

VILNIUS UNIVERSITY

MAŽVYDAS MACKEVIČIUS

COMPUTER MODELING OF CHEMICAL SYNTHESIS AT HIGH
TEMPERATURES

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VILNIAUS UNIVERSITETAS

MAŽVYDAS MACKEVIČIUS

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MODELIAVIMAS

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INTRODUCTION

The rate of a general homogeneous reaction is conventionally measured by following the decrease in concentration of reactants or the increase in concentration of the products at constant temperature. For the heterogeneous reaction, however, the concept of concentration has no longer the same significance, and the progress of reaction is usually determined in some other way. The kinetics and the mechanism studies of heterogeneous reactions thus involve measurement of changes in mass of reactants of the sample as functions of time at constant temperatures [3, 10, 19, 32]. Many equations relating the rate of solid-state reactions under isothermal and nonisothermal conditions to the bulk nucleation followed by three-dimensional growth and diffused distribution at the phase boundary (classical Fick diffusion or Prout–Tompkins model) are summarized and discussed in the literature [1, 5, 11, 34, 47]. The interpretation of the kinetic equations is extremely complicated and considers the way in which the reaction starts, by a process of nucleation, then how those nuclei grow, what reaction or interface geometry is involved, and, finally, how the reactants decay. Consequently, for the investigation of complex solid-state reactions, different novel mathematical approximations and computational models recently have been suggested [13, 35, 36].

In our dissertation, we construct two- and three-reactant models of synthesis reactions at high temperatures and provide methods of estimation of the parameters of syntheses, such as the diffusion coefficients and reaction rate coefficients, using a rather limited information from real laboratory experiments. Namely, the known data only includes the synthesis half-times at different temperatures and approximate sizes of reactant particles. We use the Fick, Arrhenius, and active mass laws. Though the validity of applying the Arrhenius law to heterogeneous reactions has been questioned, the parameters obtained from it often have practical values even if their theoretical interpretation is difficult.

Actuality

In mathematical modeling, for solving actual problems, one often uses numerical methods for differential parabolic equations. In this work, we present the results of computer modeling of synthesis at high temperatures of yttrium aluminium garnet (YAG) and synthetic calcium hydroxyapatite (CHAp), but the methods used can be applied for general two- and three-reactant synthesis reactions.

Yttrium aluminium garnet $2\text{Y}_3\text{Al}_5\text{O}_{12}$ is now widely used in optical materials because of a variety of unique optical properties. YAG doped with a transition metal or lanthanide ions is an important solid-state laser material ([14, 4, 16, 22, 27, 29, 30, 33]). The YAG powders could be synthesized by many different methods, such as solid-state reaction, sol-gel, and others [2, 17, 18, 24, 28, 41, 48, 49, 50]).

Synthetic calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (CHAp for short), is known to be one of the most important implantable materials due to its biocompatibility, bioactivity, and osteoconductivity and is used as a substitute material for human hard tissues [45, 25, 40]. However, the specific chemical, structural, and morphological properties of CHAp bioceramics are highly sensitive to the processing conditions [12, 15, 23, 43]. Several sol-gel approaches starting from nonaqueous [38, 51] and aqueous [46, 31] solutions of different precursors of calcium and phosphorus have been used for the preparation of CHAp powders.

It has been well demonstrated that many parameters of sol-gel process such as starting materials and its concentration, pH, temperature, speed of stirring, stirring time, duration of gelation, nature and concentration of complexing agents, and others should be carefully controlled [6, 7, 8, 9]

Synthesis of both materials are expensive because they require long-term support of high temperature [37, 42, 44]. Investigation of synthesis and its parameters using usual experiments would be complicated and expensive. Therefore, it is important to create theoretical mathematical models that would help to accomplish such tasks.

A one-dimensional mathematical model of YAG synthesis was presented in [20, 21, 26].

In this work, we first present general two- and three-dimensional (two-reactant) mathematical synthesis models and perform calculations for the YAG synthesis based on real data from laboratory experiments. Naturally, the three-dimensional model is more realistic, but, as was shown by

computer modeling, the results of the two-dimensional model (unlike the one-dimensional model) are rather similar to those of the three-dimensional model. So, as a consequence, the two-dimensional model is preferable as significantly simpler and less time consuming. This is also a motivation of restricting ourselves to the two-dimensional model in the case of three reactants since its extension to the three-dimensional model would be extremely complicated. Thus, investigating the CHAp synthesis, we have developed a general two-dimensional three-reactant mathematical model, which also allowed us to find the synthesis parameters.

Research object

Mathematical models for investigation of chemical synthesis at high temperatures and methods of calculating the synthesis parameters having limited data from real laboratory experiments.

The Main Aims and Tasks

- To extend the one-dimensional two-reactant synthesis model to two- and three-dimensional models.
- To construct and investigate a three-reactant synthesis mathematical model.

Tasks

- To develop general two-reactant two- and three-dimensional and three-reactant two-dimensional synthesis models and methods for calculation of synthesis parameters.
- To apply this model for finding temperature dependencies of diffusion and reaction rate coefficients and activation energies in the YAG and CHAp syntheses.
- To compare the results in one-, two-, and three- dimensional models of YAG synthesis.
- To find the optimal temperature of YAG synthesis that minimizes the energy consumption.

Methodology

For modeling, we applied the laws of physical chemistry and reduced the problems to particular state spaces by periodization of distribution of reactant particles and symmetrization of the state space.

For calculations, we applied standard and constructed new difference schemes for solving parabolic differential equation systems with partial derivatives. Computer modeling programs were written in ANCI C language with codes parallelized using the parallelization library MPI.

Scientific novelty

In this work, we developed two- and three-dimensional two-reactant models and a two-dimensional three-reactant mathematical model of chemical synthesis, parameter calculation methods, and numerical algorithms. The results obtained extend and generalize the known results for one-dimensional two-reactant model.

Practical significance

The obtained numerical algorithm provides the ability to model processes of chemical synthesis and allows one to find synthesis parameters and their dependencies on the synthesis temperature from limited data of real laboratory experiments. This method can be successfully applied in analysis of various syntheses.

Defended models, methods, and results

- Two-reactant two- and three-dimensional synthesis models and three-reactant (two-dimensional) synthesis model.
- Methods of calculating parameters of synthesis reactions at high temperatures.
- The results of calculations in concrete cases of YAP (two-reactant) and CHAp (three-reactant) synthesis.

The Structure of Dissertation

The dissertation consists of the introduction, four chapters, the list of author's publications, and references. The language of the thesis is Lithuanian.

In Chapter 1, we shortly present the laws of physical chemistry that we use to construct the diffusion–reaction equation systems modeling the synthesis reactions and check the mass preservation law for these models.

In Chapter 2, we consider one-, two-, and three-dimensional models of two-reactant synthesis reaction. Concrete calculations are performed and compared for YAG synthesis on the basis of data from real laboratory experiments in the Faculty of Chemistry of Vilnius University.

In Chapter 3, we consider the three-reactant two-dimensional model. To assure the periodicity and symmetry requirements, we consider rhombic particles and triangle synthesis space, which allow us to reduce the calculations to the triangle state space with zero Neumann boundary conditions. Concrete calculations are performed for CHAp synthesis on the basis of data from real laboratory experiments in the Faculty of Chemistry of Vilnius University.

In Chapter 4, we present numerical methods used for solving our model diffusion–reaction equation systems. In Section 4.1, the standard difference method is presented, while in Section 4.2, a newly constructed method for a triangular state space is presented, which we have used for solving equation systems of Chapter 3. At the ends of both sections, we present the plots illustrating the methods. In Section 4.3, we present the parallelization algorithm used in calculations of parameters.

1. TWO-REACTANT MODEL

1.1 *Experimental*

The YAG powders could be synthesized by many different methods, such as solid-state reaction, spray-pyrolysis, coprecipitation, sol-gel, and others. The conditions for the formation of monophasic YAG largely depend on the used synthesis method. For example, by changing the solid-state synthesis method to the sol-gel chemistry approach, the YAG formation temperature decreases from 1600 °C down to 1000 °C.

1.1.1 *Sol-gel method*

In the sol-gel synthesis, yttrium oxide was dissolved in 150 mL of 0.2 mol L⁻¹ CH₃COOH by stirring the mixture for 10 h at 55–60 °C in a breaker covered with a watch-glass. To this solution, aluminium nitrate dissolved in 50 mL of distilled water was added, and the resulting mixture was stirred for 2 h at the same temperature. In the next step, 1.2 ethanediol (25 mmol) as complexing agent was added to the above solutions. The acidic medium (pH 5) prevents the flocculation of metal hydroxides in the mixtures and no adjustment of pH was necessary. After concentrating the solutions by slow evaporation at 60–70 °C under stirring, the Y–Al acetate–nitrate–glycolate solution turned into a white transparent gel. The oven-dried 60–70 °C gel became light brown due to the initial decomposition of nitrates. The gel powders were ground in an agate mortar and preheated for 2 h at 800 °C in air. Since the gels are very combustible, slow heating (2 °C min⁻¹), especially between 150 and 400 °C, was found to be essential. After an intermediate grinding, the powders were additionally sintered at various temperatures from 1000 to 1600 °C in air. The optimum annealing time was 5 h at 1000 °C, 4 h at 1200 °C, and 3 h at 1600 °C.

