

Computer modeling of synthesis of strontium stannates at high temperatures

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Abstract In our previous papers (Mackevičius et al. in *Cent Eur J Chem* 10(2): 380–385, 2012; *J Math Chem* 50(8):2291–2302, 2012; *J Math Chem* 51(5):1249–1257, 2013), we presented a method for estimation of the diffusion and reaction rates of synthesis at high temperatures using limited information, such as synthesis time and dimensions of reactants, from real laboratory experiments. In this paper, we extend the method to the case where particles of two reactants react with the gas environment and apply it to the case of synthesis of strontium stannate SrSnO_3 . The synthesis is modeled by a reaction–diffusion system describing the dynamics of the concentrations of reactants and product in an appropriately constructed synthesis space. Solving in the latter an inverse modeling problem, we obtain explicit formulas for the diffusion coefficient and reaction rate as functions of temperature by calculating the activation energies and other parameters of synthesis. Our approach also allows us to explain why we have different reactions at different temperatures.

Keywords Three-reactant model · Diffusion coefficient · Reaction rate coefficient · Stannates

1 Introduction

Perovskite-type alkaline earth metal metastannates with the general formula of MSnO_3 ($M = \text{Ca}, \text{Sr}, \text{and Ba}$) have received increasing attention due to their applications in ceramic dielectric bodies [4,5], gas sensors [6–8], anode materials for lithium ion batteries [9–13], and photocatalysts [14–20]. Recently, alkaline earth orthostannates

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(M_2SnO_4 , where $M = Ca, Sr, \text{ or } Ba$) have been drawing more and more attention for new phosphors because of their stable crystalline structure and high physical and chemical stability. The anions SnO_4^{4-} are reported to be optically inert and could be a candidate as a host for luminescent materials. Incorporation of lanthanide ions into stannate host lattice resulted in photoluminescence (PL) and long lasting phosphorescence (LLP) [21–26].

Recently, a novel and versatile synthetic approach for the preparation of alkaline earth metal (Ca, Sr, and Ba) stannates via aqueous sol–gel (combustion) method was proposed [27]. Calcium, strontium, and barium metastannates and orthostannates were synthesized by means of an environmentally friendly aqueous sol–gel technique. It was established that monophasic alkaline earth metal metastannates ($MSnO_3$) can be obtained at $T = 800^\circ C$. On the other hand, for the preparation of monophasic alkaline earth metal orthostannates (M_2SnO_4), a slightly higher annealing temperature ($T = 1000^\circ C$) should be used. The obtained results initiated the aim of this work to investigate the possibility of computer modeling of formation of different sol–gel-derived strontium metastannates at different temperatures.

In our previous papers (Mackevičius et al. [1–3]), we presented a method for estimation of the diffusion and reaction rates of synthesis at high temperatures using limited information, such as synthesis time and dimensions of reactants, from real laboratory experiments. Two- and three-reactant models were considered, with the reactants represented by small particles. The model was not applicable to the case where one of the reactants is a gas. In this paper, we fill this gap by extending the model to the case where the particles of two reactants react with the gas environment and apply it to the case of synthesis of strontium stannate $SrSnO_3$. The synthesis is modeled by a reaction–diffusion system describing the dynamics of the concentrations of reactants and product in an appropriately constructed synthesis space. Solving in the latter an inverse modeling problem, we obtain explicit formulas for the diffusion coefficient and reaction rate as functions of temperature by calculating the activation energies and other parameters of synthesis. Our approach also allows us to explain why we have different reactions at different temperatures.

The paper is organized as follows. In Sect. 2, we give a brief description of laboratory experiments of stannate synthesis. In Sect. 3, we give some preliminaries on the parameters of reactants and construct a synthesis space for numerical calculations. In Sects. 4 and 5, we present a mathematical model for estimation of diffusion–reaction synthesis rates and state the main goal of the paper, calculation of the parameters to be estimated. In Sects. 6 and 7, we present the calculation method and results. We conclude in Sect. 8.

