

Diffusion and reaction rates of the yttrium aluminium garnet synthesis using different techniques

Feliksas Ivanauskas^{a,b}

^a *Vilnius University, Department of Mathematics and Informatics, Naugarduko str. 24, Vilnius LT-03225, Lithuania*

^b *Institute of Mathematics and Informatics, Akademijos str. 4, Vilnius LT-08663, Lithuania*

Aivaras Kareiva

Vilnius University, Department of Chemistry, Naugarduko str. 24, Vilnius LT-03225, Lithuania

Bogdan Lapcun*

Vilnius University, Department of Mathematics and Informatics, Naugarduko str. 24, Vilnius LT-03225, Lithuania

E-mail: bogdanl@vtex.lt

Received 21 December 2005; revised 8 February 2006

The mathematical model of the yttrium aluminium garnet synthesis presented in this article. The model based on a system of non-stationary diffusion equations containing a non-linear term related to kinetics of reaction. Using computer-simulation tools and known experimental results we estimated the diffusion and reaction rates of the synthesis. Also it was shown that diffusion rate is a limited stage of the synthesis.

KEY WORDS: YAG, yttrium aluminium garnet, reaction–diffusion model

AMS subject classification: 35K57, 65M06

1. Introduction

Yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) is now used widely in optical materials because it has a variety of unique optical properties. The YAG doped with a transition metal or lanthanide ions are important solid-state laser material. Moreover, the YAG powders can be used as phosphors for cathode ray tubes and high-resolution displays, in luminescence systems and window materials for a variety of lamps [4, 9, 10, 14, 15, 17, 20, 23].

*Corresponding author.

The YAG powders could be synthesized by many different methods, such as solid-state reaction, spray-pyrolysis, coprecipitation, sol-gel, and others [1, 8, 9, 11, 13, 18, 24–26]. The solid-state reaction synthesis method requires a high temperature ($> 1600^{\circ}\text{C}$), or a long reaction time, if temperature a bit less than 1600°C , and repeated mechanical mixing. Recently, we have developed a simple aqueous sol-gel synthesis method for the preparation of monophasic garnet structure compounds at 1000°C [7, 12, 16, 21]. Some of the advantages of the proposed sol-gel synthesis method, e.g. excellent homogeneity and control of stoichiometry, high-phase purity and, of course, low-sintering temperature of pure, and doped garnet samples were demonstrated in those studies.

Thus, it is clear that the conditions for the formation of monophasic YAG are dependent largely on the used synthesis method. By changing the solid-state synthesis method to the sol-gel chemistry approach, the YAG formation temperature decreases from 1600 down to 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 $\text{Y}_3\text{Al}_5\text{O}_{12}$ using sol-gel technique.

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 no longer has the same significance and the progress of reaction usually is determined in some other way. A kinetic study of heterogeneous reaction thus involves measurement of changes in mass or fraction reacted of the sample as a function of time at constant temperature [2, 3, 19]. Many equations relating the rate of solid-state reactions to are summarized in the literature. 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 and what reaction or interface geometry is involved, and finally, how the reactants decay [5]. The validity of applying the Arrhenius equation to heterogeneous reactions has been questioned, but the parameters obtained had practical value even if their theoretical interpretation is difficult [6].

The main goal of this study is to construct a mathematical model, which allows the effective computer simulation of the YAG synthesis and to determine the exact reasons responsible for the different formation temperatures of $\text{Y}_3\text{Al}_5\text{O}_{12}$ using different techniques. Developing the model, we assume, that the mass transport by diffusion, and reaction are the only limited stages of YAG synthesis. The kinetics of solid-state reactions generally cannot be assumed to follow simple rate laws that are applicable to homogeneous reactions [22]. Nevertheless, in the developed our mathematical model, the fundamental kinetic equations for the homogeneous reactions are re-examined in an attempt

to increase the reliability of the kinetic parameters obtained for solid-state reactions.

