

ANALYSIS OF THE TEMPERATURE PROFILES DURING THE COMBUSTION SYNTHESIS OF DOPED LANTHANUM GALLATE

ANALIZA TEMPERATURNIH PROFILOV MED ZGOREVALNO SINTEZO DOPIRANEGA LANTANOVEGA GALATA

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Strontium-, magnesium-, iron-doped lanthanum gallate was prepared by the citrate-nitrate combustion technique. The temperature profiles of the citrate-nitrate metal ions system were measured and analyzed by applying the Boddington method. On the basis of the temperature measurements it was possible to perform thermodynamic and kinetic analysis of the system. The Boddington parameters T_c , u , t_r , t_d , t_x , t^* , τ_{ad} , α , G that are essential for the kinetic analysis were defined by means of calculated λ , h , c_p values of the combustion system and measured values of ρ and Q . Arrhenius kinetics was assumed for the determination of the kinetic parameters such as the activation energy E_a , the exponential factor n and pre-exponential factor K_0' of the system. The activation energy for the combustion system was determined by the method of combustion-wave propagation velocity to be 34.8 kJ mol^{-1} , by the Boddington method to be 31.8 kJ mol^{-1} and by the Freeman-Carroll method to be 33.1 kJ mol^{-1} .

Key words: lanthanum gallate, self-propagating-high-temperature synthesis, citrate-nitrate combustion process, kinetic analysis, the Boddington method, Freeman-Carroll

Lantanov galat, dopiran s stroncijem, magnezijem in železom, je bil pripravljen po citratno-nitratnem postopku zgorevalne sinteze. Merjeni temperaturni profili sistema citrat-nitrat-kovinski ioni so bili analizirani po Boddingtonovi metodi. Na podlagi izračunanih vrednosti λ , h , c_p zgorevalnega sistema in merjenih vrednosti ρ in Q so bili določeni Boddingtonovi parametri T_c , u , t_r , t_d , t_x , t^* , τ_{ad} , α , G , ki so ključnega pomena za kinetično analizo. Za določitev kinetičnih parametrov, kot so aktivacijska energija E_a , eksponentni faktor n in predeksponentni faktor K_0' sistema, je bila predpostavljena Arrheniusova kinetika. Aktivacijska energija je bila določena po metodi hitrosti napredovanja zgorevalnega vala v odvisnosti od temperature z vrednostjo $34,8 \text{ kJ mol}^{-1}$, po Boddingtonovi metodi z vrednostjo $31,8 \text{ kJ mol}^{-1}$ in po Freeman-Carrollovi metodi z rezultatom $33,1 \text{ kJ mol}^{-1}$.

Ključne besede: lantanov galat, zgorevalna sinteza, citratno-nitratni postopek, kinetična analiza, Boddingtonova metoda, metoda Freeman-Carroll

1 INTRODUCTION

Lately, the oxygen ionic transfer in some doped perovskite-type oxides was investigated with special emphasis on the relationship between the oxygen-ion conductivity and the material lattice parameters¹⁻³. Among the investigated materials gallate ABO_3 with $A = \text{La}$ was found to have the highest Goldschmidt tolerance factor and correspondingly the highest oxygen ionic conductivity in relation to other $A = \text{rare-earth}$ occupations. On the B-site, the maximum specific conductivity and oxygen transfer and the minimum of the activation energy were determined in the case of Ga^{4,5}. The ionic conductivity properties of perovskites were explained in terms of their structure, i.e., the oxygen ionic conductivity increases with the free volume of the unit cell and decreases with decreasing tolerance factor owing to an increasing distortion of the perovskite structure.

The oxygen ionic conductivity of lanthanum gallates can be improved with appropriate doping owing to the generation of oxygen vacancies. Among the dopands Sr (A-site dopand) and Mg (B-site dopand) additions ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-x}$) were found to have a profound

effect on increasing the oxygen ionic conductivity – LSGM⁶. If Ga in $\text{La}_{0.9}\text{Sr}_{0.1}(\text{Ga}_{1-y}\text{M}_y)_{0.8}\text{Mg}_{0.2}\text{O}_{3-x}$ is further substituted by a transition metal ($M = \text{Cr, Mn, Fe, Co}$), the electrical properties of LSGM can be further modified. When doped with amounts $y \leq 0.1$ of Fe or Co, gallates exhibit oxygen ionic conductivities twice that of LSGM⁷, which enables these materials to be used as medium-temperature electrolytes. With increasing dopant concentration both the exchangeable oxygen and the p-type electrical conductivity increase, which is of interest for applications as mixed conductors.

