

COMBUSTIBLE PRECURSOR BEHAVIOUR IN THE LANTHANUM CHROMITE FORMATION PROCESS

TERMIČNE LASTNOSTI REAKCIJSKEGA GELA ZA PRIPRAVO LANTANOVEGA KROMITA

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Combustion-derived lanthanum chromite (LC) powders were prepared with combustion synthesis from citrate-nitrate precursor gels. The transformation process of reactive citrate-nitrate gel to the cubic perovskite modification of (LC) was investigated. The influence of the fuel/oxidant molar ratio in the precursor gel on the combustion propagation and thermal characteristics of the combustion system was studied with simultaneous thermal analysis (TG, DTG and DTA), evolved gas analysis (MS) and gas chromatography (GC). The main (MS) responses detected were attributed to H₂, H₂O and CO₂ generation. It was found that the citrate-nitrate reaction proceeds through several separate consecutive steps and the precursor thermal decomposition characteristics depended strongly on the citrate/nitrate ratio prior to the combustion. The first two steps of the thermal decomposition at approximately 150 °C and 250 °C are strongly related to the citrate-nitrate reaction, while at around 400 °C the combustion of citric acid residuals occurs. The last step of the thermal decomposition is caused by transformation of LaCrO₄ to LaCrO₃. Intermediate precursors and final powder ashes were also analyzed with X-ray diffraction.

Keywords: combustion synthesis; lanthanum chromite; citrate- nitrate, thermal characteristics

Prahove lantanovega kromita (LC) smo pripravili s samovzdrževalno reakcijo iz citratno- nitratnih gelov. Preučevali smo pretvorbo reaktivnega citratno-nitratnega gela v perovskitno modifikacijo lantanovega kromita. Vpliv razmerja gorivo/oksidant v izhodnem prekurzorju na hitrost gorenja in termične karakteristike smo spremljali s simultano termično analizo (TG, DTG in DTA), EGA analizo ter plinsko kromatografijo (GC). Pomembnejše odzive na masnem spektrometru smo pripisali nastanku H₂, H₂O in CO₂. Termični razpad gela je močno odvisen od citratno-nitratnega razmerja v gelu pred sežigom, pri njegovem gorenju pa potekajo reakcije v več zaporednih med seboj ločenih stopnjah. Prvi dve stopnji termičnega razpada pri okoli 150 °C in 250 °C sta povezani z reakcijo med citronsko kislino in nitratom. Stopnja nad 400 °C kaže na razkroj ostanka citronske kisline, zadnja stopnja termičnega razpada pa je povezana s pretvorbo LaCrO₄ v LaCrO₃. Vmesne in končne produkte gorenja smo karakterizirali z rentgensko praškovno analizo.

Ključne besede: zgorevalna sinteza, lantanov kromit, citrat-nitrat, termične lastnosti

1 INTRODUCTION

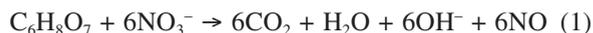
Several synthetic techniques are available for the preparation of multi-component oxides including the solid-solution-precursor method,¹ sol-gel synthesis,² co-precipitation,³ and spray drying.⁴ The solution combustion synthesis of complex metal oxides has several advantages over other conventional preparation techniques. Because it starts in a solution, it has control over the homogeneity and stoichiometry of the products. With a judicious choice of starting precursors for the combustion synthesis, particle size reduction (nano-sized) and the high degree of conversion to reactive powders may also be achieved.⁵

Combustion synthesis utilizes different redox systems, each with its own characteristics. In the precursor formation process in which an oxidant (i.e. nitrate) and fuels (i.e. glycine, urea, carbonylhydrazide, citric acid) are mixed in appropriate molar ratios, the fuels also serve as complexing agents limiting the precipitation of individual precursor components prior to ignition.⁸ The exothermic reaction between fuel and oxidant is accompanied by the release of a relatively large volume of gases leaving behind fine particulate solid residue.