2 Experimental

Tin (II) oxalate ($SrSnO_4$, Alfa Aesar, 98 %), hydrogen peroxide (H_2O_2 , Acros Organics, 35 wt% in H_2O , for analysis, stabilized), citric acid ($C_6H_8O_7$, Sigma-Aldrich, $\geq 99.5\%$) and ammonia (NH_3 , Merck, 32% in H_2O , extra pure) were used as starting materials for the synthesis of tin precursor solutions. Firstly, tin (II) oxalate was dispersed with a minimal amount of distilled water by stirring in a beaker at room tem-

perature. Secondly, 35 % hydrogen peroxide was added to the suspension resulting in a 1:12 Sn (IV) : H₂O₂ molar ratio. The beaker was heated on a hot plate at 80 °C and the mixture was stirred for 30 min until a clear and transparent solution is obtained. Citric acid (CA) was then added to the above solution in 1:6 Sn (IV) : CA molar ratio. The obtained mixture was refluxed for 1 h at 80 °C in a beaker closed with a watch glass. The resulting acidic solution was neutralized while keeping the beaker in an ice water bath by the addition of concentrated ammonia up to pH ~ 7. For the preparation of alkaline earth metal (Sr) precursor solution strontium hydroxide octahydrate (Sr(OH)₂·8H₂O, Alfa Aesar, 99 %) or strontium acetate (Sr(CH₃COO)₂, Sigma-Aldrich, ≥98 %) were used. Alkaline earth metal precursor solution was obtained by dissolving hydroxide or acetate in an aqueous solution of 3 M citric acid (Sr:CA=1:6) constantly stirring at room temperature to avoid the formation of carbonates. After complete dissolution, the concentrated ammonia was used to adjust pH ~ 7. The alkaline earth metal and citrato peroxo Sn (IV) precursors were mixed in the stoichiometric ratio 1:1 resulting in powders with nominal chemical composition of SrSnO₃. The bimetallic precursors were homogenized constantly stirring at 80 °C for 1 h. The Sr–Sn–O (Sr–Sn) containing precursor solution with pH ~ 7 was heated at ~150 °C to promote dehydration that leads to the formation of white foams gradually turning into brown–black gels. Amorphous and highly hygroscopic Sr–Sn precursor gels were dried in the oven at 150 °C for two days. During last stages of gelation, self-propagating gel combustion process started and was accompanied with evolution of gases. The resulting voluminous fluffy yellowish product was dried in the oven at 150 °C over night. Dried gel was ground in an agate mortar and preheated for 5 h at 500 °C (1 °C/min) in air. After an intermediate grinding, the samples were additionally sintered for 5 h in the temperature range of 800–1000 °C (5 °C/min) in air.

3 Description of particles and synthesis space

First, let us summarize the parameters of reactants, strontium oxide SrO and tin oxide SnO, we will need for modeling. Their molar masses are 103.619 g/mol (SrO) and 134.709 g/mol (SnO), and their densities are

$$4.70 \text{ g/cm}^3 = \frac{4.7}{103.69} \frac{\text{mol}}{\text{cm}^3} \approx 0.045 \frac{\text{mol}}{\text{cm}^3} = 0.045 \cdot 10^{-12} \frac{\text{mol}}{\mu\text{m}^3}$$

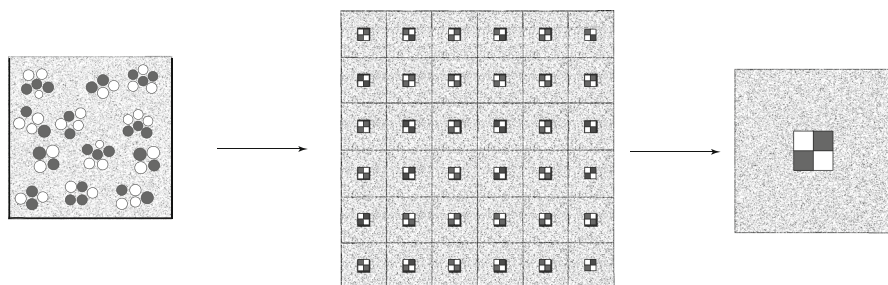
and

$$6.45 \text{ g/cm}^3 = \frac{6.45}{134.709} \frac{\text{mol}}{\text{cm}^3} \approx 0.048 \frac{\text{mol}}{\text{cm}^3} = 0.048 \cdot 10^{-12} \frac{\text{mol}}{\mu\text{m}^3},$$