Doped lanthanum gallates are usually prepared either from the corresponding oxides with a solid-state reaction at high temperatures^{8,9}, or with self-propagating high-temperature synthesis (SHS)¹⁰. Such solid-state reactions are diffusion controlled and time consuming, while the resulting powders may show a certain degree of compositional inhomogeneity. In contrast, a combustion synthesis or a self-propagating high-temperature synthesis (SHS) provides an attractive practical alternative to conventional methods. The combustion process involves the decomposition of a redox system, which then proceeds as a self-sustaining front throughout the

reactant gel mixture. The reaction conditions and the large amount of heat evolved during the reaction enable the direct production of a large number of single or multicomponent crystalline and homogeneous powders that have a narrow particle size distribution¹¹. From the variety of possible redox systems, a combustion mixture based on the citrate-nitrate combination can be potentially applied for the production of larger quantities of mixed oxides owing to its relatively non-violent combustion¹².

The theoretical physical models that explain, simulate and predict SHS reaction phenomena are based on energy and mass balances¹³. In the case where the reaction rate is used to calculate the kinetic parameters of the reaction, several mathematical models have been developed. In this respect the Boddington method¹⁴ is particularly valuable because calculations of the kinetic parameters and the preliminary thermal conductivity determinations are not necessary. Moreover, the Boddington method is not based on a specific kinetic model but predicts the same kinetic behaviour of the system at a certain value of the reactant-to-product conversion. The origin of the Boddington method is thus a mathematical analysis of the measured temperature profiles of the combustion system with respect to the heat-balance equation utilized. The Boddington method employs the following heat-balance equation:

$$\kappa \frac{\partial^2 T}{\partial x^2} - C_p \rho \frac{\partial T}{\partial t} + \Phi(T, \eta) - h(T - T_0) = 0 \quad (1)$$

In the above equation C_p is the heat capacity of the product, ρ is its density, κ is the thermal conductivity, $\Phi(T, \eta)$ is the rate of heat generation, h is an axial heat-transfer coefficient, T is the temperature, t is the time and x is the coordinate of wave propagation (the radiant heat losses are assumed to be negligible). The result of a combustion temperature profile according to the Boddington method is the calculation of the previously mentioned parameters, which finally enables a determination of the activation energy for the combustion reaction.

When the data on the fraction reacted η vs. T or t are accessible, several approaches are available for the kinetic analysis. A particularly interesting approach to kinetic parameter determination, because of its simplicity, is the Freeman-Carroll method¹⁵. This method is based on Arrhenius kinetics and utilizes the following kinetic function:

$$\frac{d\eta}{dt} = K_0' \exp\left(-\frac{E}{RT}\right)(1-\eta)^n \quad (2)$$

where K_0' is a constant and n is an exponential factor in a function of the kinetic order.

In the present work, a citrate-nitrate (fuel-oxidant) combustion synthesis method was employed to produce $\text{La}_{0.85}\text{Sr}_{0.1}(\text{Ga}_{0.9}\text{Fe}_{0.1})_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGFM) To our knowledge, this is the first time that combustion synthesis was

chosen for doped-LSGM preparation. The citrate-nitrate system was chosen due to its non-violent nature and because fine-doped LSGM-based perovskites have potential uses in the previously mentioned applications. For the chosen combustion system a complete Boddington analysis was also performed.