The remainder of the paper is organized as follows. In section 2, we describe in detail the synthesis of YAG using sol-gel and solid-state reaction methods. In section 3, a mathematical model of the YAG synthesis is presented. Under certain conditions the synthesis may be described by the system of non-stationary diffusion equations containing a non-linear term related to kinetics of reaction. Differential problems were solved numerically using finite difference technique [28]. In section 4, the problem of a determination of unknown parameters of the model (diffusion and reaction rate coefficients) is investigated. As a result the values of the parameters are located in quite small intervals. Simultaneously, it was shown that the formation of YAG using sol-gel technique requires lower diffusion rate, so it may be carried out at lower-temperature regime.

2. Experiments

2.1. Sol-gel method

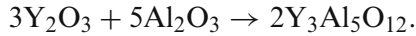
In the sol-gel synthesis, yttrium oxide was dissolved in 150 ml of 0.2 mol l^{-1} CH_3COOH by stirring the mixture for 10 h at $55\text{--}60^\circ\text{C}$ in a beaker covered with a watch-glass. To this solution, aluminium nitrate dissolved in 50 ml of distilled water was added and the resulting mixture was stirred for 2 h at the same temperature. In a following step, 1.2 ethanediol (25 mmol) as complexing agent was added to the above solutions. The acidic medium ($\text{pH} \sim 5$) prevents the flocculation of metal hydroxides in the mixtures and no adjustment of pH was necessary. After concentrating the solutions by slow evaporation at $60\text{--}70^\circ\text{C}$ under stirring the Y-Al acetate-nitrate-glycolate solution turned into a white transparent gel. The oven dried ($100\text{--}120^\circ\text{C}$) gel became light brown due to the initial decomposition of nitrates. The gel powders were ground in an agate mortar and pre-heated 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 8 h at 1000°C and 4 h at 1600°C .

2.2. Solid-state reaction method

In the solid-state reaction method, the stoichiometric mixture of metal oxides (Al_2O_3 and Y_2O_3) was carefully ground in an agate mortar and annealed at various temperatures from 1000 to 1600°C in air. The monophasic YAG was obtained only at higher temperature, after sintering oxide precursor for 8 h at 1600°C .

3. Mathematical model

Schematically the synthesis may be described by the following reaction



Summarizing section 2, it may be concluded that at preparatory stage of the synthesis (using both solid-state reaction and sol-gel methods) the reactants were milled and mixed thoroughly in some cubic volume. The structure of the reaction space becomes chaotic – exact initial position of reactants' particles is unknown. Therefore, it is quite reasonable to impose some conditions on reaction space. Let us assume that as a consequence the reaction space becomes a periodical structure in a certain sense. Let all particles are of same shape. More particularly, let particles are of cube shape and the edge of the cube is $1\ \mu\text{m}$. (Guiding by experimental data, volume of these particles must be approximately $1\ \mu\text{m}^3$.) Further, let these particles recurring periodically in x_1, x_2, x_3 directions (see figure 1 left part). As is easy to see, this assumption allows us to carry out analysis only in a periodic part V of the reaction space – see, figure 1 (right part).

We think that such transition from whole reaction space to its small part allows us to consider synthesis as a homogeneous reaction since the temperature regime is high – within the range $1000\text{--}1600^\circ\text{C}$. As is well known, reaction rate for the i th reactant in such case is defined as $\partial c_i / \partial t$, 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 .

Next we suppose that the mass transport by diffusion, and reaction are the only limited stages of the synthesis. Then the synthesis (at the certain temperature T within the range $1000\text{--}1600^\circ\text{C}$) may be described by the following system of non-stationary diffusion equations containing a non-linear term related to kinetics of reaction:

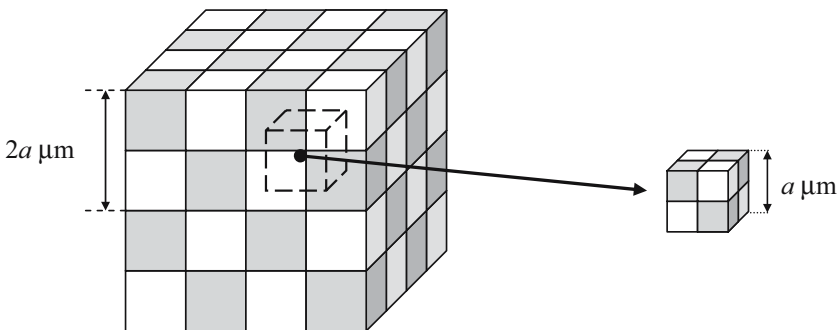


Figure 1. Physical model of the reaction space, $T = 1000^\circ\text{C}$.

$$\begin{aligned} \frac{\partial c_1}{\partial t} &= \sum_{j=1}^3 D_1 \frac{\partial^2 c_1}{\partial x_j^2} - 3kc_1c_2, \\ \frac{\partial c_2}{\partial t} &= \sum_{j=1}^3 D_2 \frac{\partial^2 c_2}{\partial x_j^2} - 5kc_1c_2, \quad x \in V, \quad t > 0, \\ \frac{\partial c_3}{\partial t} &= \sum_{j=1}^3 D_3 \frac{\partial^2 c_3}{\partial x_j^2} + 2kc_1c_2, \end{aligned} \tag{1}$$

where $c_i = c_i(x, t)$ is the concentration of the i th component; D_i and k are diffusion and reaction rate coefficients, respectively; $V = (0, a) \times (0, a) \times (0, a)$. (The quantity a defines the size of the periodical structure [cube face]; it is known that $a = 1 \mu\text{m}^3$ in sol-gel method, and $a = 10 \mu\text{m}^3$ in solid-state reaction method.) The initial conditions for c_i are

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

and the boundary conditions corresponding to non-passing condition at ∂V are

$$\left. \frac{\partial c_i}{\partial x} \right|_{x \in \partial V} = 0, \quad i = 1, 2, 3, \quad t \geq 0. \tag{3}$$

Differential problems (1)–(3) was solved numerically using finite difference technique [28]. For detailed solution the reader is referred to [27].

4. Estimation of diffusion and reaction rate coefficients

The application of the model is complicated in view of unknown parameters – diffusion and reaction rate coefficients D_i and k . Theoretical approaches to estimation of diffusion and reaction rates are quite general and/or expensive. Therefore, alternative approach is investigated. The main goal is to estimate the coefficients D_i and k using known synthesis time $t_s = 8$ and the size of the periodical structure ($a = 1$ or 10).

Remark. A half-time $t_{1/2}$ (4 h) may be considered instead of the synthesis time t_s (8 h), i.e. a time required for the half of the initial reactants to disappear:

$$\int_V (c_1(x, t_{1/2}) + c_2(x, t_{1/2})) \, dx = \frac{1}{2} \int_V (c_1(x, 0) + c_2(x, 0)) \, dx. \tag{4}$$

Now, the experimental results from section 2 may be formalized as follows:

- (i) $T = 1000, V = (0, 1) \times (0, 1) \times (0, 1) \Rightarrow t_{1/2} = 4;$
- (ii) $T = 1600, V = (0, 10) \times (0, 10) \times (0, 10) \Rightarrow t_{1/2} = 4.$

Let us make some inessential simplifications of the model. Four-dimensional problems (1)–(3) may be simplified to two-dimensional one in the following way:

$$\begin{aligned} \frac{\partial c_1}{\partial t} &= D_1 \frac{\partial^2 c_1}{\partial x^2} - 3kc_1c_2, \\ \frac{\partial c_2}{\partial t} &= D_2 \frac{\partial^2 c_2}{\partial x^2} - 5kc_1c_2, \quad x \in (0, a), \quad t > 0, \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{\partial c_3}{\partial t} &= D_3 \frac{\partial^2 c_3}{\partial x^2} + 2kc_1c_2, \\ c_i(x, 0) &= c_i^0, \quad i = 1, 2, 3, \quad x \in [0, a], \end{aligned} \quad (6)$$