respectively. Since the densities are rather similar, in our model, we shall assume for simplicity that they are both equal to their average $0.0465 \cdot 10^{-12} \frac{\text{mol}}{\mu\text{m}^3}$. Since the linear size is about 200 nm (and, thus, the volume is about $8 \cdot 10^6 \text{ nm}^3$), one particle of each reactant contains about $0.008 \cdot 0.0465 \cdot 10^{-12} \text{ mol} \approx 3.7 \cdot 10^{-16} \text{ mol}$ (Table 1).

Table 1 Parameters of particles of reactants SrO and SnO

Particle size	$\approx 200 \text{ nm} = 0.2 \mu\text{m}$
Density	$\approx 0.0465 \frac{\text{mol}}{\text{cm}^3} = 0.0465 \cdot 10^{-12} \frac{\text{mol}}{\mu\text{m}^3}$
Particle volume	$\approx 8 \cdot 10^6 \text{ nm}^3 = 0.008 \mu\text{m}^3$
Moles in one particle	$\approx 3.7 \cdot 10^{-16} \text{ mol}$

**Fig. 1** Construction of a synthesis space in the two-dimensional model

Let us now consider the first reaction



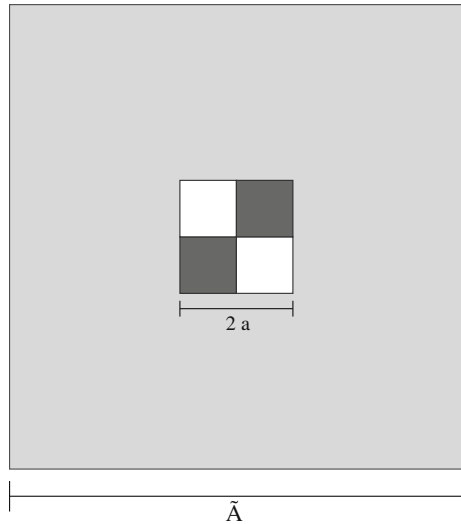
At the preparatory stage of the synthesis, the reactants are milled and mixed thoroughly in some cubic volume. The particles in the synthesis space are distributed randomly since their exact initial positions are unknown. As a result, modeling would require a huge memory size for storage. Therefore, we first assume that the particles are stored periodically. Moreover, in order to reduce the calculations to an 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 any particle. We achieve the periodicity and symmetry with a particle arrangement by taking cubic particles so that the synthesis volume V is also cubic. In Figs. 1, 2, for simplicity, we show the construction of the two-dimensional version of the synthesis space, with squares instead of cubes.

Since two moles of SrO and two moles of SnO react with one mole of O_2 , in the three-dimensional model, four particles of SrO and four particles of SnO react with $2 \times 3.7 \cdot 10^{-16} = 7.4 \cdot 10^{-16} \text{ mol O}_2$. According to the Avogadro law, one mole of gas fills a volume of $22.4 \cdot 10^{15} \mu\text{m}^3$, and molar density of the gas is $0.0446 \cdot 10^{-15} \frac{\text{mol}}{\mu\text{m}^3}$ (about 1000 times less than the density of SrO and SnO). We have that $7.4 \cdot 10^{-16} \text{ mol O}_2$ fills the volume

$$7.4 \times 10^{-16} \times 22.4 \cdot 10^{15} \mu\text{m}^3 \approx 16.6 \mu\text{m}^3.$$

The edge of a cube of such a volume is equal to $\sqrt[3]{16.6} \approx 2.55 \mu\text{m}$ —relatively large in comparison with a cube composed of eight cubes (four SrO and four SnO) with an edge of $0.4 \mu\text{m}$.