1.1.2 Solid-state method

In the solid-state reaction method, the stoichiometric mixture of metal oxides ($5\text{Al}_2\text{O}_3$ and $2\text{Y}_2\text{O}_3$) was carefully ground in an agate mortar and annealed at various temperatures from 1000 to 1600 °C in air. The monophase YAG was obtained only at higher temperature, after sintering oxide precursor for 5 h at 1600 °C.

1.2 Mathematical model

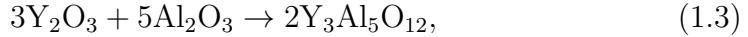
For synthesis modeling, using the second Fick's law and active mass law, we describe the two-reactant reaction



by the following diffusion–reaction equation system for concentrations $c_i = c_i(x, t)$, $x \in V$, $t \geq 0$, $i = 1, 2, 3$, of the reactants A, B and product P :

$$\begin{aligned} \frac{\partial c_1}{\partial t} &= D \sum_{j=1}^n \frac{\partial^2 c_1}{\partial x_j^2} - \frac{1}{b} k c_1 c_2, \\ \frac{\partial c_2}{\partial t} &= D \sum_{j=1}^n \frac{\partial^2 c_2}{\partial x_j^2} - \frac{1}{a} k c_1 c_2, \\ \frac{\partial c_3}{\partial t} &= D \sum_{j=1}^n \frac{\partial^2 c_3}{\partial x_j^2} + \frac{p}{ab} k c_1 c_2, \end{aligned} \quad (1.2)$$

with initial conditions $c_i(x, 0) = c_i^0(x)$, $x \in \bar{V} = V \cup \partial V$, $i = 1, 2, 3$, and boundary conditions $\frac{\partial c_i(x, t)}{\partial \mathbf{n}} = 0$, $x \in \partial V$, $t \geq 0$, $i = 1, 2, 3$. Here V is the synthesis space (two- or three-dimensional), D is the diffusion coefficient, and k is the reaction rate coefficient. For example, in the case of the YAG synthesis reaction



we clearly have $a = 3$, $b = 5$, and $p = 2$.

We analyze the relations between D and k by using the following data known from the true laboratory experiments of YAG synthesis at Vilnius University: the synthesis half-times at different temperatures and synthesis methods, and typical dimensions of the reactant particles. By the half-time

we mean the time, denoted $t_{1/2}$, in which the total concentration of initial reactants falls to one half; so, it satisfies the equation

$$\int_V (c_1(x, t_{1/2}) + c_2(x, t_{1/2})) dx = \frac{1}{2} \int_V (c_1(x, 0) + c_2(x, 0)) dx. \quad (1.4)$$

To be concrete, the half-times $t_{1/2}$ approximately equal 5, 4, and 3 hours at the temperatures $T = 1000^\circ\text{C}$, 1200°C , and 1600°C in the sol-gel synthesis method and 5 hours at 1600°C in the solid-state synthesis method. At the preparatory stage of the synthesis (using both solid-state and sol-gel reaction methods), the reactants are milled and mixed thoroughly in some cubic volume. The particles in the synthesis space are distributed randomly since their exact initial positions are unknown. As a result, modeling would require a huge memory size for storage. Therefore, we assume that the particles are periodically stored in the synthesis volume as shown in Fig. 1.1 (two-dimensional model) and Fig. 1.2 (three-dimensional model). Then, because of periodicity, it suffices to consider the reaction in the square synthesis space $V = [0, a] \times [0, a]$ or cubic synthesis space $V = [0, a] \times [0, a] \times [0, a]$, respectively, with zero boundary conditions, $\partial c_i / \partial \mathbf{n}(x) = 0$ for $x \in \partial V$, where \mathbf{n} is the normal vector to the boundary (as shown, in more detail, in Fig. 1.3 in the two-dimensional case).

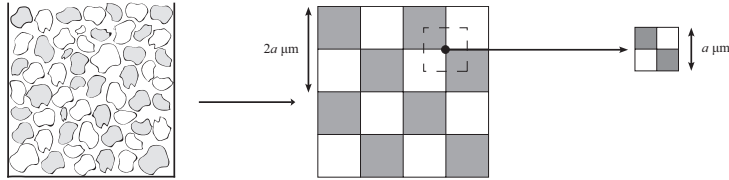


Fig. 1.1: Synthesis space in the two-dimensional model: $V = [0, a] \times [0, a]$; $a = 1 (\mu\text{m})$ for the sol-gel method and $a = \sqrt{10} (\mu\text{m})$ for the solid-state method

The typical volume of particles is $1 \mu\text{m}^3$ in the sol-gel synthesis method and $10 \mu\text{m}^3$ in the solid-state method. Therefore, in the two-dimensional model, we assume that line dimensions of particles are respectively $a = 1 \mu\text{m}$ or $a = \sqrt{10} \mu\text{m}$ (in the one-dimensional case, $a = 1 \mu\text{m}$ and $a = 10 \mu\text{m}$). This is motivated by the natural presumption that, in order to compare models of different dimensions, for the same reactant concentration values, the quantities of reactants must be the same at all dimensions.

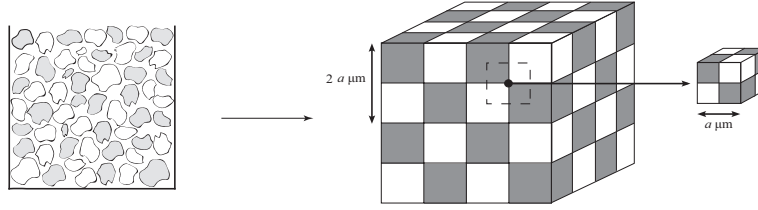


Fig. 1.2: Synthesis space in the three-dimensional model: $V = [0, a] \times [0, a] \times [0, a]$; $a = 1 (\mu\text{m})$ for the sol-gel method and $a = \sqrt[3]{10} (\mu\text{m})$ for the solid-state method

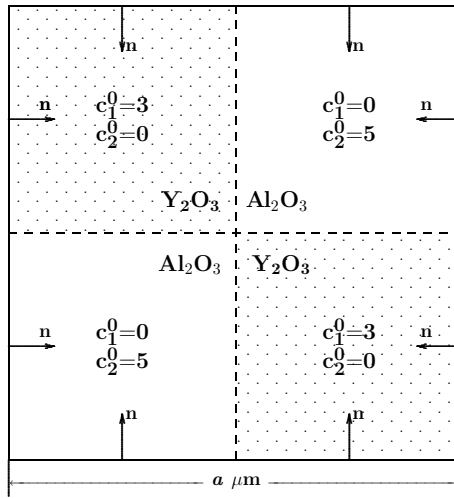


Fig. 1.3: Synthesis space in the two-dimensional two-particle model: $V = [0, a] \times [0, a]$; $a = 1 (\mu\text{m})$ for sol-gel method and $a = \sqrt{10}$ for solid-state method.

So, summarizing, we arrived at the equation system (1.2) in the synthesis space $V = [0, a] \times [0, a] \times [0, a]$ (3D) or $V = [0, a] \times [0, a]$ (2D) with the initial conditions proportional to the initial densities of the particles in the space V and zero boundary conditions, $\frac{\partial c_i}{\partial \mathbf{n}} = 0$ on ∂V .

When solving numerically the partial differential equation system (1.2), we use a standard finite difference scheme (see [39] or Section 4.1 of the dissertation).

1.3 The main goal

Our estimations are based on the Arrhenius laws describing the temperature dependence of the diffusion and reaction rate coefficients by the following relations:

$$D = D_0 \exp \left\{ -\frac{E_D}{RT} \right\}, \quad k = k_0 \exp \left\{ -\frac{E_A}{RT} \right\}. \quad (1.5)$$

Here, E_D is the diffusion activation energy, E_A is the reaction activation energy, D_0 and k_0 are constants, and $R = 8.314472$. Our main goal is to estimate the unknown parameters E_D , E_A , D_0 , k_0 by finding the coefficients D and k for temperatures $T = 1000^\circ\text{C}$, 1200°C , and 1600°C . In a sense, we solve the inverse problem for system (1.2): given the synthesis half-times $t_{1/2}$, we look for the parameters D and k of the system such that the half-time condition (1.4) is satisfied for all temperatures. Using Eq. (1.5), for any temperature T , we can find the corresponding parameters D and k , and then, by computer modeling, the corresponding synthesis half-time. This allows us to calculate the energy needed for synthesis at any given temperature and, in particular, to find the optimal temperature.