$$\left. \frac{\partial c_i}{\partial x} \right|_{x=0, x=a} = 0, \quad i = 1, 2, 3, \quad t \geq 0, \quad (7)$$

where

$$c_1^0 = \begin{cases} 3 \cdot 10^{-6}, & 0 \leq x \leq \frac{a}{2}, \\ 0, & \frac{a}{2} < x \leq 1, \end{cases} \quad c_2^0 = \begin{cases} 0, & 0 \leq x \leq \frac{a}{2}, \\ 5 \cdot 10^{-6}, & \frac{a}{2} < x \leq 1, \end{cases} \quad c_3^0 = 0.$$

For simplicity we may presume $D_1 = D_2 = D_3 \equiv D$. (It is quite reasonable since the physical measures of the reactants are similar.)

Now, assume that diffusion rate of the synthesis is infinite. In such case the reactants will be fully mixed in V instantly, and concentration becomes constant in V . Therefore, the terms related to diffusion ($D \partial^2 c_i / \partial x^2$) in (5) disappear, so this case becomes equivalent to the following problem:

$$\begin{aligned} \frac{\partial c_1}{\partial t} &= -3kc_1c_2, \\ \frac{\partial c_2}{\partial t} &= -5kc_1c_2, \quad x \in (0, a), \quad t > 0, \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{\partial c_3}{\partial t} &= 2kc_1c_2, \\ c_i(x, 0) &= \hat{c}_i^0, \quad i = 1, 2, 3, \quad x \in [0, a], \end{aligned} \quad (9)$$

$$\left. \frac{\partial c_i}{\partial x} \right|_{x=0, x=a} = 0, \quad i = 1, 2, 3, \quad t \geq 0 \quad (10)$$

and

$$\hat{c}_1^0 = \frac{3}{2} \cdot 10^{-6}, \quad \hat{c}_2^0 = \frac{5}{2} \cdot 10^{-6}, \quad \hat{c}_3^0 = 0.$$

Problems (8)–(10) was solved numerically and k was chosen such that $t_{1/2} = 4$. We obtained

$$k_T^1 = 9.2$$

for $T = 1000\text{--}1600$. It is obvious that such k_T^1 is the minimal value of the reaction rate such that $t_{1/2} = 4$, i.e. the garnet cannot be synthesized in 8 h if parameters D and k are in region G_T^4 (see, figure 2(a) and (b)) because of the low-reaction rate. In figure 2(a) and (b), this value corresponds to the line H .

Assume that reaction rate of the synthesis is infinite. In such case the reactants cannot pass through the reaction spot (middle of the interval $(0, a)$) – reaction proceeds instantly; and therefore, there is homogenous boundary condition in the center. So this case is equivalent to the following problem:

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2}, \quad i = 1, 2, \quad x \in (0, a), \quad t > 0, \tag{11}$$

$$c_i(x, 0) = c_i^0, \quad i = 1, 2, \quad x \in [0, a], \tag{12}$$

$$\left. \frac{\partial c_1}{\partial x} \right|_{x=0} = 0, \quad \left. \frac{\partial c_2}{\partial x} \right|_{x=a} = 0, \quad c_i|_{x=\frac{a}{2}} = 0, \quad i = 1, 2, \quad t \geq 0. \tag{13}$$

Problems (11)–(13) was solved numerically and D was chosen such that $t_{1/2} = 4$. We obtained

$$D_{1000}^1 = 3.3 \cdot 10^{-6} \quad \text{and} \quad D_{1600}^1 = 3.3 \cdot 10^{-4}.$$

It is obvious that such D_T^1 is the minimal value of the diffusion rate such that $t_{1/2} = 4$, i.e. the garnet cannot be synthesized in 8 h if parameters D and k are in region G_T^1 (see figure 2(a) and (b)) because of the low-difusion rate. In figure 2(a) and (b), these values correspond to the line W .