Fig. 2 The synthesis space V in the two-dimensional model



Thus, in the *three-dimensional model*, we suppose that the volume of synthesis consists of a “large” area of a cube with edge $A = 2.55 \mu\text{m}$, filled by O_2 with density

$$c_3 = 0.0446 \cdot 10^{-15} \frac{\text{mol}}{\mu\text{m}^3},$$

and in the center, we have a smaller cube with edge $2a = 0.4 \mu\text{m}$, which consists of eight (four SrO and four SnO cubes) checkered cubes with edges $a = 0.2 \mu\text{m}$ and density of the material

$$c_1 = c_2 = 0.0465 \cdot 10^{-12} \frac{\text{mol}}{\mu\text{m}^3}.$$

In order to reduce the computation time, we consider, instead, the *two-dimensional model*,¹ where O_2 fills a square of area that equals the volume in the three-dimensional model, that is, with the side equal to

$$\tilde{A} = \sqrt{16.6} \approx 4.07 \mu\text{m},$$

and where the density is the same, that is,

$$c_3 = 0.0446 \cdot 10^{-15} \frac{\text{mol}}{\mu\text{m}^2}.$$

So in a square with side $\tilde{A} = 4.07$, we will have the same amount of O_2 . We put two particles of each reactant in a square with side $2a = 0.4$, in chess order, as four squares with sides $a = 0.2 \mu\text{m}$ (see Fig. 2). In order to have the same size of particles, we have

¹ Numerical experiments in [2] showed that the results of this type models in the two- and three-dimensional cases are similar.

to multiply the densities by the length of the square side $2a = 0.4$ because, instead of the cube whose volume is equal to $(2a)^3 = 0.4^3$, we have a square of area $(2a)^2 = 0.4^2$. So, in the two-dimensional model, we suppose that the densities of reactants are

$$c_1 = c_2 = 0.4 \times 0.0465 \cdot 10^{-12} = 0.0186 \cdot 10^{-12}.$$

In the second reaction



which acts at the temperature from 1000 °C, four moles of moles of SrO and two moles of SnO react with one mole of O₂. In this case, we have to double the density c_1 of SrO in our calculations.

4 Mathematical model

We denote by C_4 the concentration of the complex 2SrSnO_3 ($2\text{Sr}_2\text{SnO}_4$) resulting from the synthesis of three complexes 2SrO (resp. 4SrO), 2SnO , and O_2 with concentrations C_1 , C_2 and C_3 in reaction (1) (resp. in reaction (2)). The reaction rate w can be expressed by the rate law as follows:

$$w = kC_1C_2C_3,$$

where k is the reaction rate coefficient (or rate constant).

The dynamics of concentrations of the reactants by diffusion is described by the second Fick law:

$$w_i = \frac{\partial C_i}{\partial t} = \sum_{j=1}^2 D_i \frac{\partial^2 C_i}{\partial x_j^2},$$

where D_i is the diffusion coefficient, n is the dimension of the model, and w_i is the rate of synthesis of the i th reactant. We denote

$$\begin{aligned} c_1 &= 2C_1, \quad c_2 = 2C_2, \quad c_3 = C_3, \quad c_4 = 2C_4 \quad \text{for } \text{SrSnO}_3, \\ c_1 &= 4C_1, \quad c_2 = 2C_2, \quad c_3 = C_3, \quad c_4 = 2C_4 \quad \text{for } \text{Sr}_2\text{SnO}_4, \end{aligned}$$

that is, $c_i = c_i(x, t)$ is the concentration of the i th reactant (SrO, SnO, O₂, and SrSnO₃ or Sr₂SnO₄ for $i = 1, 2, 3, 4$, respectively) of the synthesis at a point $x \in V$ at time t .