1.4 Calculation method

We calculate the diffusion and reaction rate coefficients as follows:

First, for each of the temperatures $T_1 = 1000^\circ\text{C}$, $T_2 = 1200^\circ\text{C}$, and $T_3 = 1600^\circ\text{C}$, we draw the graphs L_1 , L_2 , and L_3 of points (D, k) of the diffusion and reaction rate parameters for which the half-times are equal to those of the laboratory experiments by using the sol-gel synthesis method (i.e., $t_{1/2} = 5, 4$, and 3 , respectively). To this end, we use our computer program that, given any fixed D , half-time $t_{1/2}$, and particle size a , numerically solves system (1.2) until the half-time condition (1.4) is satisfied and, using the middle-point method, finds the value k such that half-time coincides with the given one. A sufficiently large discrete set of the (D, k) values is joined by a smooth curve. Finally, in the same way, we additionally draw the graph \tilde{L}_3 of the (D, k) for the solid-state method ($T_3 = 1600^\circ\text{C}$, $t_{1/2} = 5$). The difference with the previous cases is in the particle-size parameter a , which now takes the value $\sqrt[3]{10}$ (three-dimensional model), instead of $a = 1$. So, in Fig. 1.4 ($n = 2$) and Fig. 1.5 ($n = 3$), we see all four graphs : L_1 , L_2 ,

and L_3 for the sol-gel method at temperatures T_1 , T_2 , and T_3 ; and \tilde{L}_3 for the solid-state method and temperature T_3 .

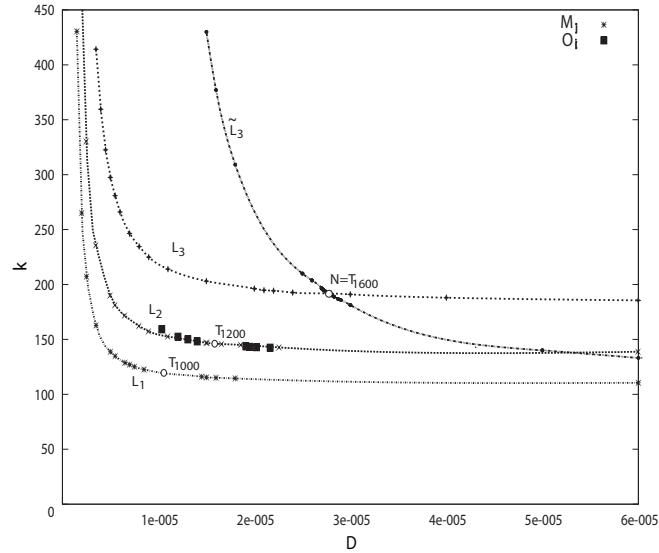


Fig. 1.4: Calculations in the two-dimensional model. The synthesis space $V = [0, a] \times [0, a]$; $a = 1$ (μm) for the sol-gel method and $a = \sqrt{10}$ (μm) for the solid-state method.

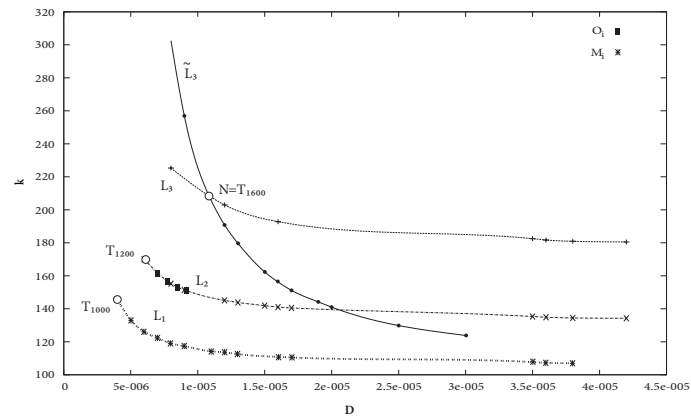


Fig. 1.5: Calculations in the three-dimensional model. The synthesis space $V = [0, a] \times [0, a] \times [0, a]$; $a = 1$ (μm) for the sol-gel method and $a = \sqrt[3]{10}$ (μm) for the solid-state method.

At the same temperature, the values of (D, k) for both synthesis methods coincide. So, the intersection of the graphs \tilde{L}_3 and L_3 gives us the first pair of the true values of (D, k) at the temperature $T_3 = 1600^\circ\text{C}$. We mark by N the intersection point.

To calculate the four unknown parameters (E_D, E_A, D_0, k_0) , we need another pair of the values of (D, k) . Recall that the graph L_1 is obtained as the spline of m calculated points $M_i = (D_{1000}^i, k_{1000}^i)$, $i = 1, \dots, m$, obtained by computer modeling, where the main condition was that the half-time is 5 h.

Now, for each pair $N = (D_{1600}, k_{1600})$, $M_i = (D_{1000}^i, k_{1000}^i)$, using the Arrhenius law for $T = 1873\text{ K}$ and $T = 1273\text{ K}$, we write and solve the following equation system with respect to unknown (E_D, E_A, D_0, k_0) :

$$D_{1600} = D_0 \exp\left\{-\frac{E_D}{R \cdot 1873}\right\}, \quad k_{1600} = k_0 \exp\left\{-\frac{E_A}{R \cdot 1873}\right\},$$

$$D_{1000}^i = D_0^i \exp\left\{-\frac{E_D^i}{R \cdot 1273}\right\}, \quad k_{1000}^i = k_0^i \exp\left\{-\frac{E_A^i}{R \cdot 1273}\right\}.$$

We denote the corresponding solutions by $(E_D^i, E_A^i, D_0^i, k_0^i)$. Substituting these values of E_D^i , E_A^i , D_0^i , k_0^i into the Arrhenius law (1.5) with $T = 1200^\circ\text{C} = 1473\text{ K}$, we get a set of points $O_i = (D_{1200}^i, k_{1200}^i)$, $i = 1, \dots, m$.

Now, comparing the points O_i with the graph L_2 , we choose the nearest one L_O . Fixing the latter, again from the Arrhenius law, the corresponding unknown E_D , E_A , D_0 , k_0 can be found uniquely.

1.5 Calculation results

For the three-dimensional model, we obtained the following calculation results:

- 1) $N = (D_{1600}, k_{1600}) = (11\text{e-}6, 209)$.
- 2) $L_O = (6\text{e-}6, 170)$;
- 3) The diffusion and reaction rates as functions of synthesis temperature T :

$$D = 9\text{e-}5 \exp(-3.3\text{e}4/(RT)), \quad (1.6)$$

$$k = 450 \exp(-1.2\text{e}4/(RT)). \quad (1.7)$$

The obtained Arrhenius law equations (1.6)–(1.7) give us the diffusion and reaction rates at temperatures $T = 1000\text{ }^\circ\text{C}$, $1200\text{ }^\circ\text{C}$, and $1600\text{ }^\circ\text{C}$, presented in Table 1, where the results in the one- and two- dimensional models are also included for comparison.

Tab. 1.1: Diffusion and reaction rate coefficients

T	1000 °C	1200 °C	1600 °C
One-dimensional model			
D	5.0e-4	5.8e-4	7.0e-4
k	113	143	199
Two-dimensional model			
D	10.5e-6	15e-6	28e-6
k	119	146	192
Three-dimensional model			
D	4e-6	6e-6	11e-6
k	146	170	209

The corresponding points (D, k) on the graphs L_1 – L_3 and \tilde{L}_3 (Figs. 1.4 and 1.5) are marked as T_{1000} , T_{1200} , T_{1600} , respectively.

In Figs. 1.6 and 1.7, we compare the graphs of the diffusion and reaction rate coefficients as functions of temperature (the Arrhenius law) in all three models.

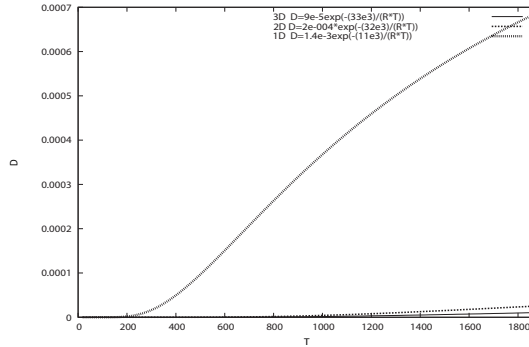


Fig. 1.6: Comparison of dependence of diffusion coefficients on the temperature in one-, two-, and three-dimensional models.