2 EXPERIMENTAL PROCEDURE

$\text{La}_{0.85}\text{Sr}_{0.1}(\text{Ga}_{0.9}\text{Fe}_{0.1})_{0.8}\text{Mg}_{0.2}\text{O}_{3-x+\delta}$ perovskite was prepared with a modified combustion synthesis based on the citrate-nitrate redox reaction. The starting substances for the reactive gel preparation were $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ga}(\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, and nitric acid (analytical reagent grade). $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (3.000 g), $\text{Sr}(\text{NO}_3)_2$ (0.173 g), $\text{Ga}(\text{NO}_3)_3 \cdot 10\text{H}_2\text{O}$ (2.559 g), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.417 g), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.263) and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (2.394 g) were dissolved separately with minimum additions of water in amounts that ensured the desired final composition. Aqueous solutions were mixed and HNO_3 (aq. 65 %, 1.25 mL) was added to ensure the initial citrate/nitrate molar ratio of 0.18. With the aim to obtain kinetic parameters from the temperature profile measurements, the reaction system was then diluted with different additions of $\alpha\text{-Al}_2\text{O}_3$ (from 0 % Al_2O_3 up to 5 % Al_2O_3 in the dry reactive mixture). A suspension (mixed nitrate solution with Al_2O_3 addition) was kept over a water bath at 60 °C under vacuum (5 mbar) until it transformed into a bright fragile xerogel.

The dried and diluted gels were gently milled and homogenized in an agate mortar and subsequently uniaxially pressed (17 MPa) into pellets (16 mm in diameter, height \approx 30 mm). The pellets were ignited at the top to start a self-sustaining combustion reaction producing doped LSGM perovskite. If the additions of Al_2O_3 exceeded 5 % the combustion system did not react in a self-sustaining mode.

The temperature profiles of the burning tablets were measured using an optical pyrometer (Ircan, model IPE 140, based on sample brightness) with a measuring range from 50 to 1200 °C and a very quick response time (1.5 ms). The accuracy of the optically measured temperature was ± 2.5 °C below 400 °C and ± 0.4 % of the measured value (in °C) above 400 °C. Since the measured systems were all ceramics with unknown exact emissivities, the emissivity was set to 0.85 and was kept constant for all the measurements. This value is close to the cited emissivities of ceramic products and Al_2O_3 in the measured temperature range. The temperature profiles of the reaction systems were measured from a distance of 10 cm with a space resolution of temperature measurements (the size of the measured spot on the sample surface) of 0.3 mm. Prior to the Boddington kinetic analysis, the experimentally measured temperature profiles were smoothed in the zone of rapid temperature change. The smoothing procedure is essential because

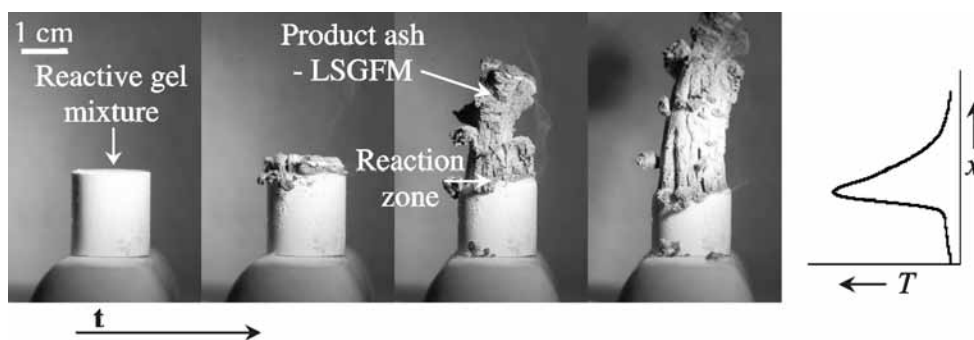


Figure 1: Self-sustaining citrate-nitrate reaction for $\text{La}_{0.85}\text{Sr}_{0.1}(\text{Ga}_{0.9}\text{Fe}_{0.1})_{0.8}\text{Mg}_{0.2}\text{O}_{3-x+\delta}$ preparation
Slika 1: Napredovanje zgorevne sinteze v sistemu za pripravo $\text{La}_{0.85}\text{Sr}_{0.1}(\text{Ga}_{0.9}\text{Fe}_{0.1})_{0.8}\text{Mg}_{0.2}\text{O}_{3-x+\delta}$

the measured values may oscillate around an average value, which makes the analysis of the temperature profile difficult. Slight temperature oscillations were ascribed to the surface roughness and to the synthesized material porosity.

