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**SYNTHESIS OF NANOMETER CRYSTALLINE LANTHANUM CHROMITE POWDERS BY THE CITRATE-NITRATE AUTOIGNITION REACTION<sup>†</sup>****Klementina Zupan, Stane Pejovnik, Jadran Maček***Faculty of Chemistry and Chemical Technology, University of Ljubljana*

<sup>†</sup>This paper is dedicated to the late Professor Drago Kolar

*Received 17-01-2001*

**Abstract**

Lanthanum chromite-based materials have a great potential for use in various high temperature applications and as SOFC (solid oxide fuel cell) separators. Submicron crystalline lanthanum chromite was prepared by the autoignition of a citrate-nitrate gel. The effect of the fuel-oxidant molar ratio and sample form prior to combustion was investigated in terms of phase formation, particle size, morphology, and agglomerate formation. Various characterization methods, including X-ray powder diffraction and thermal analysis, scanning electron microscopy and BET measurement, were used to evaluate powder characteristics. It was shown that the reaction period depends on the fuel/oxidant ratio and reaction mixture packing. The lanthanum chromite powders prepared via the combustion route exhibited surface areas of about 12 m<sup>2</sup>/g for the loose packed layer prepared samples and 8.8 to 13 m<sup>2</sup>/g for the samples prepared from a pellet.

**Introduction**

Preparation of complex metal oxides is traditionally carried out using solid state synthesis, i.e. the “calcining” method. A number of specialized powder preparation techniques such as the solid-solution-precursor method,<sup>1</sup> sol-gel synthesis,<sup>2</sup> coprecipitation,<sup>3</sup> and freeze drying<sup>4</sup> have been used for the preparation of multicomponent oxides. Each method has its own characteristic compositional homogeneity, powder morphology and degree of agglomeration. Combustion synthesis from solution offers a number of advantages since its low energy and time demands makes it a promising powder preparative technique. The critical factors of combustion synthesis are the fuel/oxidant ratio and the sample packing prior to ignition; these determine the temperature and reaction time, the degree of conversion, phase formation, particle morphology and the nature of the agglomerates. A large volume of released gas, which prevents coarsening and hard agglomerate formation, accompanies the exothermic effect during the fuel and nitrate reaction. In comparison with some explosive mixtures like

combinations of nitrates with urea or glycine, the citrate- nitrate gel combustion reactions are more controllable due to their much weaker exothermic reactions, thus allowing the preparation of larger amounts of the product.

Due to its chemical stability at elevated temperatures and its electrical properties, lanthanum chromite is of potential use as a material in high temperature applications such as the interconnect in solid oxide fuel cells and the electronic conductors for heating elements. However, lanthanum chromite-based materials are difficult to process into a dense gas-tight separator between the electrodes. Some of the difficulties with the interconnect formation can be diminished if the powder particles are small ( $<1\mu$ ).

In the present contribution the fuel oxidant ratios in the reaction mixtures varied and the burning proceeded either in the pellet form or in the loose packed layer form. The influence of sample form prior to combustion on the powder characteristics, phase formation and degree of conversion for undoped lanthanum chromite prepared by citrate-nitrate gel combustion synthesis is described. The applied method was derived from a citrate-gel precursor synthesis<sup>5</sup> and was first used to prepare the oxide superconductor in an Y-Ba-Cu-O system.<sup>6</sup>

### Experimental

Samples with the nominal composition  $\text{LaCrO}_3$  were prepared by combustion synthesis of citrate- nitrate gel. In the combustion synthesis, the starting materials (analytical reagent grade) were  $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . They were mixed in an appropriate molar ratio, dissolved in a minimum quantity of water, and 2.9 M citric acid solution was added. The citrate- nitrate ratios in the reaction mixtures were 0.28, 0.23 and 0.18. The dish was kept over a water bath at  $60\text{ }^\circ\text{C}$  under vacuum (2.7 kPa) until the solution transformed into a dark violet gel. To study the influence of sample packing prior to combustion synthesis, the gels were prepared in two different ways: one gel was prepared as a loose packed layer (height  $\sim 5\text{mm}$ ) while the other was uniaxially pressed (17 MPa) into a pellet (27 mm in diameter, height 15 mm,  $\rho=1.7\text{ g/cm}^3$ ). The samples were placed in an  $\text{Al}_2\text{O}_3$  crucible and ignited at one end of the reaction mixture to give lanthanum chromite powders. The reaction mixture composition and its form before ignition are summarized in Table 1.