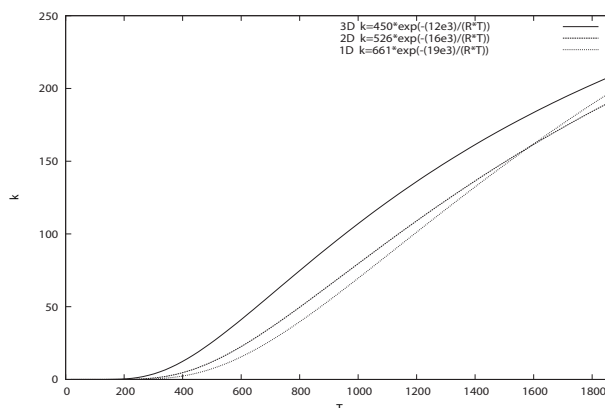


Fig. 1.7: Comparison of dependence of reaction rate coefficients on the temperature in one-, two-, and three-dimensional models.

We see that reaction rate coefficients are rather similar in all models, although the diffusion coefficients are not. The latter difference can be explained by noticing that, in the one-dimensional model, the diffusion actually begins through a single point, while in the two- and three-dimensional models, the “diffusion surface” is essentially larger.

1.6 Optimization of the energy consumption

Our approach allows us to find the optimal synthesis temperature in the sense of minimal energy consumption. We are given the powers (Table 1.2, column 3) needed to achieve various temperatures (column 2) in the YAG synthesis. The energy outly was calculated for the high-temperature chamber furnace Nabertherm LHT. From Eqs. (1.6) and (1.7) we can get the diffusion and reaction rates (columns 4 and 5) needed for specific temperature and then calculate the corresponding half-times (column 6) by computer modeling. To calculate the total energy consumption E_T (column 7) under given synthesis temperature T , we take into account the energy consumed for preheating from room temperature, for which the five times higher furnace power is used for half an hour. For simplicity, we assume that the total synthesis time is twice the half-time, although in real experiments, the reaction time

Tab. 1.2: The energy consumption in YAG synthesis

No.	T ($^{\circ}\text{C}$)	P_T (kW)	D	k	$t_{1/2}$ (h)	E_T (MJ)
1	1000	648	4e-6	146	5	7.8
2	1100	667	5e-6	157	4.47	7.3
3	1200	720	6e-6	170	4	7.2
4	1300	975	7e-6	181	3.63	9.0
5	1400	1260	8e-6	191	3.37	11
6	1500	1512	10e-6	200	3.17	13
7	1600	1800	11e-6	209	3	14.4

is somewhat longer.¹ To be precise, we use the formula

$$E_T = P_T(2.5 + 2t_{1/2}),$$

where P_T is the power used at the synthesis temperature T . Having plotted a graph of energy vs. temperature (Fig. 1.8), we see that the minimal energy consumption in the YAG synthesis is achieved at the temperature $T \approx 1170^{\circ}\text{C}$.

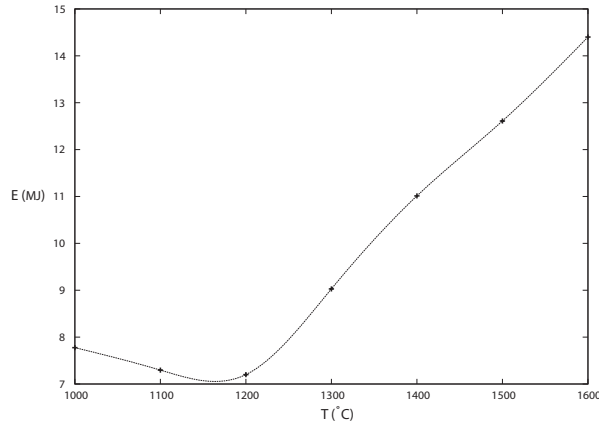


Fig. 1.8: Energy consumption vs. temperature.

¹ Theoretically, the total reaction time is infinite.

2. THREE-REACTANT MODEL

2.1 *Experimental*

In the sol–gel process phosphoric acid, H_3PO_4 , and calcium acetate monohydrate, $\text{Ca}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}$, were selected as P and Ca precursors, respectively. Calcium acetate was first dissolved in 0.2 M CH_3COOH at room temperature (20°C) or at 65°C . To these solutions, phosphoric acid was added and the resulting mixtures were stirred for 1 h at the same temperatures. In the following step, tartaric acid as complexing agent was added to the above solutions. After concentrating the solutions by slow evaporation at 20°C or 65°C under stirring the Ca–P–O sols turned into the transparent gels. The oven-dried (100°C) gel powders were ground in an agate mortar and annealed for 5 h at $800\text{--}1300^\circ\text{C}$ in air.

2.2 *Mathematical model*

For synthesis modeling, using the second Fick’s law and active mass law, we describe the two-reactant reaction



by the following diffusion–reaction equation system for concentrations $c_i = c_i(x, t)$, $x \in V$, $t \geq 0$, $i = 1, 2, 3, 4$, of the reactants A, B, C and product P :

$$\begin{aligned}
\frac{\partial c_1}{\partial t} &= D \sum_{j=1}^2 \frac{\partial^2 c_1}{\partial x_j^2} - \frac{1}{bc} k c_1 c_2 c_3 \\
\frac{\partial c_2}{\partial t} &= D \sum_{j=1}^2 \frac{\partial^2 c_2}{\partial x_j^2} - \frac{1}{ac} k c_1 c_2 c_3, \\
\frac{\partial c_3}{\partial t} &= D \sum_{j=1}^2 \frac{\partial^2 c_3}{\partial x_j^2} - \frac{1}{ab} k c_1 c_2 c_3, \\
\frac{\partial c_4}{\partial t} &= D \sum_{j=1}^2 \frac{\partial^2 c_4}{\partial x_j^2} + \frac{p}{abc} k c_1 c_2 c_3.
\end{aligned} \tag{2.2}$$

with initial conditions $c_i(x, 0) = c_i^0(x)$, $x \in \bar{V} = V \cup \partial V$, $i = 1, 2, 3, 4$, and boundary conditions $\frac{\partial c_i(x, t)}{\partial \mathbf{n}} = 0$, $x \in \partial V$, $t \geq 0$, $i = 1, 2, 3, 4$. Here V is the two-dimensional synthesis space, D is the diffusion coefficient, and k is the reaction rate coefficient. For example, in the case of the CHAp synthesis reaction



we have $a = 10$, $b = 3$, $c = 2$, and $p = 1$.

We analyze the relations between D and k by using the following data known from the true laboratory experiments at Vilnius University: the synthesis times at different temperatures and typical dimensions of the reactant particles. In our model, for calculations, we use the synthesis half-time, which is the time, denoted $t_{1/2}$, in which the total concentration of initial reactants falls to one half; so, it satisfies the equation

$$\begin{aligned}
&\int_V (c_1(x, t_{1/2}) + c_2(x, t_{1/2}) + c_3(x, t_{1/2})) dx \\
&= \frac{1}{2} \int_V (c_1(x, 0) + c_2(x, 0) + c_3(x, 0)) dx.
\end{aligned} \tag{2.4}$$

Theoretically, the total concentration of initial reactants, although decays exponentially, always remains positive, and therefore the “full” synthesis time is infinite. Practically, we assume that the synthesis is over when the total concentration of initial reactants becomes “sufficiently small,” namely, the

unreacted part is less than $0.1\% \approx 2^{-10}$. From experiments we know that the “full” synthesis times are approximately 6, 8, 10, and 16 hours at the temperatures $T = 1200^\circ\text{C}$, 1100°C , 1000°C , and 900°C , respectively. So, in our calculations, we assume that the synthesis half-times are one-tenth of the corresponding “full” times, that is, 0.6, 0.8, 1.0, and 1.6 hours at the temperatures $T = 1200^\circ\text{C}$, 1100°C , 1000°C , and 900°C , respectively.

As before, in order to have a model appropriate for calculations, we first have to store the particles periodically. Moreover, to reduce the calculations to a small area with zero Neumann boundary condition (zero normal derivative), we have to store the particles symmetrically with respect to any edge of the boundary of the area. Unlike the two-reactant case, this appeared to be impossible with square-form or rectangular particles. Happily, in the three-reactant case, we succeeded to achieve the periodicity and symmetry by taking rhombic particles so that the synthesis volume V is triangular as is shown in Fig. 2.1.

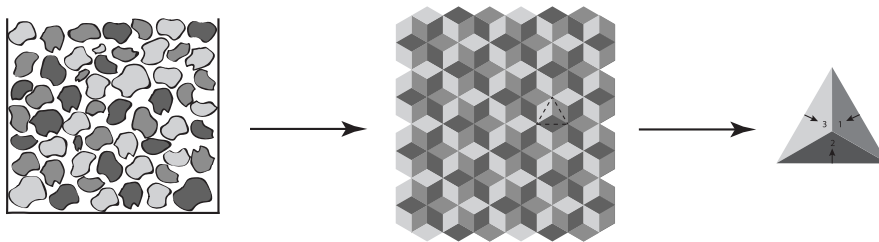


Fig. 2.1: Construction of a synthesis space in the two-dimensional three-reactant model.