3 RESULTS AND DISCUSSION

Combustion synthesis is a relatively new approach to doped-gallate preparation, i.e., gallates are normally prepared via a solid-state reaction. Very few reports are found in the literature describing lanthanum-gallate-based materials prepared via a combustion route^{16,17} and none deal with citrate-nitrate-derived doped lanthanum gallates.

One of the reasons why citrate-nitrate combustion synthesis for doped gallates preparation was neglected is that the preparation of pure lanthanum gallate is practically impossible. Regardless of the citrate/nitrate (c/n) molar ratio used (from fuel-lean $0.13 < c/n < 0.25$ to fuel-rich mixtures $0.25 < c/n < 0.33$) or small additions of various fuels (e.g. urea), the heat evolved during the combustion was not sufficient to trigger a self-sustaining combustion reaction. Only if dopand elements (Fe or Co) that are known for their catalytic activity towards citrate-nitrate combustion are added to the fuel-lean initial mixture ($c/n = 0.18$) can the self-sustaining combustion be achieved (**Figure 1**). Such a system was then the basis for the Boddington kinetic analysis.

To confirm citrate-nitrate combustion as an appropriate synthesis route for LSGFM preparation, the final ash product, as well as the intermediate products, was submitted for XRD analysis (**Figure 2**). Intermediates were prepared by careful heating of small amounts of the initial xerogel in air up to a predetermined temperature. According to **Figure 2** it is apparent that the intermediate precursors were amorphous at temperatures below 740 °C. At higher temperatures some crystalline phases appeared. The main crystalline phase found in intermediates treated above 740 °C was identified as the perovskite $\text{La}_{0.895}\text{Sr}_{0.105}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$. Additionally, only traces of residual secondary phases

$\text{SrLaGa}_3\text{O}_7$ and SrLaGaO_4 were found with XRD. If the intermediate preparation temperatures were increased, the secondary phases were almost completely dissolved in the LSGFM perovskite structure. The relatively low amounts of secondary phases in the intermediates prepared above 740 °C make, in our opinion, the combustion synthesis favourable when compared to preparation processes that are based on the diffusion of components in the solid state (in the latter case the amount of secondary phases is normally greater).

The entire range of as-measured temperature profiles for the chosen citrate-nitrate combustion system with different additions of Al_2O_3 diluting agent (λ) are shown in **Figure 3**. Altering the amount of diluting agent influences many parameters pertaining to the combustion reaction, such as the wave velocity and the combustion temperature, as summarized in **Table 1**. According to the results in **Figure 3** and **Table 1**, a greater addition of diluting agent lowers the peak combustion temperature, as well as the rate of propagation of the combustion reaction. However, the general shape of the temperature profile did not change with any variation in the amount of diluent. Another interesting fact is the relatively rapid

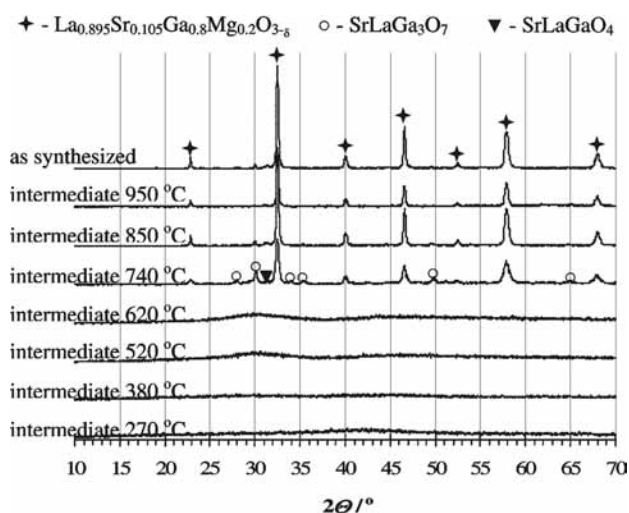


Figure 2: XRD patterns of intermediates and as-synthesized LSGFM
Slika 2: Rentgenogrami vmesnih produktov ter LSGFM sintetizirane materiala