Generally, combustion synthesis can be performed in slow reaction mode, in thermal explosion mode, or self-propagating mode.⁹ The first mode is characterised by a relatively slow, almost flameless reaction, and by the formation of an amorphous ash as a solid product. The second type of reaction occurs almost simultaneously throughout the mixture. In the self-propagating mode, the reaction is initiated at one end of the reaction mixture and propagates through the volume in the form of a combustion wave.^{9,10} The combustion reaction mode depends on the fuel/oxidant ratio¹⁰ and the reaction mixture packing prior to ignition.¹¹

The thermal transformation behaviour of citrate-based gel precursors has attracted the attention of many authors.^{12–17} Because of its less severe exothermic nature, the citrate-nitrate gel combustion reactions are the most widely used. Considering that citrate oxidation and nitrate reduction is complete, the reaction gas products (i.e. CO₂, N₂ and H₂O) are formed, although the oxidation state of product species is not restricted to one value but may vary. For instance, the oxidation state of nitrogen in the reaction product may vary from 0 (N₂) to 4+ (NO₂), meaning that there is no uniform chemical

description of the citrate-nitrate combustion. Although metal ions may affect the oxidation state and thus the appearance of volatile products, the citrate-nitrate redox/decomposition reaction is normally explained with a simplified reaction:¹⁶



Lanthanum chromite (LC) is one of the representative perovskites that has attracted much attention in recent years. Its potential is based on its refractory properties (melting point >2400 °C), relatively high electrical conductivity and high temperature corrosion resistance.¹⁸ The combustion synthesis of lanthanum chromite has been successfully applied by some authors.^{6,7,8} Different combustion systems for LC synthesis for stoichiometric fuel/nitrate ratios are shown in **Table 1**.

The main objective of this paper is an attempt to clarify how the citrate-nitrate gel transformation process including the combustion reaction and end LC product properties are affected by experimental conditions owing to different citrate/nitrate initial ratios.

2 EXPERIMENTAL PROCEDURES

The lanthanum chromite powders were prepared with the modified citrate nitrate combustion synthesis. The starting substances (analytical reagent grade) for reactive gel preparation were aqueous solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and citric acid. All three precursors were mixed to prepare solution which was kept over a water bath at 60 °C under vacuum ($p = 5\text{--}7$ mbar) until

it transformed into a dark violet gel (at least 3 h). The initial citrate/nitrate molar ratios in the starting solution were altered from c/n 0.13 to 0.33, as indicated in **Table 2**. The corresponding citrate nitrate gel was then crushed and pressed into pellets ($\Phi = 12$ mm, $h = 30$ mm, $p = 17$ MPa). The pellets were ignited at the top to start an auto-ignition reaction with the flame of a very small gas burner. The reaction period and maximum temperature (Pyrometer Omega Engineering OS3722 type, 900–3000 °C temperature range) were measured.

The amounts of chromium in the samples were determined with atomic absorption spectrometry. The amount of water in the reactive gels was determined with Karl-Fisher titration, while spectrophotometry was used for determination of the nitrate (after its reduction to nitrite). The thermal behaviour (TG, DTG, DTA) of the reactive gels was studied with thermogravimetric analysis (Netzsch STA 409 apparatus and TG-50 Thermobalance) at a heating rate of 10 K/min supported by mass spectrometry (Evolved gas analysis, with a Pfeiffer mass spectrometer); Agilent Micro GC 3000A, Gas Chromatograph. Differential Scanning Calorimetry analyses (DSC) were performed on Mettler standard cell DSC 20 at a heating rate of 10 K/min). The products of synthesis were determined by the X-ray powder diffraction technique using a Philips PW-1710 apparatus. A Micromeritics Gemini II 2370 was used to determine specific surface areas by the BET method. The crystallite size was determined with the Scherer method. The width of peaks at half size was automatically determined according to the program algorithm.