In Fig. 2.2, we show in more detail the complex of three rhombic particles with triangular synthesis space that satisfies the symmetry requirement. The rhombic particles are bounded by dashed lines, and the synthesis space by solid lines.

According to chemists, the typical size of particles is about $600\text{ nm} = 0,6\ \mu\text{m}$. Taking the longer diagonal of rhombus equal to $1\ \mu\text{m}$, the shorter one is $\sqrt{3}/3 \approx 0,6\ \mu\text{m}$. Thus, we can assume that the side of the triangular is approximately $1\ \mu\text{m}$. So, summarizing, we arrive at the equation system (2.2) in the triangular synthesis space V shown in Fig. 2.3, with the initial conditions in the three inner triangles proportional to the initial densities of the three reactants and zero Neumann boundary conditions, $\frac{\partial c_i}{\partial \mathbf{n}} = 0$ on ∂V , where \mathbf{n} is the normal vector to the boundary.

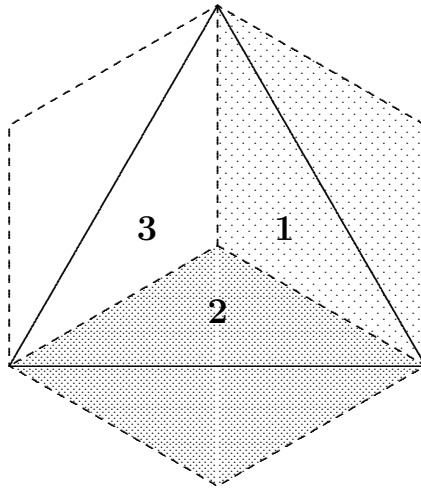


Fig. 2.2: Two-dimensional three-reactant model: rhombic particles and triangular synthesis space.

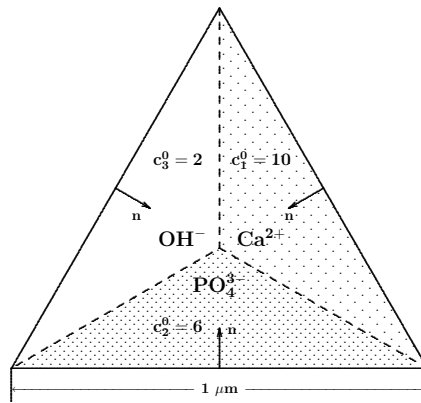


Fig. 2.3: The synthesis space in the three-reactant model.

For numerical solving the partial differential equation system (2.2) with zero Neumann boundary conditions in the triangular area, we have constructed a finite difference technique described in Section 4.2 of the dissertation.

2.3 The main goal

Our estimations are again based on the Arrhenius law describing the temperature dependence of the diffusion and reaction rate coefficients by the following relations:

$$D = D_0 \exp \left\{ -\frac{E_D}{RT} \right\}, \quad k = k_0 \exp \left\{ -\frac{E_A}{RT} \right\}, \quad (2.5)$$

where E_D is the diffusion activation energy, E_A is the reaction activation energy, D_0 and k_0 are constants, and $R = 8.314472$.

The other problem that arises in the CHAp (three-reactant) model is that the synthesis is possible by using the sol-gel method only. Therefore, we cannot obtain one pair of parameters (D, k) as the intersection of two curves corresponding to the same temperature. However, we are given **four** values of half-times at **four** different temperatures. In view of this, we have to modify the method of calculation of the synthesis parameters.

2.4 Calculation method

We calculate the diffusion and reaction rate coefficients as follows:

First, for the temperatures $T_1 = 1200^\circ\text{C}$, $T_2 = 1100^\circ\text{C}$, $T_3 = 1000^\circ\text{C}$, and $T_4 = 900^\circ\text{C}$, we draw the corresponding graphs L_1 , L_2 , L_3 , and L_4 of points (D, k) of the diffusion and reaction rate parameters for which the half-times are equal to those of the laboratory experiments by using the sol-gel synthesis method (i.e., $t_{1/2} = 0.6, 0.8, 1.0, \text{ and } 1.6$, respectively). To this end, we use our computer program that, given any fixed D , half-time $t_{1/2}$, and particle size a , numerically solves the system (2.2) until the half-time condition (2.4) is satisfied and, using the middle-point method, finds the value k such that half-time coincides with the given one. For each temperature T , a sufficiently large discrete set of the (D, k) values is joined by a smooth curve. All four graphs, L_1 , L_2 , L_3 , and L_4 , are shown in Fig. 2.4.

To calculate the four unknown parameters (E_D, E_A, D_0, k_0) , we proceed as follows. For any pair $(D_1, k_1) \in L_1$ and any pair $(D_2, k_2) \in L_4$, using the Arrhenius law for $T_1 = 1473\text{ K}$ and $T_4 = 1173\text{ K}$, we write and solve the following equation system with respect to unknown (E_D, E_A, D_0, k_0) :

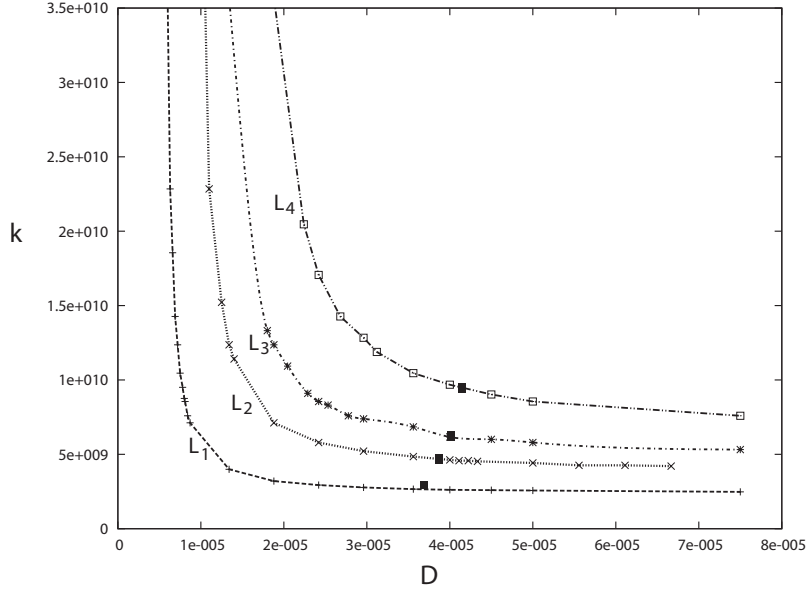


Fig. 2.4: Calculations in the three-reactant model in the triangular synthesis space V with edge $a = 1$ (μm) shown in Fig. 2.3.

$$D_1 = D_0 \exp \left\{ -\frac{E_D}{R \cdot T_1} \right\}, \quad D_2 = D_0 \exp \left\{ -\frac{E_D}{R \cdot T_4} \right\},$$

$$k_1 = k_0 \exp \left\{ -\frac{E_A}{R \cdot T_1} \right\}, \quad k_2 = k_0 \exp \left\{ -\frac{E_A}{R \cdot T_4} \right\}.$$

This way, we get the set of possible collections of the parameters

$$(E_D^i, E_A^i, D_0^i, k_0^i), \quad i = 1, 2, \dots$$

Repeating this for curves L_2 and L_3 , we get another set of possible collections of the parameters, $(E_D^j, E_A^j, D_0^j, k_0^j)$, $j = 1, 2, \dots$

Using the weighted least-squares method, we look for the minimal value of the sum

$$w_1(E_D^i - E_D^j)^2 + w_2(E_A^i - E_A^j)^2 + w_3(D_0^i - D_0^j)^2 + w_4(k_0^i - k_0^j)^2, \quad (2.6)$$

where we choose the weight coefficients w_i , $i = 1, 2, 3, 4$, so that the summands are approximately of the same order. The collections of parameters minimizing the sum (2.6), say $(E_D^{i_0}, E_A^{i_0}, D_0^{i_0}, k_0^{i_0})$ and $(E_D^{j_0}, E_A^{j_0}, D_0^{j_0}, k_0^{j_0})$,

can both serve as estimates of (E_D, E_A, D_0, k_0) ; the first collection represents the curves L_1 and L_4 , while the second one represents L_2 and L_3 . To equate their “contribution,” we finally take the average values of parameters: $(E_D, E_A, D_0, k_0) = ((E_D^{i_0} + E_D^{j_0})/2, (E_A^{i_0} + E_A^{j_0})/2, (D_0^{i_0} + D_0^{j_0})/2, (k_0^{i_0} + k_0^{j_0})/2)$. Now we can use these values to calculate D and k for arbitrary temperature T . Their values for temperatures T_i , $i = 1, 2, 3, 4$, are marked in Fig. 2.4 by “■”.