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Samples were characterized by X-ray powder diffraction using a Philips PW-1710 apparatus. Data were collected in 15 to 75° 2 $\theta$  range in steps of 0.04° for 1s per step. TG analysis was performed on a NETZSCH STA 409C. A Micromeritics Gemini II 2370 apparatus was used to determine the specific surface areas using the BET method. The samples were also analyzed by SEM (Scanning Electron Microscope, Jeol T300).

**Table 1:** Experimental conditions for the combustion synthesis

Sample	c/n*	Sample packing prior combustion
NA	0.18	loose packed layer
NB	0.23	loose packed layer
NC	0.28	loose packed layer
NA1	0.18	pellet
NB1	0.23	pellet
NC1	0.28	pellet

\* citrate/nitrate ratio

### Results and discussion

Calculations of the stoichiometric fuel/oxidant ratio were based on the assumption that the oxidation state of the product species is not restricted to one value but may vary. By comparison with the reaction scheme of Zhang and coworker,<sup>7</sup> compositions with c/n ratios of 0.23 and 0.18 are in the stoichiometric region, while the ratio 0.28 is considered fuel-rich. Their calculations of the stoichiometric fuel/ oxidant ratio were also based on the assumption that the oxidation state of the 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 (as in N<sub>2</sub>) to 4+ (NO<sub>2</sub>).

The specific surface areas (SSA) of products, shown in Table 2, decrease with increasing citrate content in the reaction mixture. Furthermore, visual observation revealed that mixtures with c/n ratios of 0.18 and 0.23 burned at higher temperatures than the mixture with a c/n ratio of 0.28. The reaction period for the layer-formed precursors is shorter (from 4 to 10 seconds) than for the pellet-formed ones (from 20 to 120 seconds) due to the fact that the heat transfer to the surface of the pellet is retarded. Examples of combustion of NA and NA1 samples prepared from different forms of the

precursor are shown in Fig 1. The maximum black body temperature of both samples was estimated to be 1230 °C.

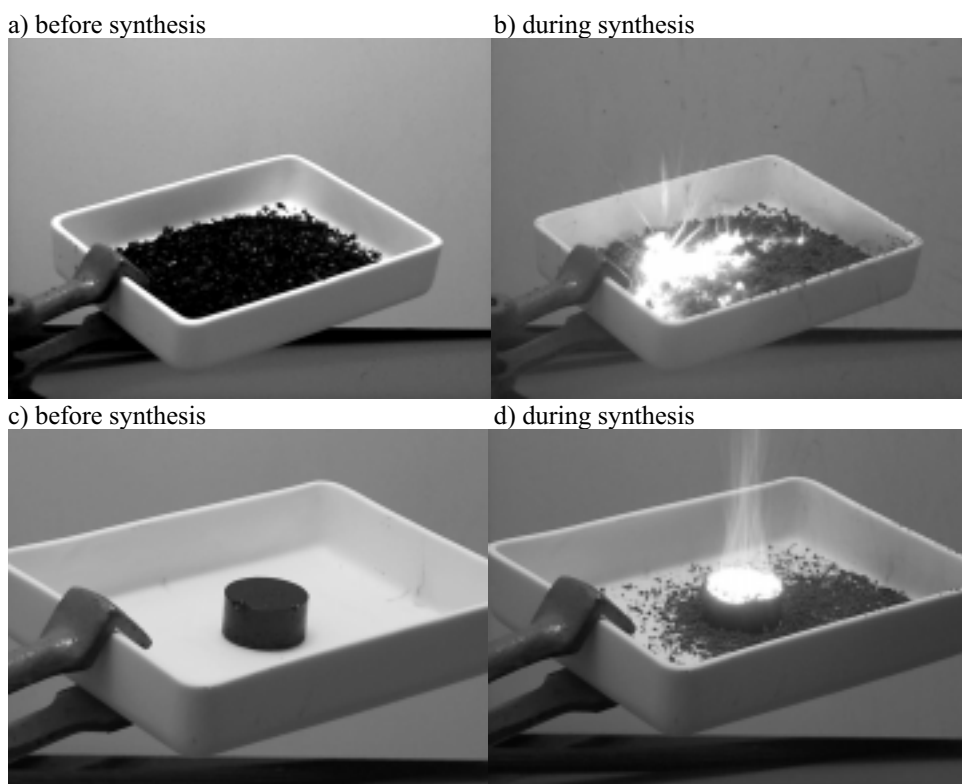


Figure 1: Photographs of the combustion synthesis of NA samples prepared in a loose packed layer (a, b) and NA1 prepared in pellet form (c, d)