product cooling. The samples cooled down from their peak temperature to 50 °C in approximately 40–60 s. The fast cooling was ascribed to the very porous structure formed after the combustion (**Figure 1**). The determination of the parameters' peak combustion temperature (T_c) and the combustion propagation velocity (u) is essential for the wave-velocity analysis. For the activation-energy calculation the following equation was utilized:

$$\frac{u^2}{T_c^2}(1-\lambda) = f(\eta)K_0\alpha\frac{C_p}{Q_0}\frac{R}{E}\exp\left(-\frac{E}{RT_c}\right)$$

where $f(\eta)$ is a function that depends on the kinetic order of the reaction, α is the thermal diffusivity of the product, C_p is the heat capacity of the product, Q_0 is the heat of reaction for an undiluted system, λ is the weight fraction of diluent, E is the activation energy, R is the general gas constant and K_0 is a constant. As the parameters u and T_c are altered if the reaction system is diluted with an inert substance, the activation energy can then be calculated from the slope in the plot of $\ln((1-\lambda)^{0.5}(u/T_c))$ vs. $1/T_c$. From the best-fit linear slope of the experimental combustion parameters, an apparent combustion activation energy of 34.8 kJ/mol was calculated (**Figure 4**).

Table 1: Reaction parameters of citrate-nitrate SHS systems

Tabela 1: Parametri citratno-nitratne zgorevalne reakcije

λ/wt	T_c/K	$u \cdot 10^3 / (\text{cm s}^{-1})$	$(\partial T/\partial t) / \text{K} \cdot \text{s}^{-1}$	$(\partial T/\partial x) / \text{K} \cdot \text{cm}^{-1}$
0	907.2	18.33	177	9655
0.01	871.5	19.71	149	7557
0.02	834.6	17.07	146	8552
0.03	725.5	12.17	129	10596
0.04	715.7	9.09	103	11329
0.05	700.5	7.63	96	12575

In order to obtain kinetic information from the temperature profiles, a variety of calculations were

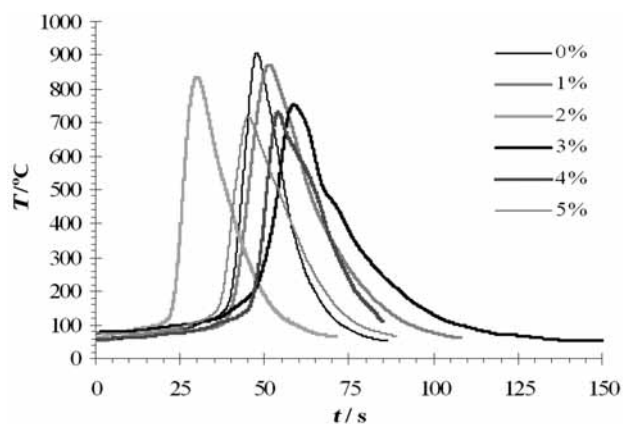


Figure 3: Measured temperature profiles of citrate-nitrate SHS systems with different additions of diluent

Slika 3: Merjeni temperaturni profili citratno-nitratnega sistema z različnimi dodatki sredstva za redčenje

performed on the basis of the experimental data. First, the temperature profiles in the zone of rapid temperature change were smoothed. From the smoothed version of the temperature profiles, the first and the second derivatives $\partial T/\partial t$ and $\partial^2 T/\partial t^2$ of each smoothed profile were calculated. The peak value in the plot of $\partial T/\partial t$ vs. t corresponds to the maximum heating rate achieved during the reaction. If this value were divided by the measured wave-velocity value (u), the maximum thermal gradient $(\partial T/\partial x)_{\text{max}}$ in the propagating coordinate could be calculated (**Table 1**).