2.5 Calculation results

For the three-reactant model, we obtained the diffusion and reaction rates as functions of synthesis temperature T :

$$D = 6.5\text{e-}5 \exp(-5.6\text{e}3/(RT)), \quad (2.7)$$

$$k = 8.7\text{e}11 \exp(-5.5\text{e}4/(RT)). \quad (2.8)$$

The obtained Arrhenius law equations (1.6)–(1.7) give us the diffusion and reaction rates at temperatures $T = 900^\circ\text{C}$, 1000°C , 1100°C , and 1200°C , presented in Table 1.

Tab. 2.1: Diffusion and reaction rates

T	900°C	1000°C	1100°C	1200°C
D	$3.7\text{e-}5$	$3.9\text{e-}5$	$4\text{e-}5$	$4.1\text{e-}5$
k	$3\text{e}9$	$4.6\text{e}9$	$6.8\text{e}9$	$9.4\text{e}9$

3. CONCLUSIONS

Using the second Fick's, active mass, and Arrhenius laws, we presented and analyzed two-reactant (two- and three-dimensional) and three-reactant (two-dimensional) models of synthesis reactions at high temperatures in the forms of diffusion–reaction equation systems describing the dynamics of concentrations of reactants and products. Based on these models, we provided methods for calculation of diffusion and reaction-rate coefficients of such reactions when limited data (half-times and approximate sizes of reactant particles) from real laboratory experiments are given. Applying these methods for concrete YAG (two-reactant) and CHAp (three-reactant) synthesis reactions that were realized in real laboratory experiments, we obtained the following results:

1. We obtained explicit formulas for diffusion and reaction rate coefficients expressing their dependence of on the temperature, provided by Eqs. (1.6)–(1.7) for YAG and Eqs. (2.7)–(2.8) for CHAp. At the same time, we have calculated activation energies, important data that can be used to analyze other syntheses.

2. In YAG synthesis, for reaction rate coefficients, we see similar results in all dimensions. However, for diffusion coefficients, we the results are similar only for two- and three-dimensional models. Since calculations in the three-dimensional case are significantly more time-consuming than in the two-dimensional case, the two-dimensional model seems to be a good choice for much simpler and less time-consuming calculations.

3. Using Eqs. (1.6)–(1.7), we have found the parameters D and k in the YAG synthesis and, by computer modeling, the corresponding half-times for several temperatures. Having them, we calculated the energies consumed at these temperatures and found the optimal temperature.

Published Works on the Topic of the Dissertation

The main results of the thesis are published in four articles in referred journals (three of them with ISI citation index):

1. M. Mackevičius, F. Ivanauskas, A. Kareiva, Computer modeling of yttrium aluminium garnet synthesis (in Lithuanian), *Liet. matem. rink.*, **51**(spec. issue – Proc. Lith. Math. Soc.):291–294 (2010).
2. M. Mackevičius, F. Ivanauskas, A. Kareiva, Mathematical approach to investigation of synthesis processes at high temperatures, *Central European Journal of Chemistry*, **10**(2):380–385 (2012).
3. M. Mackevičius, F. Ivanauskas, A. Kareiva, D. Jasaitis, A closer look at the computer modeling and sintering optimization in the preparation of YAG, *Journal of Mathematical Chemistry*, **50**(8):2291–2302 (2012).
4. M. Mackevičius, F. Ivanauskas, A. Kareiva, I. Bogdanovičienė, Computer modeling of synthesis of calcium hydroxyapatite (CHAp), *Journal of Mathematical Chemistry*, **51**(5):1249–1257 (2013).

About the author

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2007–2012 Software developer at Sintagma.

2012– Software developer at Tieto Lietuva.

CHEMINIŲ SINTEZIŲ PRIE AUKŠTŲ TEMPERATŪRŲ MODELIAVIMAS

Reziumė

Homogeninių reakcijų dydis yra randamas stebint sintezėje dalyvaujančių medžiagos dalelių mažėjimą arba naujai susidariusios medžiagos prieaugį, esant pastoviai temperatūrai. Tačiau heterogeninėse reakcijose koncentracijos sąvoka nėra taip pat reikšminga, o reakcijos rezultatai yra apskaičiuojami kitokiais metodais. Heterogeninių reakcijų mechanizmo bei kinetikos studijavimas priverčia atsižvelgti į dalelių kiekio pasikeitimus kintant laikui [3, 10, 19, 32]. Daugybė lygčių, susijusių su kietafazių reakcijomis prie izoterminių ir neizoterminių sąlygų (Fick arba Prout–Tompkins modelis) yra aprašyti ir išnagrinėti [1, 5, 11, 34, 47]. Kinetiką aprašančių lygčių interpretavimas yra sudėtingas, nes atsižvelgiama į sąlygas, prie kurių pradeda vykti cheminė sintezė, kaip naujai susidariusios medžiagos dalių kiekis auga arba kiek dalelių susinaudoja vykstant reakcijai. Šioms kietafazių reakcijų problemoms spręsti buvo pasiūlytos naujos matematinės aproksimacijos bei skaitiniai modeliai [13, 35, 36]. Turėdami ribotus duomenis iš realių laboratorinių eksperimentų, mes pritaikėme mūsų modelį skirtingų sintezių parametrų skaičiavimams, tokių kaip difuzijos bei reakcijų greičio koeficientų radimui. Tarp realių laboratorinių eksperimentų parametrų mes turėjome tik sintezės puslaikius prie skirtingų temperatūrų bei apytiksliai dalelių dydžius. Savo skaičiavimuose mes naudojome Fick'o, Arrhenius'o ir veikiančių masių dėsniais.

Darbo aktualumas

Dažnai matematiniam modeliavimui, sprendžiant aktualias problemas yra naudojami diferencialinių parabolinių lygčių skaitiniai sprendimo metodai. Darbe nagrinėjamas itrio aliuminio granato (YAG) ir sintetinio kalcio hidroksiapatito (CHAp) sintezės prie aukštų temperatūrų matematinis modeliavimas. Abi medžiagos yra svarbios dėl savo unikalių savybių.

Pavyzdžiui, itrio aliuminio granatas $2Y_3Al_5O_{12}$ yra plačiai naudojama optinė medžiaga, kuri turi daugybę unikalių savybių (žr., pavyzdžiui, [14,

4, 16, 22, 27, 29, 30, 33]). YAG milteliai galibūti pagaminti skirtingais metodais, tokiais kaip kietafazių reakcijų, zolių-gelių ir kiti metodai (žr., pavyzdžiui, [2, 17, 18, 24, 28, 41, 48, 49, 50]). Sintetinis kalcio hidroksiapatitas, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ yra žinomas kaip vienas iš svarbiausių implantuojamų medžiagų dėl savo biologinio suderinamumo ir aktyvumo ir yra naudojamas kaip pakaitalinė medžiaga žmogaus kietųjų audinių [45, 25, 40]. Dėl savo cheminės struktūros CHAp pagaminimas priklauso nuo pasirinktų procesų [12, 15, 23, 43]. CHAp gali būti pagamintas skirtingais zolių-gelių metodais, pavyzdžiui, nevandeniniu [38, 51] ir vandeniniu [46, 31].

Zolių-gelių proceso parametrų, tokių kaip pradinis medžiagų kiekis, pH, temperatūra, maišymo greitis, maišymo laikas ir kt. turi būti kruopščiai kontroliuojami [6, 7, 8, 9].

Abiejų medžiagų sintetinimas yra brangus, kadangi jų pagaminimas reikalauja ilgalaikio aukštos temperatūros palaikymo (žr., pavyzdžiui, [37, 42, 44]). Įprastais eksperimentais nagrinėti sąlygas bei ieškoti parametrų, prie kurių įmanoma pagaminti minėtas medžiagas, būtų labai sudėtinga ir brangu. Todėl svarbu sukurti teorinius matematinius modelius, kurių pagalba būtų galima atlikti šitas užduotis.

Darbe vienamatis modelis išplėtotas dvimačiam ir trimačiam atvejams. Natūralu, kad trimatis atvejis yra tikslesnis ir tikroviškesnis, tačiau kaip parodė mūsų kompiuteriniai eksperimentai, dvimačiu atveju, skirtingai nuo vienamačio atvejo, rezultatai yra panašūs ir todėl gali būti naudojami modeliavimui kaip paprasteni ir reikalaujantys ženkliai mažiau kompiuterinio laiko.

Nagrinėjant sintetinio kalcio hidroksiapatito sintezę, sukurtas bendras dvimatis matematinis modelis, leidžiantis ieškoti sintezei reikalingų parametrų trijų reagentų atveju.

Tyrimų objektas

Tyrimų objektas – matematiniai modeliai, skirti cheminių sintezių prie aukštų temperatūrų parametrų radimui.