Table 1: An overview of LC preparation using combustion synthesis route and characteristic synthesis conditions

Tabela 1: Pregled načinov priprave LC z zgorevalno sintezo s pogoji priprave

Reducing agent	Molar ratio fuel/nitrate	Combustion temperature (°C)	SSA/(m ² /g)	Reference
TFTA-C ₄ H ₁₆ N ₆ O ₂	0.19	1100 ± 100	8.7	6
urea	0.28	1000–1050	8.2–8.1*	7
glycine	0.55	1750	17	8
(NH ₄) ₂ Cr ₂ O ₇ + glycine	0.55	1250	29	8
apdefaultCitric acid	0.18	1230	14.8	19

* calculated from the particle size

Table 2: Sample preparation conditions

Tabela 2: Pogoji priprave vzorcev

Sample	Initial ratio c/n^{**}	Combustion temperature [°C]	Combustion velocity [g/s]	SSA ^{***} /(m ² /g)	d_{110} /nm
A0.13	0.13		No self-sustaining reaction	19.1	24
B0.15	0.15		No self-sustaining reaction	23.0	18.7
C0.16	0.16		0.05	24.3	16.4
D0.18	0.18	1174	0.11	19.8	17.9
E0.23	0.23	1380	0.18	10.4	30.0
F0.28	0.28	1329	0.07	16.6	18.4
G0.33	0.33	1198	0.04	13.9	17.0

** citrate/nitrate

*** specific surface area

3 RESULTS AND DISCUSSION

The influence of the citrate/nitrate molar ratio on the reaction dynamic was determined by following the chemical composition of the various precursors and intermediates. The amounts of metal ions, water and nitrate were determined as described in the experimental procedure. To calculate the amount of citrate in the reactive gels, we performed an EGA analysis of the gases emitted by the gels during drying over a water bath. This analysis showed that under drying conditions there were no carbon oxides released from the gels, indicating that the citrate did not undergo decomposition during the gel formation. From the spectrophotometric-volumetric-water content analysis and by assuming that citrate when treated over a water bath did not decompose, the chemical formulae of the reactive citrate-nitrate gel can be calculated for the reactive gels (Table 3).

According to the results summarized in Table 3, dehydration of the starting reaction solution was accompanied by the loss of some nitrates, increasing the c/n molar ratio. It is also clear that gels lose water more easily when the c/n ratio is high; e.g. the water content in the dried gel is lower. It was also observed that pellets prepared from mixtures with a relatively high c/n ratio were less hygroscopic than those with a relatively low c/n ratio. The final c/n ratio also influences the combustion temperature and velocity (Table 2). Both were highest in the case of sample E0.23 with a final c/n ratio

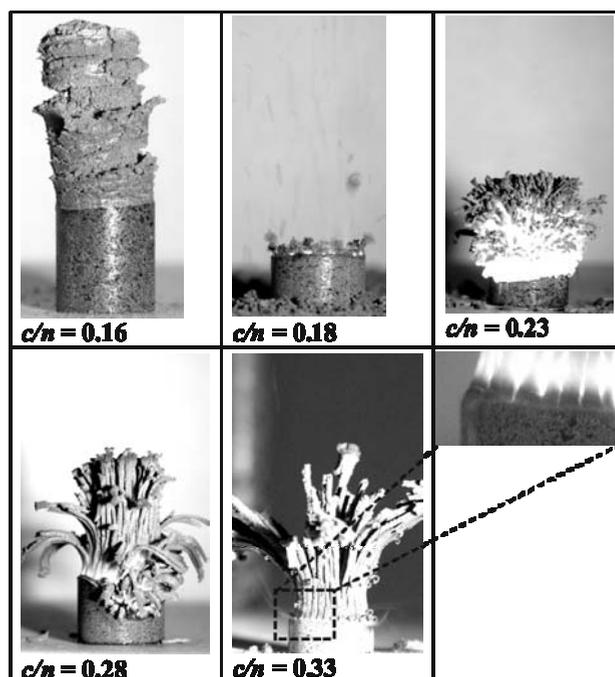


Figure 1: Photographs of gel combustion for different citrate-nitrate ratios

Slika 1: Fotografije gorenja gelov z različnimi citratno nitratnimi razmerji

of 0.27 (i.e. 0.18 g/s was the combustion velocity and 1380 °C was the combustion peak temperature) and

