_2 = \begin{cases}
0, & 0 \leqslant x_1 \leqslant 1/2, 0 \leqslant x_2 \leqslant 1/2, \\
0, & 1/2 \leqslant x_1 \leqslant 1, 1/2 \leqslant x_2 \leqslant 1, \\
5 \times 10^{-6}, & 0 \leqslant x_1 < 1/2, 1/2 \leqslant x_2 \leqslant 1, \\
5 \times 10^{-6}, & 1/2 < x_1 \leqslant 1, 0 \leqslant x_2 < 1/2,
\end{cases}
$$

$$c^0_3 = 0.$$

Also we took $h_1 = h_2 = 0.02$ for $T = 1000\,°C$ and $h_1 = h_2 = 0.2$ for $T = 1600\,°C$, $\tau = 10$.

In both cases for simplicity we took $D_1 = D_2 = D_3 = D$.

Finite difference schemes were solved using stream sweeping method. The stability of this method was proved in [25].

## 4. Results

As we mentioned in section 1, the first question appeared was to determine the values of the diffusion and rate constants of YAG synthesis. We proceed from requirement that

$$t_{1/2} = 4. \tag{17}$$

Thereby we selected values of unknown constants such as the value of half time was as in [17]. The results (at $1000\,^\circ$C and $1600\,^\circ$C) are presented in figures 4–7. In these figures triangled curves express dependability between required constants $D$ and $k$. (If one of the required constant is known then the other constant is obtained easily.) One can see that diffusion constant $D$ is bounded below in both cases at both temperature regimes and this lower bound (dash-dot line) increases 100 times while temperature increases from $1000\,^\circ$C to $1600\,^\circ$C.

Further, we noticed that the run of YAG synthesis was more or less different at different points of got dependability curves. So, such a situation has initiated to divide $D-k$ plane into areas and thereby more precisely localise values of the unknown constants. Let us define a domination concept.

**Definition.** Diffusion (reaction) is dominating process of the YAG synthesis if for the fixed constants $v_{\mathrm{dif}}(v_{\mathrm{reac}})$

$$I(t^*) = \frac{I_3(t^*)}{I_1(t^*) + I_2(t^*)} = \frac{\int_V c_3(x, t^*)\mathrm{d}x}{\int_{V_1^0} c_1(x, t^*)\mathrm{d}x + \int_{V_2^0} c_2(x, t^*)\mathrm{d}x} \leqslant v_{\mathrm{dif}} \quad (\geqslant v_{\mathrm{reac}}),$$
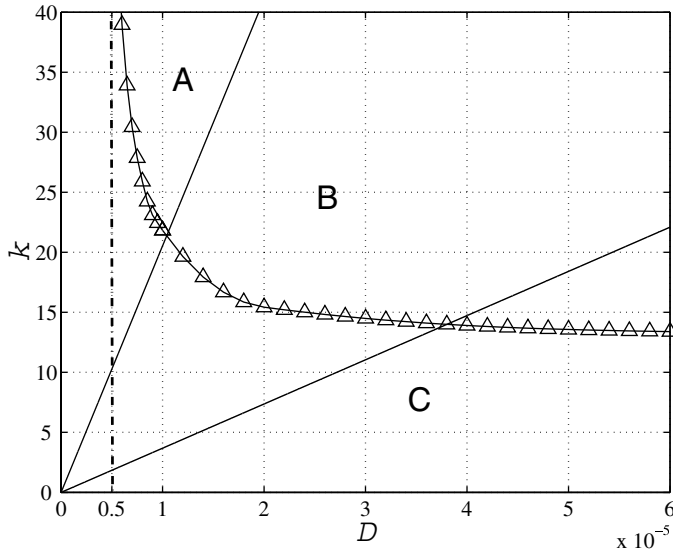