Darbo tikslai

Apibendrinti ir išplėtoti dviejų reagentų sintezės vienamatį matematinį modelį dvimačiam ir trimačiam atvejams.

Sukurti ir išnagrinėti trijų reagentų matematinį modelį.

Darbo uždaviniai

- Sukurti ir ištirti YAG (dviejų reagentų) vienamačio modelio dvimatį ir trimatį analogus.
- Rasti aktyvacijos energijas dvimačiame ir trimačiame YAG sintezės modeliuose.
- Rasti YAG sintezės dvimačio ir trimačio modelių difuzijos ir reakcijos koeficientų priklausomybes nuo temperatūros.
- Palyginti vienamačio, dvimačio ir trimačio YAG sintezės matematinio modeliavimo parametrų rezultatus.
- Rasti YAG sintezės optimalią temperatūrą, minimizuojančią energijos sąnaudas.
- Sukurti CHAp (trijų reagentų) dvimatį matematinį modelį.
- Rasti CHAp sintezės aktyvacijos energijas ir difuzijos bei reakcijos greičio koeficientų priklausomybes nuo temperatūros.

Tyrimų metodika

Atlikdami tyrimus, taikėme diferencialinių lygčių su dalinėmis išvestinėmis skaitinius sprendimo metodus. Kompiuterinių eksperimentų programos parašytos ANSI C kalba, naudojant skaičiavimų lygiagretinimo biblioteką MPI.

Darbo mokslinis naujumas

Disertacijoje sukurti ir išnagrinėti dvimačio bei trimačio dviejų reagentų ir dvimačio trijų reagentų cheminės sintezės matematiniai modeliai ir jų parametrų skaičiavimo metodika bei skaitiniai algoritmai. Atlikto darbo rezultatai apibendrina ir išplėtoja iki šiol gautus rezultatus vienamačiame dviejų reagentų modelyje.

Kadangi pereinant tiek prie didesnių sintezės erdvės dimensijų, tiek prie didesnio reagentų skaičiaus žymiai padidėja skaičiavimų trukmė, ypatingas dėmesys buvo skiriamas sprendimo pagreitiniui, sudarant efektyvesnius skaičiavimo algoritmus ir skaidant bei lygiagretinant uždavinius.

Darbo rezultatų praktinė reikšmė

Sudaryti ir realizuoti skaitiniai algoritmai, leidžiantys modeliuoti cheminės sintezės difuzijos–reakcijos procesus, rasti jų parametrus, turint ribotus laboratorijose gautus duomenis. Algoritmai pagrįsti lygiagretumo principu. Rastos difuzijos ir reakcijos koeficientų priklausomybės nuo temperatūros. Apskaičiuotos aktyvavimo energijos, svarbios kitų sintezės uždavinių analizei.

Gynimui pateikiama

- Dviejų reagentų dvimatis bei trimatis ir trijų reagentų dvimatis sintezės modeliai.
- Sintezės parametrų šiuose modeliuose skaičiavimo metodai.
- Parametrų skaičiavimų rezultatai konkrečiais YAP (dviejų reagentų) ir CHAp (trijų reagentų) sintezės atvejais.

Disertacijos struktūra

Disertaciją sudaro įvadas, keturi skyriai ir literatūros sąrašas. Skyriai yra suskirstyti į poskyrius. Disertacijos apimtis – 79 psl.

1 skyriuje trumpai pagrindiniai disertacijoje naudojami fizikinės chemijos dėsniai ir nuostatos, trumpai apibūdinti matematiniai cheminių reakcijų modeliai – atitinkamos difuzijos-reakcijos lygčių sistemos, jiems patikrintas masės tvermės dėsnis.

2 skyriuje nagrinėjami dviejų reagentų sintezės reakcijos vienamatis, dvimatis ir trimatis modeliai. Konkretūs reakcijos parametrų skaičiavimai atlikti ir palyginti YAG sintezės atveju, remiantis duomenimis iš realių laboratorinių eksperimentų VU Chemijos fakultete.

3 skyriuje nagrinėjamas trijų reagentų dvimatis modelis. Sukonstruotos periodiškumo ir simetrijos reikalavimus atitinkančios reagentų dalelių formos ir sintezės erdvė (rombinės dalelės ir trikampė erdvė), leidžiančios atlikti skaičiavimus trikampėje srityje su Neumanno kraštinėmis sąlygomis.

4 skyriuje aprašyti skaitiniai metodai bei algoritmai, naudoti difuzijos–reakcijos lygčių sistemoms spręsti. 4.1 poskyryje trumpai aprašytas standartinis skirtuminis metodas intervalui, kvadratui ir kubui, naudotas 2 skyriaus uždaviniams spręsti. 4.2 poskyryje aprašytas naujai sukonstruotas skirtuminis metodas trikampe sričiai, reikalingas 3 skyriaus uždaviniams spręsti. Abiejų poskyrių pabaigoje pateikti metodus iliustruojantys grafikai. 4.3 poskyryje pateiktas parametrų skaičiavimų lygiagretinimo algoritmas.

REFERENCES

- [1] B. Adnadevic, B. Jankovic, and D. M. Minic, Kinetics of the apparent isothermal and non-isothermal crystallization of the alpha-Fe phase within the amorphous Fe₈₁B₁₃Si₄C₂ alloy, *J. Phys. Chem. Solids*, **71**(7):927–934, 2010.
- [2] T. Aichele, T. Lorenz, R. Hergt, and P. Gornert, Garnet layers prepared by liquid phase epitaxy for microwave and magneto-optical applications: A review, *Cryst. Res. Technol.*, **38**(7–8):575–587 (2003).
- [3] B. N. Arzamasov and V. N. Simonov, Circulation method for depositing diffusion coatings, *Met. Sci. Heat Treat.*, **52**(9–10):403–407, 2011.
- [4] J.L. Bates and J.E. Garnier, Electrical Conductivity of MgAl₂O₄ and Y₃Al₅O₁₂, *J. Am. Ceram. Soc.*, **64**:C138–C141 (1981).
- [5] H. Belhouchet, M. Hamidouche, N. Bouaouadja, V. Garnier, and G. Fantozzi, Kinetics of mullite formation in zircon and boehmite mixture, *Annal. Chimie-Sci. Mater.*, **35**(1):17–25, 2010.
- [6] I. Bogdanoviciene, A. Beganskiene, K. Tõnsuaadu, J. Glaser, H.-J. Meyer, and A. Kareiva, Calcium hydroxyapatite, (Ca₁₀(PO₄)₆(OH)₂, HA) ceramics prepared by aqueous sol-gel processing, *Mater. Res. Bull.*, **41**:1754–1762 (2006).
- [7] I. Bogdanoviciene, K. Tõnsuaadu, and A. Kareiva, Influence of gelation temperature on the properties of sol-gel derived calcium hydroxyapatite ceramics, *Polish J. Chem.*, **83**:47–55 (2009).
- [8] I. Bogdanovičienė, A. Beganskienė, A. Kareiva, R. Juškėnas, A. Selskis, R. Ramanauskas, K. Tõnsuaadu, and V. Mikli, Influence of heating conditions on the formation of sol-gel derived calcium hydroxyapatite, *Chemija*, **21**:98–105 (2010).

- [9] I. Bogdanovičienė, K. Tõnsuaadu, V. Mikli, I. Grigoravičiūtė-Puronienė, A. Beganskienė, and A. Kareiva, pH impact on the sol-gel preparation of calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, using a novel complexing agent DCTA, *Centr. Eur. J. Chem.*, **8**:1323–1330 (2010).
- [10] P. Budrugaec, An iterative model-free method to determine the activation energy of non-isothermal heterogeneous processes, *Thermochimica Acta*, **511**(1–2):8–16, 2010.
- [11] C. Chen, W. L. Gong, W. Lutze, and I. L. Pegg, Kinetics of fly ash geopolymerization, *J. Mater. Sci.*, **46**(9):3073–3083, 2011.
- [12] C.K. Chua, K.F. Leong, K.H. Tan, F.E. Wiria, and C.M. Cheah, Development of tissue scaffolds using selective laser sintering of polyvinyl alcohol/hydroxyapatite biocomposite for craniofacial and joint defects, *J. Mater. Sci.: Mater. Med.*, **15**:1113–1121 (2004).
- [13] C. J. Deng, J. M. Cai, and R. H. Liu, Kinetic analysis of solid-state reactions: Evaluation of approximations to temperature integral and their applications, *Solid State Sci.*, **11**(8):1375–1379, 2009.
- [14] J. Dong, P. Deng, and J. Xu, Study of the effects of Cr ions on Yb in Cr,Yb:YAG crystal, *Optics Commun.*, **170**(4–6):255–258, 1999.
- [15] L. Gan, J. Wang, A. Tache, N. Valiquette, D. Deporter, and R. Pilliar, Calcium phosphate sol-gel-derived thin films on porous-surfaced implants for enhanced osteoconductivity. Part II: Short-term in vivo studies, *Biomater.*, **25**:5313–5321 (2004).
- [16] E. Garškaitė, D. Jasaitis, and A. Kareiva, Sol-gel preparation and electrical behaviour of Ln: YAG (Ln = Ce, Nd, Ho, Er), *J. Serb. Chem. Soc.*, **68**(8–9):677–684 (2003).
- [17] C.J. Harlan, A. Kareiva, D.B. Macqueen, R. Cook, and A.R. Barror, Yttrium substituted alumoxanes: A *chemie duce* route to $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM), *Adv. Mater.*, **9**(1): 68–71 (1997).
- [18] A. Ikesue, K. Yoshida, and K. Kamata, Transparent Cr⁴⁺-doped YAG ceramics for tunable lasers, *J. Am. Ceram. Soc.*, **79**(2):507–509 (1996).
- [19] F. Ivanauskas, A. Kareiva, and B. Lapcun, On the modeling of solid state reactions. Synthesis YAG, *J. Math. Chemistry*, **37**(4):365–476, 2005.