The SSA of the pellet-formed powders increased from 8.8 to 13.1 m<sup>2</sup>/g with decreasing c/n ratio, while the SSA of the layer formed powders varied between 11.3 to 13.1 and was not markedly influenced by the citrate- nitrate ratio. During combustion, samples with higher c/n ratios liberate a lower amount gas, which diminishes the coarsening of the reaction products, resulting in a higher surface area. Better contact between the particles in pellet leads to the autocatalytic reaction and more pronounced effect of escaping gas than in loose reaction mixture.

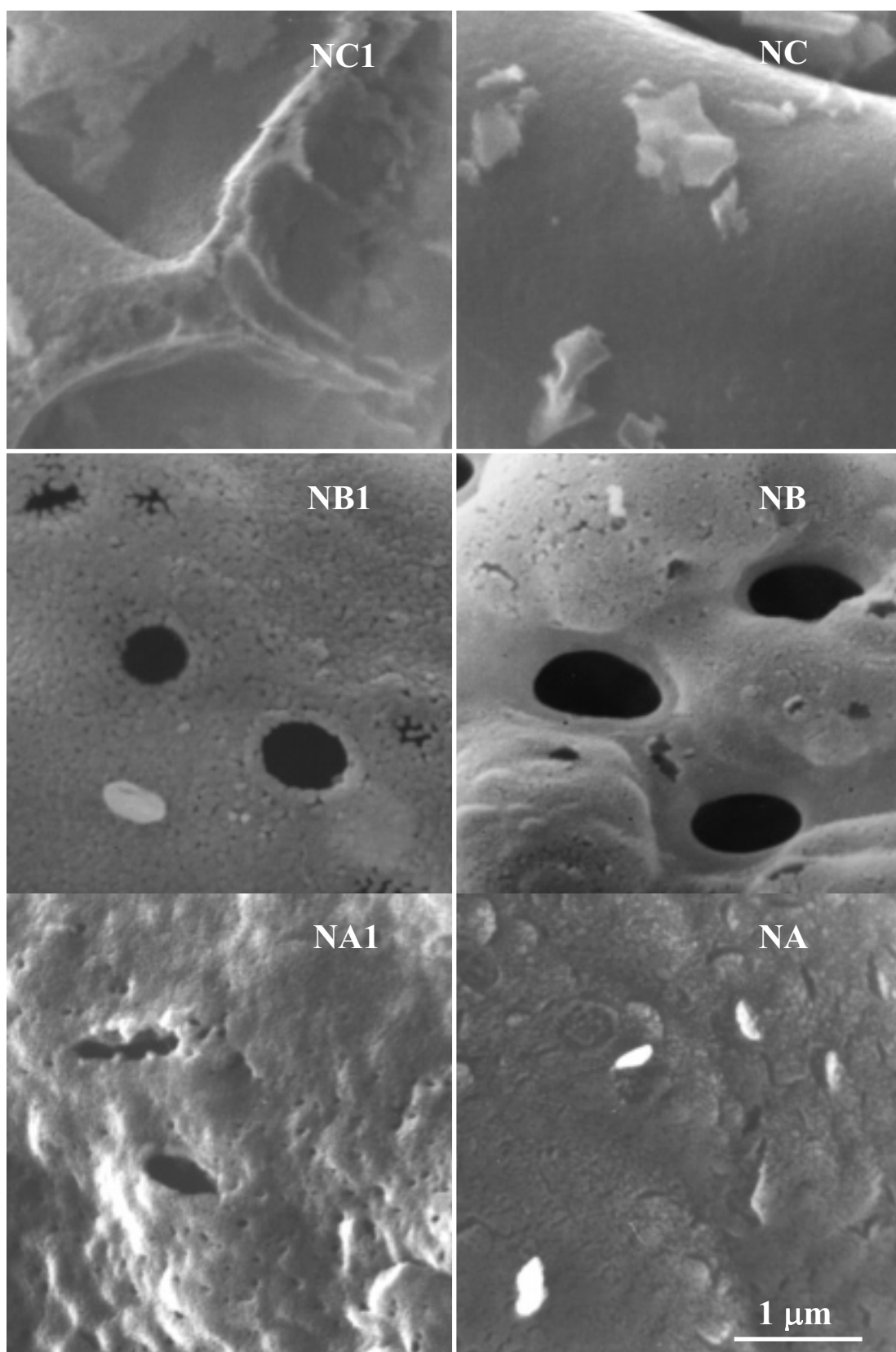


Figure 2: SEM micrographs of as prepared samples

**Table 2:** Specific surface area for all samples

Sample	SSA (m <sup>2</sup> /g)
NA	13.1
NB	10.2
NC	8.75
NA1	13.1
NB1	11.3
NC1	11.9

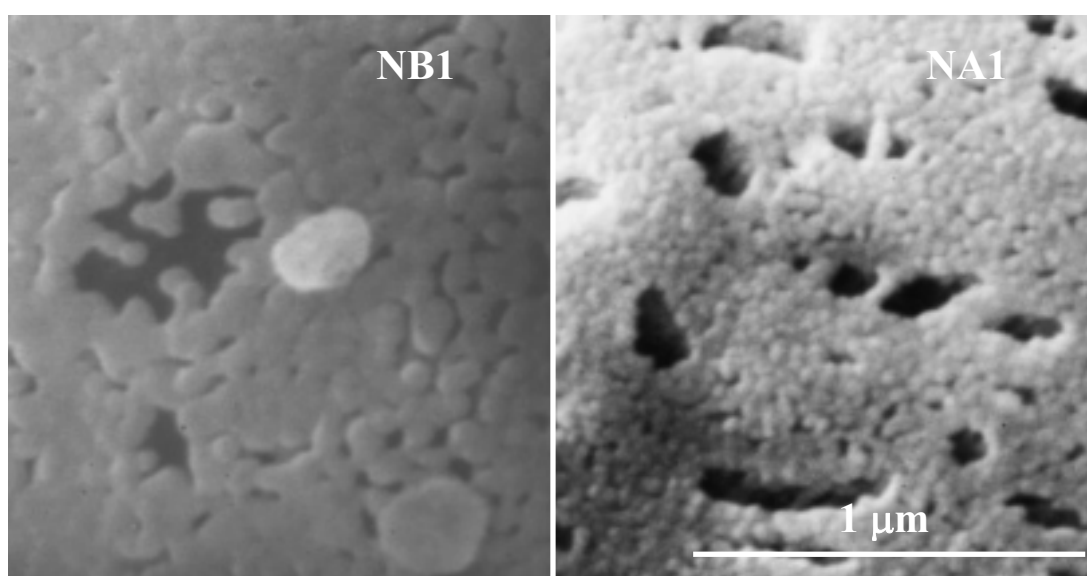


Figure 3: SEM micrographs of samples NB1 and NA1

As expected from the different experimental conditions the scanning electron micrographs of the products (given in Fig 2) show marked differences also. Samples prepared from the mixture with a c/n ratio of 0.28 are composed of dense agglomerates. Due to the lower combustion temperature, neither SEM micrograph shows any grain structure. Samples prepared from the pellet form with c/n ratios of 0.18 and 0.23 are composed of fine particles, while those in the layer form have a less pronounced grain structure. The NB1 sample is composed of particles from 80 to 250 nm in size with partial sintering observed during synthesis, whereas the porous structure of the sample NA1 is more uniform and composed of spherical particles about 50 nm in size (Fig 3).

The thermal behavior of the prepared products depends on the citrate-nitrate ratio and the precursor form prior to combustion (Fig.4.). Total mass loss increases with increasing citrate/ nitrate ratio. Minor mass losses (from 0.11 to 3.8%) were observed during thermal analysis of the pelletised samples, while mass losses of 1.5 to 12.62% for the layer form of the precursor indicates a lower degree of conversion of these samples. The optically indicated lower combustion temperature and shorter reaction time at this temperature for sample NC was confirmed by a noticeable mass loss (6.9%) in the temperature region from 400 to 600 °C due to the removal of the organic residues. The NA and NB samples prepared in the layer form showed mass losses of 1.5 and 1.9%, respectively, due to weak contact between the reaction mixture particles. Mass losses of 0.1 and 0.9% in the pelletised samples NA1 and NB1, respectively, indicate a higher degree of conversion in these samples.