At the same time, the following conclusion follows. The difference between D_{1000}^1 and D_{1600}^1 (100 times) explains the low-temperature formation of $Y_3Al_5O_{12}$ using sol–gel technique: since sol–gel method requires lower diffusion rate ($D_{1000}^1 \leq D_{1600}^1$), therefore, it may be carried out at lower-temperature regime.

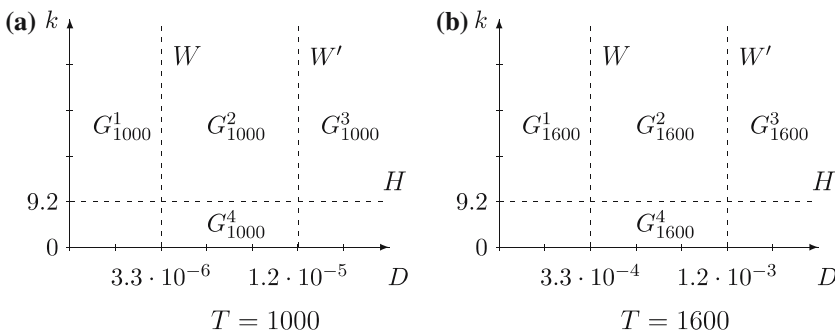


Figure 2. Phase plane $D - k$.

Now, let us consider the diffusion stage of the reaction separately. Let us define diffusion that guarantees the delivery of the reactants to the reaction spot over 8 h exactly. It may be defined in the following way:

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2}, \quad i = 1, 2, \quad x \in (0, a), \quad t > 0, \quad (14)$$

$$c_i(x, 0) = c_i^0, \quad i = 1, 2, \quad x \in [0, a], \quad (15)$$

$$\left. \frac{\partial c_i}{\partial x} \right|_{x=0, x=a} = 0, \quad i = 1, 2, \quad t \geq 0. \quad (16)$$

Problems (13)–(15) was solved numerically and D was chosen such that $t_s = 8$, and

$$\int_{V_1^0} c_1(x, t_s) + \int_{V_2^0} c_2(x, t_s) dx = \frac{1}{2} \int_V (c_1(x, 0) + c_2(x, 0)) dx,$$

$$V_i^0 = \{x : c_i(x, 0) = 0\}, \quad i = 1, 2.$$

We obtained

$$\tilde{D}_{1000} = 1.2 \cdot 10^{-5} \quad \text{and} \quad \tilde{D}_{1600} = 1.2 \cdot 10^{-3}.$$

In figure 2(a) and (b) these values correspond to line W' . This value is boundary in the sense that to the right of the line W' should be a place where only reaction is the limited stage of the synthesis.

5. Conclusions

- We develop a mathematical model, which allows the effective computer simulation of YAG synthesis. The 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 estimated diffusion and reaction rate constants proceeding from value of half-time at 1600 and 1000°C, and the size of the milled particles. There are regions in the phase plane D – k where the garnet cannot be synthesized in 8 h: $k \leq 9.2$ (because of low reaction rate) and $D \leq 3.3 \cdot 10^{-6}$ (because of low diffusion rate) at 1000°C; and $k \leq 9.2$ (because of low reaction rate) and $D \leq 3.3 \cdot 10^{-4}$ (because of low diffusion rate) at 1600°C. Also the region indicated where reaction is the only limited stage of the synthesis: $D \geq 1.2 \cdot 10^{-5}$ at 1000 and $D \geq 1.2 \cdot 10^{-3}$ at 1600°C.

At the same time, the exact reason responsible for the different formation temperatures of $Y_3Al_5O_{12}$ using different techniques was

determined. It was shown that the formation of YAG using sol–gel technique requires lower diffusion rate, so it may be carried out at lower-temperature regime.

Acknowledgments

The authors thank the Lithuanian Science Foundation for the financial support in the framework of the research programme ‘Modelita’ (Registration #C-03048) at Vilnius University.