Figure 4. Dependence between $D$ and $k$ in one-dimensional case, $T = 1000\,^\circ$C. Domination areas: (A) reaction domination, (B) reaction compete with diffusion, (C) diffusion domination.
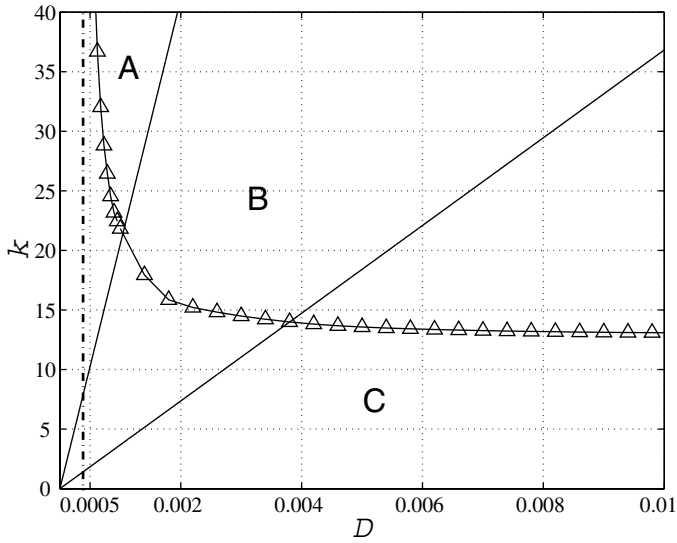
Figure 5. Dependence between $D$ and $k$ in one-dimensional case, $T = 1600\,^{\circ}\text{C}$. Domination areas: (A) reaction domination, (B) reaction compete with diffusion, (C) diffusion domination.
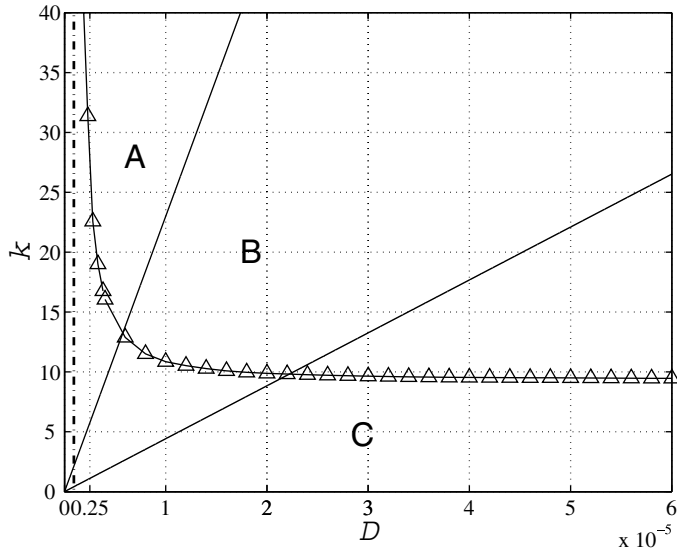


Figure 6. Dependence between $D$ and $k$ in two-dimensional case, $T = 1000\,^{\circ}\text{C}$. Domination areas: (A) reaction domination, (B) reaction compete with diffusion, (C) diffusion domination.

where $t^* : I_1(t^*) + I_2(t^*) = \max_{0 \leqslant t \leqslant t_{1/2}}(I_1(t) + I_2(t))$, $V_i^0 : c_i^0 = 0, x \in V_i^0$. $\nu_{\text{dif}}$ and $\nu_{\text{reac}} > 0$ were obtained empirically using constructed computational model: $\nu_{\text{diff}} = 0.25$ and $\nu_{\text{reac}} = 0.75$.
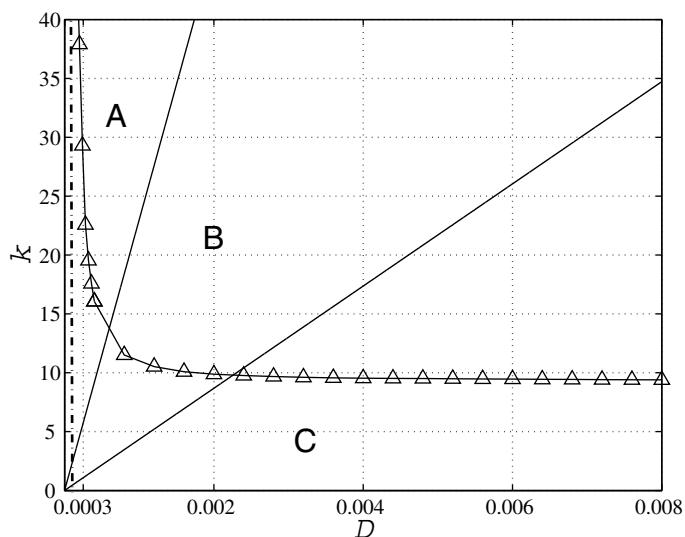
Figure 7. Dependence between $D$ and $k$ in two-dimensional case, $T = 1600\,^\circ$C. Domination areas: (A) reaction domination, (B) reaction compete with diffusion, (C) diffusion domination.

In figures 4–7 we show diffusion and reaction domination areas denoted A, B, and C. In the introduction we assume that diffusion and reaction are the limited stages of the synthesis, so, more particularly, there is approximate equality in rights of these stages. Therefore we made conclusion that the values of required constants is in area B. That is

(a) in one-dimensional case

$$1 \times 10^{-5} \leqslant D \leqslant 4 \times 10^{-5} \quad \text{for} \quad T = 1000\,^\circ\text{C},$$
$$1 \times 10^{-3} \leqslant D \leqslant 4 \times 10^{-3} \quad \text{for} \quad T = 1600\,^\circ\text{C}.$$

(b) in two-dimensional case

$$5 \times 10^{-6} \leqslant D \leqslant 2 \times 10^{-5} \quad \text{for} \quad T = 1000\,^\circ\text{C},$$
$$5 \times 10^{-4} \leqslant D \leqslant 2 \times 10^{-3} \quad \text{for} \quad T = 1600\,^\circ\text{C}.$$

## 5. Conclusions

- We construct a mathematical model which allows the effective computer simulation of YAG synthesis. Developed model is based on non-stationary diffusion equations containing a non-linear term related to kinetic of reaction. The numerical solution of the derived PDE was carried out using finite difference techniques.

- We offered possible solution to the problem of determination of diffusion and reaction rate constants proceeding from value of half-time. We

got dependability curves for diffusion and reaction rates and offered possible method to localize values of diffusion and reaction rate constants precisely enough.

## 6. Acknowledgment

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