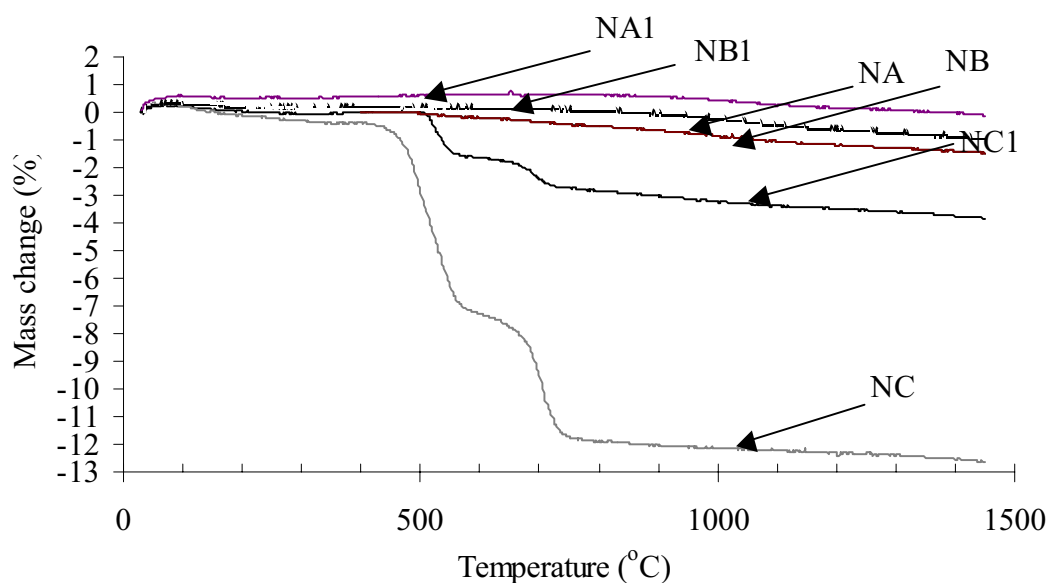


Figure 4: TG of all samples after combustion synthesis

The phase composition of all samples was determined by X-ray diffraction. The as-prepared samples were not well crystallized, being mainly composed of a perovskite crystalline phase. In layer formed precursors NA and NB, a secondary phase  $\text{La}_2\text{CrO}_6$  was found. In the samples NC and NC1 prepared from the mixture with a c/n ratio 0.28  $\text{LaCrO}_4$  was detected.

After calcination at 600 °C the sample NC (Fig 5a) contains two main phases: lanthanum chromate ( $\text{LaCrO}_4$ ), and lanthanum chromite ( $\text{LaCrO}_3$ ). According to the results of the liquid mix technique, mixtures of  $\text{LaCrO}_4$  and  $\text{LaCrO}_3$  often form at calcination temperatures below 600 °C.<sup>8</sup> Several secondary phases for example  $\text{CrOOH}$ ,  $\text{La}_2\text{CrO}_6$  and  $\text{Cr}_3\text{O}_4$  were found due to the low temperature of the synthesis and the poor contact between the gel particles in the layer form. Some peaks in that sample also remained undetermined. After heat treatment at 750 °C a chromite phase and traces of a chromium rich phase ( $\text{LaCr}_2\text{O}_6$ ) were found in the sample NC. By contrast after calcination at 600 °C and 750 °C the only phase determined for sample NA1 was lanthanum chromite (Fig 5b).