References

- [1] T. Aichele, T. Lorenz, R. Hergt and P. Gornert, *Cryst. Res. Technol.* 38 (2003) 575.
- [2] M.E. Brown, *Introduction to Thermal Analysis. Techniques and Applications* (Chapman and Hall, London, 1988).
- [3] G.W. Chadzynski, V.V. Kutarov and P. Staszczuk, *J. Therm. Anal. Calorim.* 76 (2004) 633.
- [4] J. Dong, P. Deng and J. Xu, *Optics Commun.* 170 (1999) 255.
- [5] J.R. Frade and M. Cable, *J. Mater. Sci.* 32 (1997) 2727.
- [6] A.K. Galwey and M.E. Brown, *Thermochim. Acta* 386 (2002) 91.
- [7] E. Garskaite, D. Jasaitis and A. Kareiva, *J. Serb. Chem. Soc.* 68 (2003) 677.
- [8] C.J. Harlan, A. Kareiva, D.B. Macqueen, R. Cook and A.R. Barron, *Adv. Mater.* 9 (1997) 68.
- [9] A. Ikesue, K. Yoshida and K. Kamata, *J. Am. Ceram. Soc.* 79 (1996) 507.
- [10] S.M. Kaczmarek, G. Domianiak-Dzik, W. Ryba-Romanowski, J. Kisielewski and J. Wojtkowska, *Cryst. Res. Technol.* 34 (1999) 1031.
- [11] B.H. King and J.W. Halloran, *J. Am. Ceram. Soc.* 78 (1995) 2141.
- [12] A. Leleckaite and A. Kareiva, *Opt. Mater.* 26 (2004) 123.
- [13] Y. Liu, Z.F. Zhang, B. King, J. Halloran and R.M. Laine, *J. Am. Ceram. Soc.* 79 (1996) 385.
- [14] M. Malinowski, M. Kaczkan, A. Wnuk and M. Szuflińska, *J. Lumin.* 106 (2004) 269.
- [15] R. Manalert and M.N. Rahaman, *J. Mater. Sci.* 31 (1996) 3453.
- [16] I. Mulioliene, S. Mathur, D. Jasaitis, H. Shen, V. Sivakov, R. Rapalaviciute, A. Beganskiene and A. Kareiva, *Opt. Mater.* 22 (2003) 241.
- [17] R.C. Pullar, M.D. Taylor and A.K. Bhattacharya, *J. Eur. Ceram. Soc.* 19 (1999) 1747.
- [18] Z. Sun, D. Yuan, H. Li, X. Duan, H. Sun, Z. Wang, X. Wei, H. Xu, C. Luan, D. Xu and M. Lv, *J. All. Comp.* 379 (2004) L1.
- [19] H. Tanaka, *Thermochim. Acta* 267 (1995) 29.
- [20] C.W. Thiel, H. Cruguel, Y. Sun, G.J. Lapeyre, R.M. Macfarlane, R.W. Equall and R.L. Cone, *J. Lumin.* 94–95 (2001) 1.
- [21] M. Veith, S. Mathur, A. Kareiva, M. Jilavi, M. Zimmer and V. Huch, *J. Mater. Chem.* 9 (1999) 3069.
- [22] S. Vyazovkin and C.A. Wight, *Ann. Rev. Phys. Chem.* 48 (1997) 125.
- [23] S.F. Wuister, C.D. Donega and A. Meijerink, *Phys. Chem. Chem. Phys.* 6 (2004) 1633.
- [24] M. Yada, M. Ohya, M. Machida and T. Kijima, *Chem. Commun.* issue 18 (1998) 1941.
- [25] J.M. Yang, S.M. Jeng and S. Chang, *J. Am. Ceram. Soc.* 79 (1996) 1218.
- [26] X. Zhang, H. Liu, W. He, J. Wang, X. Li and R.I. Boughton, *J. All. Comp.* 372 (2004) 300.
- [27] F. Ivanauskas, A. Kareiva and B. Lapcun, *J. Math. Chem.* 37 (2005) 367–378.
- [28] A.A. Samarskij, *Theory of Finite Difference Schemes* (Dekker, New York, 2002).