Table 3: Chemical composition of the dried gels

Tabela 3: Kemijska sestava sušenih gelov

Sample	Proposed chemical formula of the reactive gel	c/n ratio in the reactive gel	Intermediate preparation temperature /°C	Amount of nitrate %
A0.13	$\text{LaCr}(\text{NO}_3^-)_{4.11}(\text{C}_6\text{H}_8\text{O}_7)_{0.78}(\text{H}_2\text{O})_{5.80}$	0.19	180 380	15.58 8.03* 0.05**
B0.15	$\text{LaCr}(\text{NO}_3^-)_{4.51}(\text{C}_6\text{H}_8\text{O}_7)_{0.90}(\text{H}_2\text{O})_{5.18}$	0.20	180 380	15.73 7.98* 0.04**
C0.16	$\text{LaCr}(\text{NO}_3^-)_{4.56}(\text{C}_6\text{H}_8\text{O}_7)_{0.96}(\text{H}_2\text{O})_{5.16}$	0.21	180 320	15.44 7.98* 0.06**
D0.18	$\text{LaCr}(\text{NO}_3^-)_{4.69}(\text{C}_6\text{H}_8\text{O}_7)_{1.08}(\text{H}_2\text{O})_{4.93}$	0.23	180 310	14.45 7.87* 0.05**
E0.23	$\text{LaCr}(\text{NO}_3^-)_{5.10}(\text{C}_6\text{H}_8\text{O}_7)_{1.38}(\text{H}_2\text{O})_{4.84}$	0.27	170 300	14.12 7.69* 0.05**
F0.28	$\text{LaCr}(\text{NO}_3^-)_{5.25}(\text{C}_6\text{H}_8\text{O}_7)_{1.68}(\text{H}_2\text{O})_{3.99}$	0.32	170 290	15.83 0.3* 0.04**
G0.33	$\text{LaCr}(\text{NO}_3^-)_{5.35}(\text{C}_6\text{H}_8\text{O}_7)_{1.98}(\text{H}_2\text{O})_{3.91}$	0.37	160 240	15.86 0.2* 0.04**

* first stage intermediates, ** second stage intermediates

decreased mutually with higher or lower c/n ratios. In the case of samples A0.13 and A0.15, the final c/n ratio did not allow a self-sustaining reaction. The critical c/n ratio for this particular combustion system is between 0.19 and 0.20.

For better understanding of gel transformation behaviour during dried gel decomposition, a series of thermo-analytical tests were performed. DSC and TG in combination with EGA were used to examine the thermal stabilities of the gels and for the determination of the gases exiting the reaction mixture. These tests are probably not an ideal model of the combustion process, because the initial masses and reaction periods for complete burning are not equivalent in the two cases. Nevertheless, thermal analysis provides good insight into the combustion reaction, especially if we compare the combustion behaviour of gels with different c/n molar ratios, as indicated in **Figure 1**.

The DSC curves of the dried gels performed in air atmosphere are presented in **Figure 2**, indicating that the combustion process proceeds during several steps. The first, more pronounced step is an endothermic effect at approximately 110–130 °C. This endothermic peak is attributed to liquid phase formation (as indicated in Figure 1 for sample G0.33) prior to the combustion reaction itself. Similar results were also reported for other combustion systems.¹⁷