Then a complete Boddington analysis¹⁴ of the temperature profiles obtained was performed, including the calculations of t_r and t_d (the rise time of a general adiabatic fore-wave and the remote decay time, respectively) in order to determine the two other values t_x (thermal relaxation time) and t^* using the relationships $t_x = t_d - t_r$ and $1/t^* = 1/t_r - 1/t_d$. The parameters t_x and t^* include the thermodynamic values and can be further expressed as $t^* = \alpha/u^2$ and $t_x = \rho C_p/h$, where α represents the effective thermal diffusivity (**Table 2**).

Table 2: Experimentally determined parameters of the Boddington analysis for the citrate-nitrate combustion

Tabela 2: Parametri citratno-nitratne zgorevalne reakcije določeni z Boddingtonovo metodo

λ/wt	t_r/s	t_d/s	t_x/s	t^*/s	$\tau_{\text{ad}}/\text{K}$	$\alpha \cdot 10^3 / \text{cm}^2 \cdot \text{s}^{-1}$
0	2.579	11.274	8.695	3.343	1392	1.124
0.01	2.369	12.005	9.636	2.951	1319	1.147
0.02	2.968	13.351	10.383	3.817	1296	1.113
0.03	2.952	13.850	10.898	3.752	1271	0.556
0.04	4.625	14.327	9.701	6.831	1222	0.565
0.05	5.733	15.432	9.698	9.124	1093	0.532

The temperature rise of the combustion system without heat losses, the value τ_{ad} (**Table 2**), was calculated by integrating the temperature profile, as described in¹⁸. If the combustion system is under adiabatic

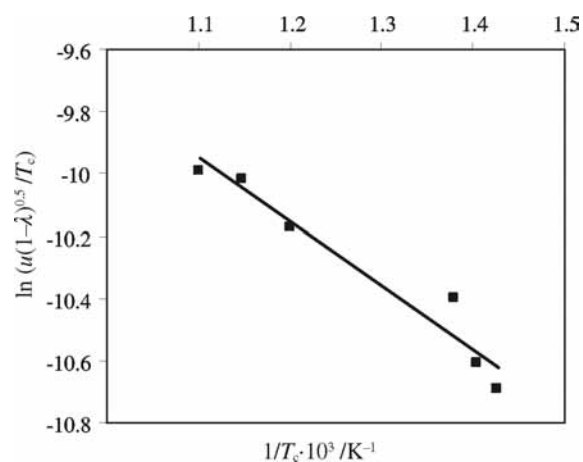


Figure 4: Wave-velocity analysis for combustion-derived LSGFM with different additions of Al_2O_3

Slika 4: Analiza hitrosti napredovanja zgorevalnega vala za sintezo LSGFM ob različnih dodatkih Al_2O_3

conditions, the value of τ_{ad} should be close to the value of T_c . However, if data from **Tables 1 and 2** are compared, τ_{ad} and T_c differ substantially. One reason for this is the incompletely adiabatic conditions during the reaction, i.e., during the citrate-nitrate combustion some volatile products are also formed¹⁹, carrying off a certain amount of heat. This implies that Eq. (1) should be changed in such a way as to describe the heat balance of the citrate-nitrate combustion, also taking into account the heat losses due to hot-gas formation. Nevertheless, the proposed Boddington heat-balance equation can still be used for the kinetic analysis and for the estimation of the η vs. T (or t) relationship (**Figure 5**). The function η vs. t was calculated in accordance with the following re-arranged Boddington heat-balance equation:

$$G = t_x^{-1} (T - T_0) + \partial T / \partial t - t^* \partial^2 T / \partial t^2$$

Since G also equals $t_{ad}(\partial\eta/\partial t)$, it was possible to calculate the reaction rate by dividing the values of G by the adiabatic temperature rise. Finally, by integrating the experimentally determined reaction rate, the fraction reacted η was calculated.

The calculated η vs. t data showed that the citrate-nitrate combustion is a relatively rapid process. In an undiluted sample the elapsed time interval from 10 % conversion to 90 % conversion was approximately 4.1 seconds, or, expressed in distance, equal to 0.75 mm.

