



Phase formation and electrical properties of the LaCoO_3 obtained by water-based sol-gel method with citric acid

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Abstract

In the present work the LaCoO_3 formation from gel precursors obtained by water-based sol-gel method with citric acid was studied. As precursors La and Co nitrates were used. The obtained gels were analyzed by TG/DTA and TG/EGA. The decomposition of the gels takes place in two main steps with the evolution of the same volatile compounds (H_2O , CO_2 and NO_2) leading to the conclusion that two types of bonding of the components in the gels occurred. The decomposition of the gels takes place up to 400°C . The gels thermally treated at 600°C lead to single pure perovskite rhombohedral phase of lanthanum cobalt oxide (LaCoO_3). Some electrical properties of LaCoO_3 measured in “operando” conditions, i.e. in gas flow, at atmospheric pressure (by using the differential step technique DST) are presented and discussed.

Keywords: sol-gel method, LaCoO_3 , electrical properties

I. Introduction

LaCoO_3 has a lot of potential applications such as: oxygen permeable membranes, materials for electrodes in combustion cells with solid electrolytes (SOFC) and can be used as chemical sensors or in catalysis.

In order to prepare LaCoO_3 , the oxide-mixing method followed by solid state reaction between the metal oxides components is still used. This method offer lower manufacturing cost and more simple preparation process but usually requires annealing temperature higher than 1000°C in order to ensure the complete reaction of the starting oxides and the obtaining of the final product as a single phase. In the literature data in order to overcome the inevitable disadvantages of the solid state reaction procedure, some methods including sol-gel, hydrothermal and coprecipitation techniques have been proposed [1–8].

The main objective of this work was to prepare LaCoO_3 by sol-gel method, aqueous route, starting with inorganic salts in the presence of citric acid as chelating agent.

II. Experimental

Precursors gel preparation

Lanthanum cobalt oxide was prepared from gel precursors obtained by sol-gel method, inorganic-carboxylic route. A lanthanum cobalt citrate (La-Co-CA) precursor with La : Co : CA = 1 : 1 : 1 was prepared by the following procedure. An aqueous solution of 0.25 M of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 M of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was realized. To this solution solid citric acid was added in the molar ratio of citric acid/total cations of 1, and the mixture was intensively stirred until a clear solution was formed. The solution was gelled at 100°C for 24 h. The La-citric (La-CA) and Co-citric (Co-CA) mono-component gels were also obtained by a similar procedure.

Gel and powder characterization

The thermal behaviour of the precursor gels was determined by TG/DTA using a Netzsch-STA 409C/CD instrument coupled with a Balzers Thermastar GSD 300D mass spectrometer. The measurements were carried out in Al_2O_3 crucibles, air atmosphere, at the maximum temperature of 740°C and the heating rate of $5^\circ\text{C}/\text{min}$.

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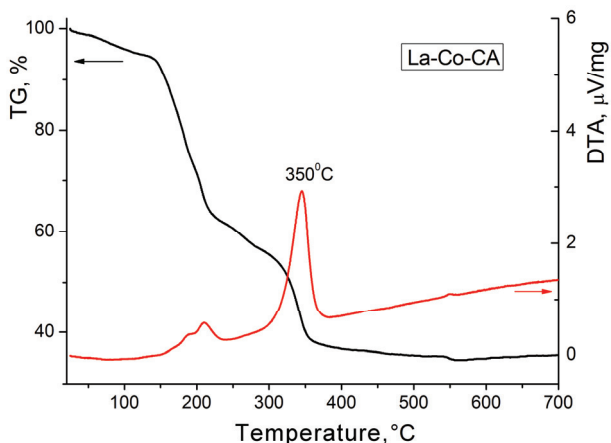


Figure 1. The DTA/TG curves of the thermal decomposition of La-Co-CA gel

The structural evolution of the annealed samples were determined by X-ray diffraction, using a CuK α ($\lambda = 0.1540$ nm) radiation source in a Bruker AXS D4

Endeavor X-ray diffractometer. The diffraction angle (2θ) ranging between 10° and 90° was scanned.

The particle size and morphology of the samples was characterized with a JEOL JSM-5800 scanning microscope.