The first exothermic peak took place in the temperature range between 130 °C and 170 °C, depending on the gel composition (c/n ratio). The exothermicity of this step increased with the increasing c/n molar ratio; however, for samples A0.13 and B0.15 this exothermic peak was hardly noticeable. Contrary to the first exothermic effect, the second step occurred over a broader temperature range, from 180 °C to 300 °C, and was more pronounced if the c/n ratio was small. This step could be represented by two successive peaks (samples A0.13 and

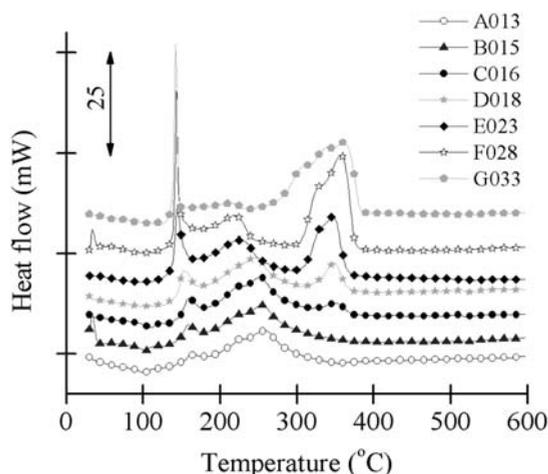


Figure 2: DSC thermal analysis plots of different citrate-nitrate gels taken in air

Slika 2: DSC analize gelov z različnimi citratno nitratnimi razmerji v zraku

B0.15) or was only slightly detectable if the c/n ratio was high (sample G0.33). The third exothermic peak was proceeding in the temperature range between 250 °C and 400 °C; the intensity of this reaction step increased with increasing c/n molar ratio. According to the literature data describing reactions in similar citrate-nitrate reaction systems,^{19,20} the third step is not related to the citrate-nitrate combustion reaction, but is rather a consequence of residual fuel burning with air.

Heat effects during citrate-nitrate combustion were usually accompanied by losses of mass of the reactive gel. Mass changes were measured with TG-DTG analysis and are presented in **Figure 3**. TG analysis confirmed that the c/n molar ratio in the gel prior to combustion has a major influence on the thermal decomposition behaviour of the citrate-nitrate precursors. The TG-DTG curves revealed several consecutive steps in mass loss if the c/n ratio was between 0.13 and 0.23 and was in accordance with DSC curves; i.e. every heat effect had its response in an equivalent mass loss. The first temperature range of higher rate mass loss occurred between 120 °C and 160 °C. This step was followed by the second stage of mass loss between 180 °C and 300 °C. The final mass loss was achieved in the temperature range between 300 and 400 °C. With an increasing c/n ratio, the DTG peaks in the temperature ranges of 120–160 °C and 300–400 °C rose, while those between 180 °C and 300 °C became less evident. Finally, if the c/n ratio was as high as 0.28 (samples F0.28 and G0.33), only two stages of rapid mass loss were detected at approximately 120 °C and in the range from 300 °C to 350 °C. Final mass losses for all samples were found to be between 64.9 % and 70.1 %.

Previous work by Couty et al.¹² proposed the existence of two types of citrate-nitrate combustion reactions. Type I occurs with reaction mixtures containing catalytically active metal ions, such as Fe, Ni, Ag, Cu, and Co, and is characterized by continuous dynamic reaction. Type II proceeds over several stages, in which an intermediate semi-decomposed precursor occurs. According to this classification, our reaction system is related to Type I reactions. Nevertheless, the thermal analysis data given in **Figures 2 and 3** show that our reaction system can correspond to both reaction types, depending on the c/n ratio. If the last step of mass loss or heat effect between 300 °C and 400 °C is a consequence of the removal of the citric acid residual step rather than citrate-nitrate combustion reaction, higher c/n ratios favour single-step combustion, while lower c/n ratios favour a several stage process.