The kinetic parameters obtained were used to calculate the activation energy of the citrate-nitrate combustion process. Due to the dependence of the T - η relationship on inert diluent additions¹⁴, the activation energy could be calculated by plotting the experimentally determined values of $\partial\eta/\partial t$ vs. the reciprocal of the absolute temperature at a fixed value of η . The magnitude of the slope in such a diagram should equal $-E/R$. The temperature dependence of the reaction rate at

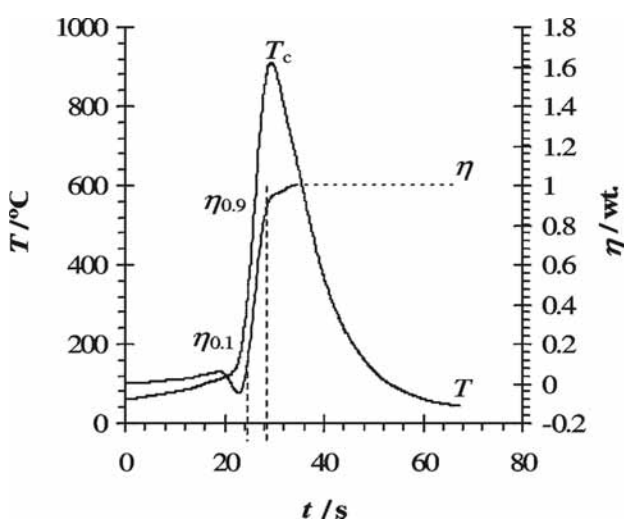


Figure 5: Temperature profile and time dependence of the fraction reacted for the undiluted sample

Slika 5: Merjeni temperaturni profil ter izračunana stopnja konverzije za pravilo LSGFM v neredčenem sistemu

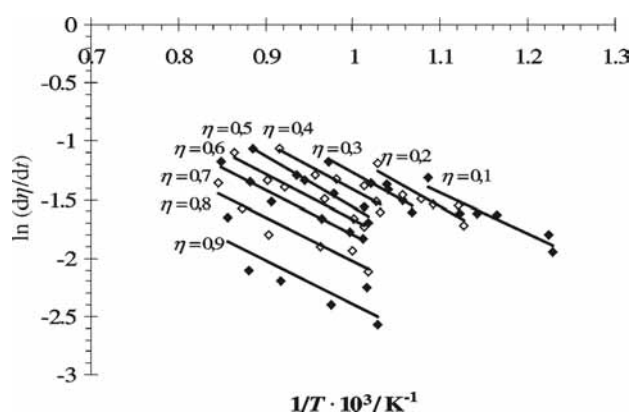


Figure 6: Temperature dependence of the reaction rate $\ln(\partial T/\partial t)$ for different values of η in the citrate-nitrate combustion system

Slika 6: Temperaturna odvisnost reakcijske hitrosti $\ln(\partial T/\partial t)$ pri različnih vrednostih η v citratno-nitratnem zgozvalnem sistemu

different η values is shown in **Figure 6**. From this it is evident that the slopes of the middle data sets (from $\eta = 0.4$ to $\eta = 0.8$) agree fairly well with each other. On the other hand, the slopes at lower values of η (from $\eta = 0.1$ to $\eta = 0.3$) and the slopes at the highest η values ($\eta = 0.9$) exhibited different (normally slightly lower) values compared to the middle data sets. Taking into account only the slopes of the middle data sets, the activation energy of 31.8 kJ/mol was deduced for the citrate-nitrate combustion system.

The third technique used for the kinetic analysis of the investigated citrate-nitrate system was the Freeman-Carroll method¹⁵. When predetermined $\partial\eta/\partial t$ vs. T data are used, this method enables the activation energy to be determined, as well as the parameters n and K_0' from Eq. (2). First, the parameter n was calculated from the slope in the plot of $(\Delta \ln(d\eta/dt))/(\Delta 1/T)$ vs. $(\Delta \ln(1-\eta))/(\Delta 1/T)$. Then the activation energy and the parameter K_0' of the system were calculated from the plots of $\ln(d\eta/dt \cdot 1/(1-\eta)^n)$ vs. the reciprocal of the absolute temperature. The magnitudes of the slope in such a diagram equal $-E/R$, while the intercept on the ordinate gives the value of $\ln K_0'$ (**Figure 7**). Parameters n , E and K_0' were determined for the undiluted system, as well as for all systems with various additions of diluent. The average n , K_0' and E values for all the investigated systems were calculated as $(0.52, 5.97) \text{ s}^{-1}$ and 33.1 kJ/mol, respectively.