Combining the second Fick law and the active mass law for reaction (1), we get the following partial differential equation system on the synthesis space V :

$$\frac{\partial c_1}{\partial t} = \sum_{j=1}^2 D_1 \frac{\partial^2 c_1}{\partial x_j^2} - \alpha_1 k c_1 c_2 c_3, \quad (3)$$

$$\frac{\partial c_2}{\partial t} = \sum_{j=1}^2 D_2 \frac{\partial^2 c_2}{\partial x_j^2} - \alpha_2 k c_1 c_2 c_3, \quad (4)$$

$$\frac{\partial c_3}{\partial t} = \sum_{j=1}^2 D_3 \frac{\partial^2 c_3}{\partial x_j^2} - \alpha_3 k c_1 c_2 c_3, \tag{5}$$

$$\frac{\partial c_4}{\partial t} = \sum_{j=1}^2 D_4 \frac{\partial^2 c_4}{\partial x_j^2} + \alpha_4 k c_1 c_2 c_3, \tag{6}$$

where

$$\begin{aligned} \alpha_1 = \frac{1}{2}, \alpha_2 = \frac{1}{2}, \alpha_3 = \frac{1}{4}, \alpha_4 = \frac{1}{2} & \text{ for SrSnO}_3, \\ \alpha_1 = \frac{1}{2}, \alpha_2 = \frac{1}{4}, \alpha_3 = \frac{1}{8}, \alpha_4 = \frac{1}{4} & \text{ for Sr}_2\text{SnO}_4, \end{aligned}$$

with the initial conditions $c_i(x, 0) = c_i^0(x)$, $x = (x_1, x_2) \in \bar{V} = V \cup \partial V$, $i = 1, 2, 3, 4$, and some boundary conditions (to be stated below) on the boundary ∂V of V . For simplicity, we assume that all the diffusion coefficients coincide, that is, $D_1 = D_2 = D_3 = D_4 = D$.

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

$$\int_V (c_1(x, t_{1/2}) + c_2(x, t_{1/2}) + c_3(x, t_{1/2})) dx = \frac{1}{2} \int_V (c_1(x, 0) + c_2(x, 0) + c_3(x, 0)) dx. \tag{7}$$

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 of SrSnO_3 are approximately 2.5, 3.5, 5, and 6 h at the temperatures $T = 1000, 900, 800,$ and 750°C , respectively, and 5 h at the temperature $T = 1000^\circ\text{C}$ for Sr_2SnO_4 . So, in our calculations, we assume that the synthesis half-times are one-tenth of the corresponding “full” times, that is, 0.25, 0.35, 0.5, and 0.6 h at the temperatures $T = 1000, 900, 800,$ and 750°C , respectively for SrSnO_3 , and 0.5 h at $T = 1000^\circ\text{C}$ for Sr_2SnO_4 .

Summarizing, we arrive at the equation system (3)–(6) in the three-reactant square synthesis space V shown in Fig. 2, with the initial conditions in the inner square 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.

When solving numerically the partial differential equation system (3)–(5) in the square area, we use a finite difference technique, which is rather complicated to be given here.

5 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:

$$D = D_0 \exp \left\{ -\frac{E_D}{RT} \right\}, \quad k = k_0 \exp \left\{ -\frac{E_A}{RT} \right\}. \quad (8)$$

Here, E_D is the diffusion activation energy, E_A is the reaction activation energy, D_0 and k_0 are constants, and $R = 8.314472$ is the universal gas constant. Our main goal is to estimate, for SrSnO_3 , the unknown parameters by finding the possible values of the coefficient pairs (D, k) for temperatures $T = 1000, 900, 800,$ and 750°C . In a sense, we solve the inverse problem for system (3)–(5): given the synthesis half-time $t_{1/2}$ at some temperature T , we look for the parameters D and k of the system such that the half-time condition (7) is satisfied. Then from the obtained data, using Eq. (8), we can find approximate values of the parameters E_D, E_A, D_0, k_0 and, in particular, the true values of parameters D and k for any given temperature T (see Sect. 6).

Remark. We cannot perform such calculations for Sr_2SnO_4 since, at the moment, we only know one half-time for one temperature $T = 1000^\circ\text{C}$. However, in view of this information, our model allows us to explain why the second reaction is impossible at lower temperatures (see Sect. 7).