The EGA data during thermal decomposition of various citrate-nitrate gels in a synthetic air atmosphere are shown in **Figure 4**. Synthetic air (Ar/O_2) was used instead of air (N_2/O_2) since N_2 is one of the gaseous products of the reactive gel thermal decomposition. The main mass spectrometry (MS) responses detected were at mass/charge ratio (m/e) 2, 18, 28, 30 and 44

(expressed in atomic mass units). Signals at m/e 2, 18 and 44 were attributed to H_2 , H_2O and CO_2 evolution, respectively. We excluded any NO_2 formation during combustion gel transformation because no fragmental signal at m/e 46 was detected, meaning that the signal at m/e 30 can be related to NO evolution. An indication of CO evolution was indicated by the analysis of fragmental peak at m/e 12 caused by CO_2 and the CO fragmental response. Even if the corresponding CO_2 fragmental response was subtracted from the signal at m/e 12, there was some residual peak showing the CO evolution pattern. Further, the EGA signal at m/e 28 could be caused by CO and/or N_2 evolution and partially due to CO_2 fragmental response. However, if the N_2 fragmental peak is examined carefully, and the fragmental contributions of CO and NO are subtracted from the signal, there was some residual peak contributed to N_2 generation. Therefore, it is apparent that the peak at m/e 28 follows both CO and N_2 evolution.

According to the EGA results, the gaseous products during citrate-nitrate gel decomposition were H_2O , CO , CO_2 , NO , N_2 and H_2 . In all cases, NO and N_2 were detected during the first stage of thermal decomposition in the temperature range between 160 °C and 200 °C. Some NO and N_2 were also evolved in the second

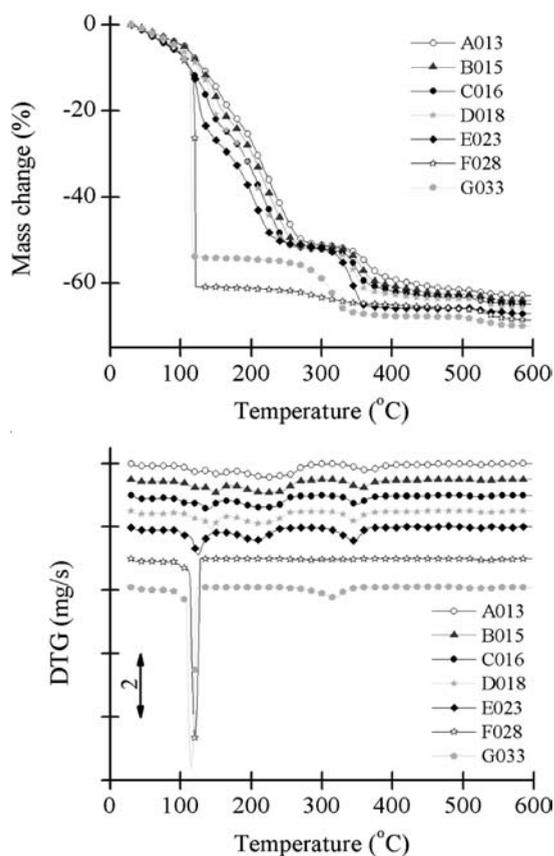


Figure 3: Mass changes of different citrate-nitrate gels taken in an air atmosphere followed by TG-DTG analysis

Slika 3: Spremembe mase gelov za različna citratno nitratna razmerja v zraku posnete z TG-DTG analizo