- [20] F. Ivanauskas, A. Kareiva, and B. Lapcun, Diffusion and reaction rates of the yttrium aluminum garnet synthesis using different techniques, *J. Math. Chemistry*, **42**(2):191–199, 2007.
- [21] F. Ivanauskas, A. Kareiva, and B. Lapcun, Computational modeling of the YAG synthesis, *J. Math. Chemistry*, **46**(2):427–442, 2009.
- [22] S.M. Kaczmarek, G. Domianiak-Dzik, W. Ryba-Romanowski, J. Kisielewski, and J. Wojtkowska, Changes in optical properties of Ce: YAG crystals under annealing and irradiation processing, *Cryst. Res. Technol.*, **34**(8), 1031–1036 (1999).
- [23] S.B. Kim, Y.J. Kim, T.L. Yoon, S.A. Park, I.H. Cho, E.J. Kim, I.A. Kim, and J.-W. Shin, The characteristics of a hydroxyapatite–chitosan–PMMA bone cement, *Biomater.*, **25**:5715 (2004).
- [24] B.H. King and J.W. Halloran, Polycrystalline yttrium aluminum garnet fibers from colloidal sols, *J. Am. Ceram. Soc.*, **78**(8), 2141–2148 (1995).
- [25] E. Landi, G. Celotti, G. Logroscino, and A. Tampieri, Carbonated hydroxyapatite as bone substitute, *J. Eur. Ceram. Soc.*, **23**:2931–2937 (2003).
- [26] B. Lapcun, Modelling of the YAG synthesis, Ph.D. thesis, Vilnius University, Vilnius, 2007.
- [27] A. Leleckaite and A. Kareiva, Synthesis of garnet structure compounds using aqueous sol–gel processing, *Opt. Mater.*, **26**(2):123–128 (2004).
- [28] Y. Liu, Z.F. Zhang, B. King, J. Halloran, and R.M. Laine, Synthesis of yttrium aluminum garnet from yttrium and aluminum isobutyrate precursors, *J. Am. Ceram. Soc.* **79**:385–394 (1996).
- [29] M. Malinowski, M. Kaczkan, A. Wnuk, and M. Szuffiska, Emission from the high lying excited states of Ho^{3+} ions in YAP and YAG crystals, *J. Lumin.*, **106**:269–279 (2004).
- [30] R. Manalert and M.N. Rahaman, Sol–gel processing and sintering of yttrium aluminum garnet, *J. Mater. Sci.*, **31**:3453–3458 (1996).
- [31] F. Miyaji, Y. Kono, and Y. Suyama, Formation and structure of zinc-substituted calcium hydroxyapatite, *Mater. Res. Bull.*, **40**:209–220 (2005).

- [32] H. H. Mohamed, C. B. Mendive, R. Dillert, and D. W. Bahnemann, Kinetic and mechanistic investigations of multielectron transfer reactions induced by stored electrons in TiO₂ nanoparticles: A stopped flow study, *J. Phys. Chem. A*, **115**(11):2139–2147, 2011.
- [33] I. Muliuolienė, S. Mathur, D. Jasaitis, H. Shen, V. Sivakov, R. Rapolavičiūtė, A. Beganskienė, and A. Kareiva, Evidence of the formation of mixed-metal garnets via sol-gel synthesis, *Opt. Mater.*, **22**, 241–250 (2003).
- [34] K. Muraleedharan, V. M. A. Mujeeb, M. H. Aneesh, T. Gangadevi, and M. P. Kannan, Effect of pre-treatments on isothermal decomposition kinetics of potassium metaperiodate, *Thermochimica Acta*, **510**(1–2):160–167, 2010.
- [35] A. Perejon, P. E. Sanchez-Jimenez, J. M. Criado, and L. A. Perez-Maqueda, Kinetic analysis of complex solid-state reactions. A new deconvolution procedure, *J. Phys. Chem. B*, **115**(8):1780–1791, 2011.
- [36] W. Preis, Modelling of surface exchange reactions and diffusion in composites and polycrystalline materials, *Montash. Chemie*, **140**(9):1059–1068, 2009.
- [37] R.C. Pullar, M.D. Taylor, and A.K. Bhattacharya, The sintering behaviour, mechanical properties and creep resistance of aligned polycrystalline yttrium aluminium garnet (YAG) fibres, produced from an aqueous sol-gel precursor, *J. Eur. Ceram. Soc.*, **19**:1747–1758 (1999).
- [38] S.R. Ramanan and R. Venkatesh, A study of hydroxyapatite fibers prepared via sol-gel route, *Mater. Lett.*, **58**:3320–3323 (2004).
- [39] A. A. Samarskii, The Theory of Difference Schemes, Marcel Dekker, New York, 2001.
- [40] M. Shirkhazadeh, Microneedles coated with porous calcium phosphate ceramics: effective vehicles for transdermal delivery of solid trehalose, *J. Mater. Sci.: Mater. Med.*, **16**:37–45 (2005).
- [41] Z. Sun, D. Yuan, H. Li, X. Duan, H. Sun, Z. Wang, X. Wei, H. Xu, C. Luan, D. Xu, and M. Lv, Synthesis of yttrium aluminum garnet (YAG) by a new sol-gel method, *J. Alloys Comp.*, **379**(1–2), L1–L3 (2004).

- [42] H. Tanaka, Thermal analysis and kinetics of solid state reactions, *Thermochim. Acta*, **267**:29–44 (1995).
- [43] A.C. Tas and F. Aldinger, Formation of apatitic calcium phosphates in a Na-K-phosphate solution of pH 7.4, *J. Mater. Sci.: Mater. Med.*, **16**:167–174 (2005).
- [44] C.W. Thiel, H. Cruguel, Y. Sun, G.J. Lapeyre, R.M. Macfarlane, R.W. Equall, and R.L. Cone, Systematics of 4f electron energies relative to host bands by resonant photoemission of rare earth doped optical materials, *J. Lumin.*, **94–95**:1–6 (2001).
- [45] M. Vallet-Regi, Ceramics for medical applications, *J. Chem. Soc. Dalton Trans.*, **2**:97–108 (2001).
- [46] H.K. Varma and S.S. Babu, Synthesis of calcium phosphate bioceramics by citrate gel pyrolysis method, *Ceram. Int.*, **31**:109–114 (2005).
- [47] F. Xia, J. Brugger, and A. Pring, Arsenian pyrite formation: Solid-state diffusion or dissolution-precipitation replacement?, In: *Smart Science for Exploration and Mining, Proc. 10th Biennial SGA Meeting of The Society for Geology Applied to Mineral Deposits*, Ed. by P. J. Williams et al., **2**:700–702, 2010.
- [48] M. Yada, M. Ohya, M. Machida, and T. Kijima, Synthesis of porous yttrium aluminium oxide templated by dodecyl sulfate assemblies, *Chem. Commun.*, **18**:1941–1942 (1998).
- [49] J.-M. Yang, S.M. Jeng, and S. Chang, Fracture behavior of directionally solidified $Y_3Al_5O_{12}/Al_2O_3$ eutectic fiber, *J. Am. Ceram Soc.*, **79**(5):1218–1222 (1996).
- [50] X. Zhang, H. Liu, W. He, J. Wang, X. Li, and R.I. Boughton, Synthesis of monodisperse and spherical YAG nanopowder by a mixed solvothermal method, *J. Alloys Comp.*, **372**(1–2):300–303 (2004).
- [51] H. Zreiqat, R. Roest, S. Valenzuela, A. Milev, and B. Ben-Nissan, Human bone derived cell (HBDC) behaviour of sol-gel derived carbonate hydroxyapatite coatings on titanium alloy substrates, *Bioceramics*, **17**(1):541–544 (2005).