6 Calculation method

We calculate the diffusion and reaction rate coefficients as follows. First, for the temperatures $T_1 = 1000^\circ\text{C}$, $T_2 = 900^\circ\text{C}$, $T_3 = 800^\circ\text{C}$, and $T_4 = 750^\circ\text{C}$, 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., $t_{1/2} = 0.25, 0.35, 0.5,$ and 0.6 , respectively). To this end, we use our computer program which, given any fixed D , half-time $t_{1/2}$, and particle size a , numerically solves the system (3)–(5) until the half-time condition (7) 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. So, all four graphs, $L_1, L_2, L_3,$ and L_4 , are shown in Fig. 3.

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 $T_1 = 1000^\circ\text{C} = 1273\text{K}$ and $T_4 = 750^\circ\text{C} = 1023\text{K}$, we write and solve the following equation system with respect to unknown (E_D, E_A, D_0, k_0) :

$$\begin{aligned} D_1 &= D_0 \exp \left\{ -\frac{E_D}{R \cdot T_1} \right\}, \\ D_2 &= D_0 \exp \left\{ -\frac{E_D}{R \cdot T_4} \right\}, \end{aligned}$$

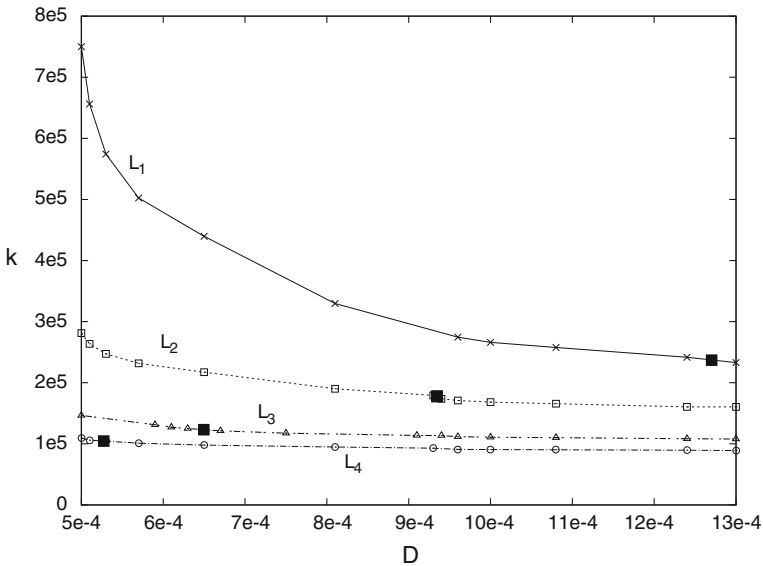


Fig. 3 Calculations in the *square* synthesis space V shown in Fig. 2

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

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

This way, we get the set of possible collections of the parameters $(E_D^i, E_A^i, D_0^i, k_0^i)$, $i = 1, 2, \dots$. Repeating this for curves L_2 and L_3 , we get another set of possible collections of the parameters, $(\bar{E}_D^j, \bar{E}_A^j, \bar{D}_0^j, \bar{k}_0^j)$, $j = 1, 2, \dots$.

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

$$w_1(E_D^i - \bar{E}_D^j)^2 + w_2(E_A^i - \bar{E}_A^j)^2 + w_3(D_0^i - \bar{D}_0^j)^2 + w_4(k_0^i - \bar{k}_0^j)^2, \quad (9)$$