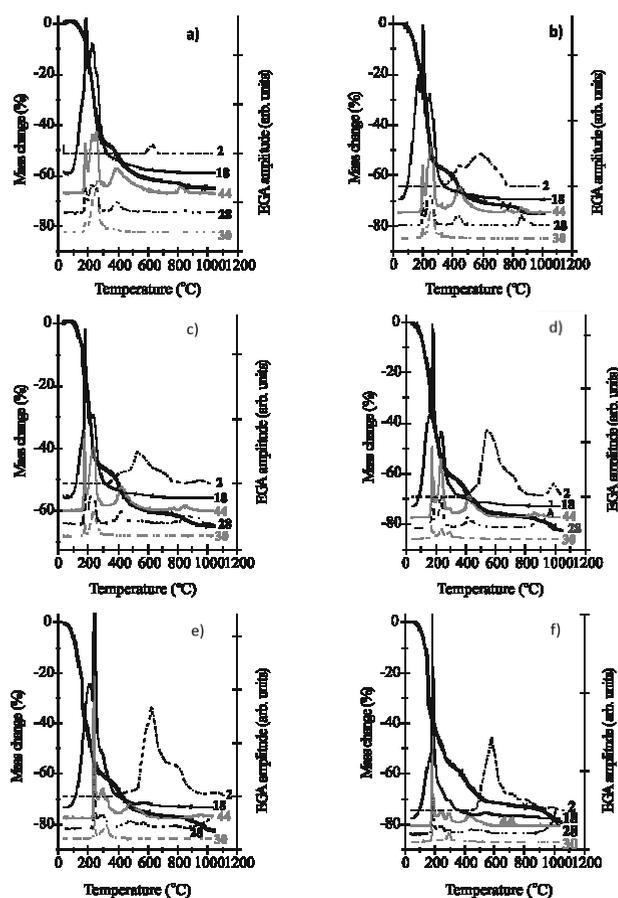


Figure 4: Evolved gas analysis by mass spectrometry for various precursors taken in synthetic air ($\varphi(O_2) = 20\%$, $\varphi(Ar) = 80\%$). (a) Sample A0.13, (b) Sample C0.16, (c) Sample D0.18, (d) Sample E0.23, (e) Sample F0.28, (f) Sample G0.33

Slika 4: Analiza EGA različnih prekurzorjev v sintetičnem zraku (20 vol.% O_2 , 80 vol.% Ar) (a) Vzorec A0.13, (b) Vzorec C0.16, (c) Vzorec D0.18, (d) Vzorec E0.23, (e) Vzorec F0.28, (f) Vzorec G0.33

temperature range, while in the third temperature range above 350 °C no NO and N_2 were detected. This confirms the assumption made on the basis of DSC and TG data that the mass loss between 300 °C and 400 °C is not a consequence of citrate-nitrate combustion itself but rather of pyrolysis of the residual citrate. The EGA results were in good agreement with the GC analysis that was performed simultaneously with the EGA analysis.

During the late stages of combustion, some H_2 was detected. H_2 evolution was not caused by citrate decomposition but was probably generated by the water gas shift (WGS) reaction. Some H_2 evolves due to the water gas shift reaction as a possible catalytic effect of lanthanum chromium oxide. At this late stage, the combustion of CO , H_2O and CO_2 products together with lanthanum chromium oxide in the reaction system leads to the WGS reaction.^{21, 22}

An insight into the course of the citrate-nitrate combustion can also be obtained by following the nitrate amount in the reactive precursors. The results of nitrate

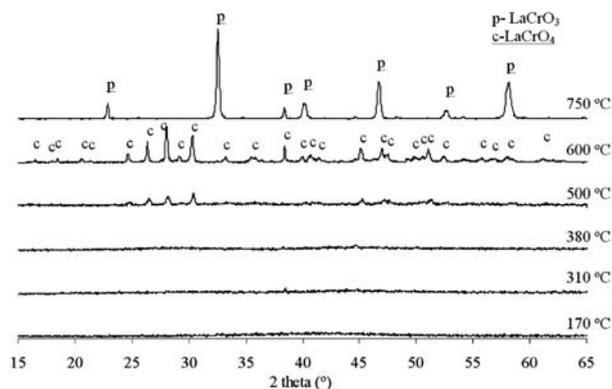


Figure 5: Phase development in E0.23 precursor during thermal treatment in air

Slika 5: Nastanek kristalnih faz v prekurzorju E0.23 pri termični obdelavi v zraku

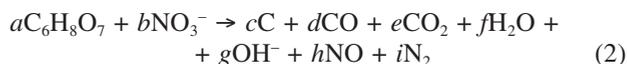
content in different precursors together with the precursors' characteristics are summarized in **Table 3**. The intermediate preparation temperature was chosen on the basis of thermal analysis results, e.g. at a temperature that a step of TG-DTG analysis was completed. As the combustion proceeds, citrate and nitrate are consumed, resulting in their diminishing content in the precursor. It is evident that the amount of nitrates in the precursors is negligible before the third stage of mass loss occurs (between 300 °C and 400 °C).