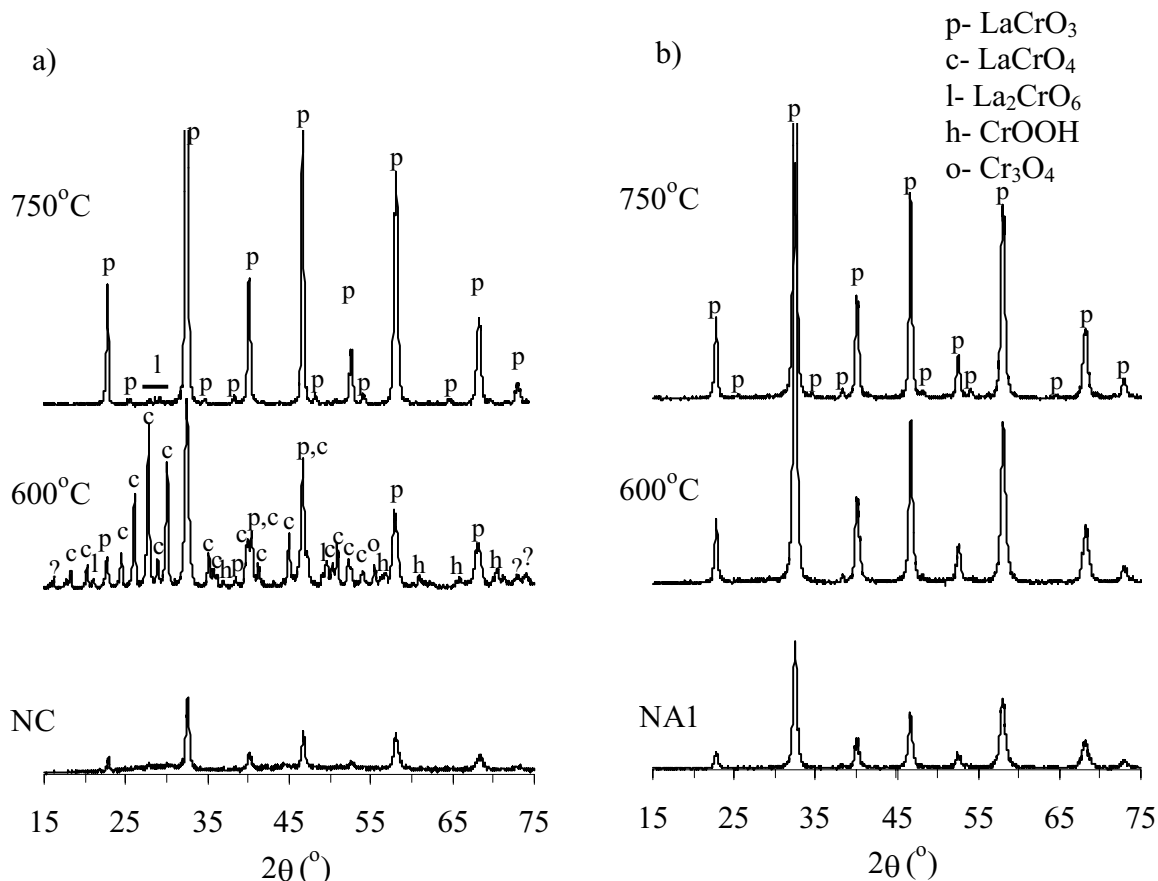


Figure 5: X-ray diffraction patterns of as -prepared samples a) NC and b) NA1 , calcined at 600 °C and 750 °C.



### Conclusions

The fuel/ oxidant ratio and the reaction mixture form prior to the combustion (loose powder layer or compacted pellet) influence lanthanum chromite powder properties after combustion. Temperature gradients during synthesis, the relatively short times at combustion temperature, and the poor contacts between the gel particles in the layered form of the precursors result in a lower degree of conversion. The best products are obtained where a citrate/ nitrate ratio of 0.18 or 0.23 is used and the combustion is performed in a pellet form. In this case, the total mass loss after the combustion does not exceed 1%.

### Acknowledgements

Authors wish to thank the Ministry of Science and Technology for the financial support of the project.

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### Povzetek

Materiali na osnovi lantanovega kromita so primerni za uporabo pri visokih temperaturah, pri katerih deluje tudi povezovalni element v gorivnih celicah s trdnim elektrolitom. Nanometerski lantanov kromit smo pripravili z zgovalno sintezo citratno nitratnega gela. Ugotavljali smo vpliv molskega razmerja gorivo- oksidant in obliko zgovalne zmesi pred sintezo na fazno sestavo, stopnjo pretvorbe, velikost delcev, morfologijo ter nastanek aglomeratov v produktu po sintezi.