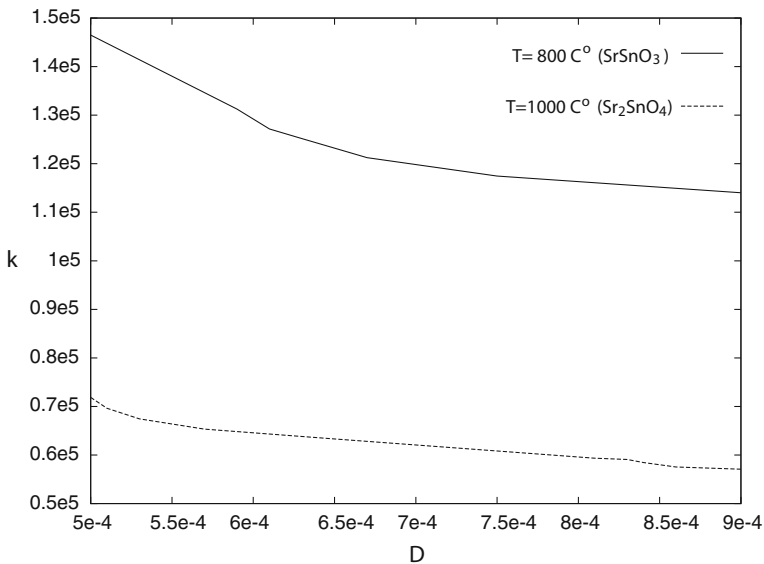
where we choose the weight coefficients w_i , $i = 1, 2, 3, 4$, so that the summands are approximately of the same order. The collections of parameters minimizing the sum (9), say $(E_D^{i_0}, E_A^{i_0}, D_0^{i_0}, k_0^{i_0})$ and $(\bar{E}_D^{j_0}, \bar{E}_A^{j_0}, \bar{D}_0^{j_0}, \bar{k}_0^{j_0})$, can both serve as estimates of (E_D, E_A, D_0, k_0) . We finally take the average values of parameters: $(E_D, E_A, D_0, k_0) = ((E_D^{i_0} + \bar{E}_D^{j_0})/2, (E_A^{i_0} + \bar{E}_A^{j_0})/2, (D_0^{i_0} + \bar{D}_0^{j_0})/2, (k_0^{i_0} + \bar{k}_0^{j_0})/2)$. 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. 3 by “■”.

7 Calculation results

For the three-reactant model of SrSnO_3 , we obtained the diffusion and reaction rates as functions of synthesis temperature T :

Table 2 Diffusion and reaction rates

T	750 °C	800 °C	900 °C	1000 °C
D	5.3e-4	6.5e-4	9.3e-4	1.3e-3
k	1.0e5	1.3e5	1.8e5	2.3e5

**Fig. 4** Comparison of possible (D, k) for SrSnO_3 and Sr_2SnO_4 at 5h of synthesis

$$D = 4.6e-2 \exp(-3.8e4/(RT)), \quad (10)$$

$$k = 6.9e11 \exp(-3.5e4/(RT)). \quad (11)$$

The obtained Arrhenius law Eqs. (10)–(11) give us the diffusion and reaction rates at temperatures $T = 750, 800, 900,$ and 1000 °C, presented in Table 2.

In Fig. 4, we have plotted the curves of possible (D, k) in the synthesis of SrSnO_3 [Eq. (1)] and Sr_2SnO_4 [Eq. (2)] at the temperatures 800 and 1000 °C, respectively. The “full” synthesis time was 5 h in both cases. We see that, even at higher temperature, the corresponding possible values of (D, k) , including the unknown true value, in the synthesis of Sr_2SnO_4 are significantly lower than those in the synthesis of SrSnO_3 . Therefore, at 800 °C, the values (D, k) for Sr_2SnO_4 would be yet lower. Theoretically, lower values of the diffusion and reaction rate coefficients make the reaction much slower, whereas practically the reaction becomes impossible at all.

8 Conclusions

Using the second Fick, active mass, and Arrhenius laws, we presented and analyzed a new mathematical model of synthesis reactions with two solid particle reactants (SrO

and SnO) in gas (O_2) environment in the form of diffusion–reaction equation system describing the dynamics of concentrations of reactants and product. Based on limited data (half-times and approximate sizes of solid reactant particles) from real laboratory experiments, we have obtained explicit formulas, given by Eqs. (10)–(11), for diffusion and reaction rate coefficients expressing their dependence on the temperature. At the same time, we have calculated the activation energies, important data that can be used to analyze other syntheses.

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