The sequence of crystalline phases formed during the course of thermal treatment of the precursor E0.23 was followed by XRD analysis (**Figure 5**). It is apparent that the intermediate precursors were amorphous at temperatures below 500 °C. The first crystalline phase found in intermediates treated above 500 °C corresponded to LaCrO_4 , and was completely crystallized at 600 °C. Lanthanum chromite in a perovskite form was identified after intermediate precursors were heated to 750 °C.

The degree of crystallization of combustion reaction products is a consequence of the reaction temperature and time. The highest combustion velocity and reaction temperature for sample E0.23 causes the highest degree of sample crystallization. From X-ray broadening of the peaks, average crystallite sizes in as-synthesized samples were calculated to be (24, 19, 16, 19, 30, 18 and 17) nm [plane perovskite (110)] for samples A0.13, D0.18, E0.23, F0.28 and G0.33, respectively.

A simplified reaction between nitrate and citrate proposed by Courty et al.¹² Eq. (1) implies a complete oxidation of the citrate without any residual carbon. However, if the citrate oxidation is performed under conditions where the stoichiometry of Eq. (1) does not apply, a part of residual organic fuel may be left in the product. An indication of residual carbon presence after the reaction is the formation of CO, H_2O and CO_2 at relatively high temperatures (1000 °C). By analogy with the reaction scheme proposed by Wang et al.¹⁷ for the nitrate-EDTA precursor and with the respect to our data obtained by the thermal analysis, the general reaction

between nitrate and citrate may be represented by Eq. (2).



Stoichiometric factors a - i depend on the conditions during the reaction. The above reaction between nitrate and citrate may be solved in various stoichiometries. However, kinetically preferred models should be based on smallest possible number of reacting molecules. By solving the above equation, the amount of the residual mass when citrate and nitrate are decomposed can be calculated. Such prediction can also be applied to the reactive gels, which (in addition to citrate and nitrate) contain metal ions and water as well. With respect to the calculated c/n ratio, the stoichiometric factors a - i in the case of sample E0.23 are 1, 4, 1, 1, 4, 2, 4, 2 and 2, respectively; the c/n ratio in the case of sample E0.23 is the closest to the stoichiometric ratio.

4 CONCLUSIONS

The citrate-nitrate combustion is very sensitive to the fuel/oxidant molar ratio prior to the reaction. The highest combustion velocity and highest combustion temperature were achieved in the case of sample E0.23 with c/n molar ratio 0.27. If the c/n ratio differs from this ratio, either up or down, the combustion rate and temperature decrease. The critical c/n ratio that still enables the self-sustaining citrate-nitrate combustion is between 0.21 and 0.23. The citrate-nitrate reaction proceeds through several separate steps. Prior to combustion, the reactive precursor melts. During thermal treatment, the citrate-nitrate decomposition takes place in the temperature range between 150 °C and 300 °C. In the temperature range between 300 °C and 400 °C, the residual citrate or its decomposition products are eliminated. According to the EGA results, the CO_2 evolution during combustion is always accompanied by CO evolution. Nitrogen leaves the reaction system partly as NO and also as N_2 . During the late stages of combustion, some H_2 evolves due to the water gas shift reaction as a possible catalytic effect of lanthanum chromium oxide. The two main crystalline phases formed in samples during the combustion process were LaCrO_4 at 500 °C and LaCrO_3 at 750 °C.

Acknowledgements

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