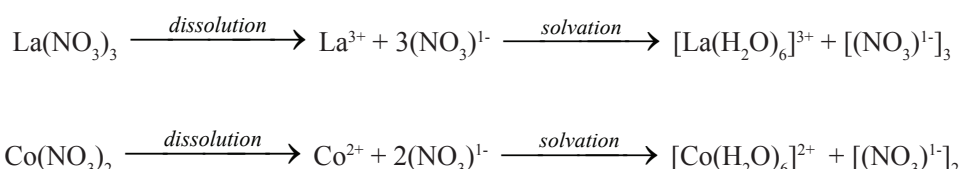
The *ac* electrical conductivity of the sample was measured in situ, *in operando* conditions, by using a special reaction cell coupled to a semiautomatic RLC bridge Tesla BM 484 (at 1592 Hz) and the differential step technique (DST). As shown previously [9], it consists of successive heating-cooling cycles of the same sample in various atmospheres that in our case were dry helium and dry oxygen.

III. Results and discussion

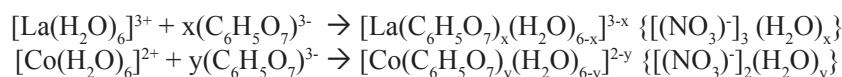
In the experimental conditions presented above an amorphous red La-Co-CA gel was obtained.

Based on the literature data [10] the following gelation mechanism could be considered as:

- 1) Dissolution of metal salts in water. In the salts solution with $\text{pH} = 2$, aquo-cations are formed:



- 2) Complexation and chemically controlled condensation in the presence of citric acid:



- 3) Formation of metals-citric acid chelate:

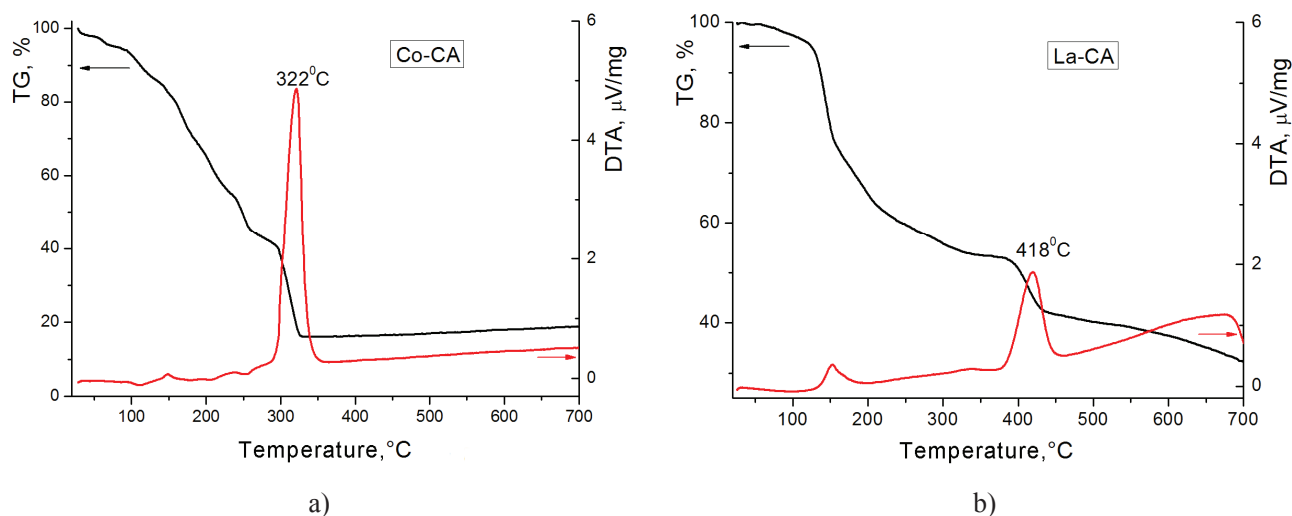
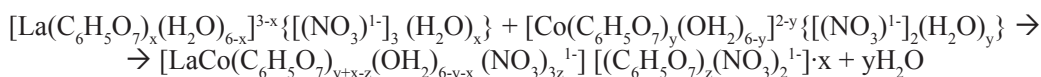


Figure 2. The TG/DTA curves of the thermal decomposition of monocomponent gels: a) Co-CA and b) La-CA