The results of the calculation of the activation energy obtained from wave-velocity measurements (34.8 kJ/mol), the temperature-profile analysis (31.8 kJ/mol) and the Freeman-Carroll kinetic analysis (33.1 kJ/mol) are in good agreement, implying that any of the three techniques described can be used for a determination of the kinetic parameters. However, the good correlation between the E values obtained with different methods is not surprising, because all the methods are based on a similar assumption concerning the kinetic law (the Freeman-Carroll analysis uses data obtained from a

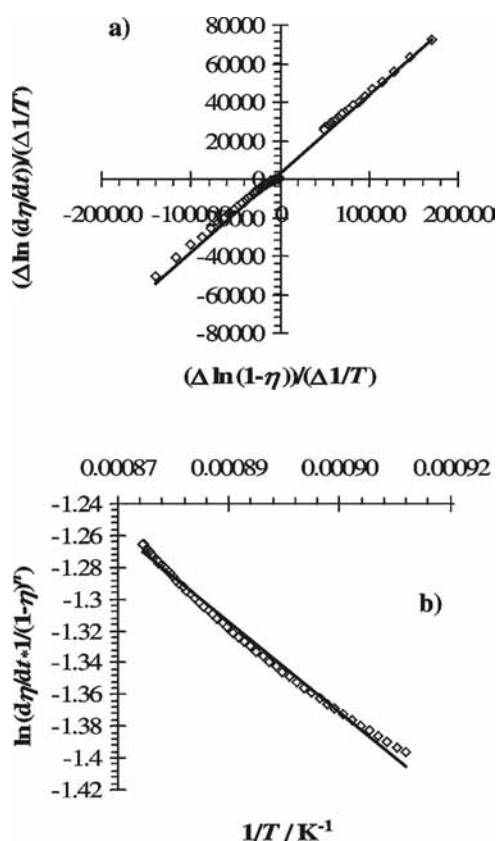


Figure 7: Determination of n , E and K_0' according to the Freeman-Carroll method, demonstration on a sample with $\lambda = 0.01$ wt.: a) determination of the parameter n , b) determination of K_0' and E
Slika 7: Določitev n , E in K_0' z metodo Freeman-Carroll v sistemu $\lambda = 0,01$ a) določitev parametra n , b) določitev K_0' in E

temperature-profile analysis). For a further validation the values of the kinetic parameters should be related to those deduced by applying an analogous or at least a similar method. As is implicit in the model on which the Boddington analysis is based, the processes which govern the rate of conversion are assumed to be chemical reactions and diffusion processes. Using this model all the reactions are treated simultaneously by applying a general function $f(\eta)$ that describes sufficiently the time dependence of the conversion equivalent h . The calculated value of the exponent n implies that there are several (at least two) processes that determine the rate of conversion. Either we have more than one reaction, each determined by its own kinetic law, affecting the rate, which leads to an overall exponent value of 0.5, or the diffusion process is the rate-limiting factor. This would also explain the relatively low value of the activation energy.

4 CONCLUSIONS

Sr-, Mg-, Fe-doped lanthanum gallate was prepared for the first time via citrate-nitrate combustion synthesis. This was successful only after the addition of an appropriate amount of a doping element, which is also

catalytically active toward the citrate-nitrate combustion. The main benefits of combustion-derived powders are a single-step process that is relatively quick, and the practical absence of secondary phases in the LSGFM after the synthesis.

A kinetic analysis of the burning system was made using three methods – wave-velocity measurements, temperature-profile analysis and the Freeman-Carroll analysis – all based on the kinetic law. The kinetic parameters obtained with the different methods are in good agreement, meaning that any of the three techniques described can be used for determining the kinetic parameters. The average n and E calculated values (≈ 0.5 and 31–35 kJ/mol, respectively) may be denoted as apparent values, and this implies that the diffusion process is the probably the rate-limiting factor.

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