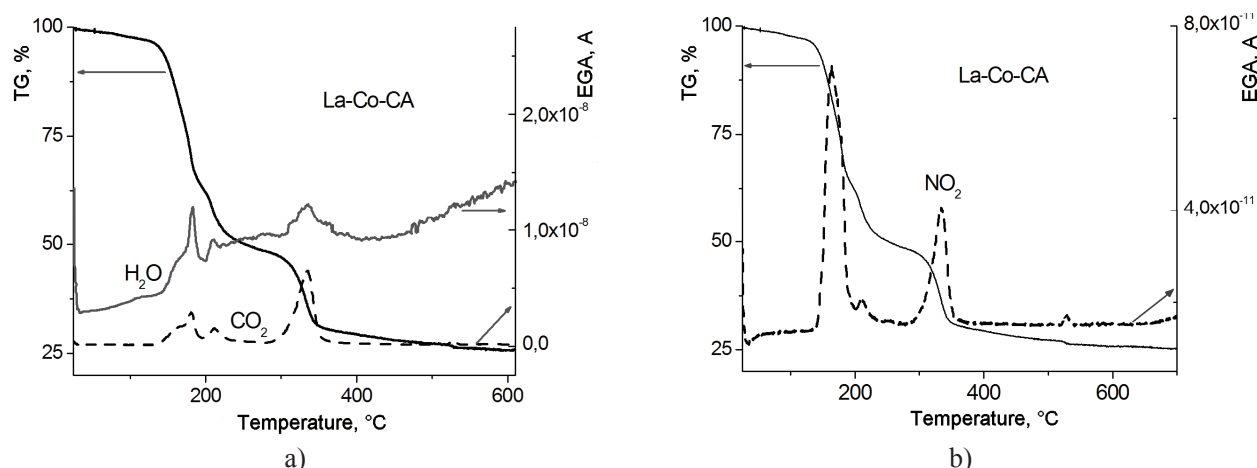


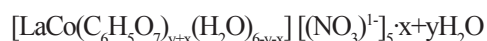
Figure 3. TG/EGA curves of La-Co-CA gel, evolution of a) H₂O and CO₂ and b) NO₂

DTA/TG analysis of the obtained La-Co-CA gel is presented in Fig. 1. The total weight loss is 68%. It starts at 80°C with evaporation of absorbed water and occurs stepwise. Over the temperature of 400°C there is a low change in weight loss slope without thermal effects. On the DTA curve, a strong exothermic effect, with a maximum at 350°C is observed, indicating that the thermal events can be primarily associated with the gel-compounds decomposition accompanied with the burning out of the organic residues.

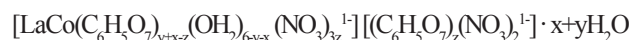
Based on the thermal behaviour of the binary gel, the thermal behaviour of the mono-component gel was also studied. The TG/DTA curves of the mono-component Co-CA and La-CA gels are presented in the Fig. 2a and Fig. 2b, respectively. An important exothermal effect in the case of the Co nitrate-citric acid (Co-CA) gel is observed at 322°C, while for the La nitrate-citric acid (La-CA) gel a similar effect occurs at 418°C. The main decomposition effect of the binary La-Co complex (La-Co-CA) gel lies between the decomposition effects of the mono-component complexes. Thus,

it can be concluded that in the case of the binary system a mixture of phases does not occur, but a complex gel was formed.

The thermal decomposition of the gel precursors after drying at 80°C was followed by simultaneous thermal analysis (thermogravimetry and differential thermal analysis) coupled with a mass spectrometer for the analysis of evolved gases (EGA). The TG/EGA curve for the La-Co-CA gel is presented in Fig. 3. The TG/EGA results show that the complex gel decomposes at two different temperatures (200°C and 350°C), with the evolution of the same gases (NO₂, CO₂ and H₂O). This means that the water, citric acid and nitric reagents are bound on two different ways in the complex gel. The initially proposed formula based on literature [10] date was the following:



In this formula citric acid is bound on the position of a coordinated ligand. But, based on the TG/AEG results the real formula could be the following:



In this formula citric acid and the nitrate are bound on two positions as weakly bound ligands (I) and as coordinated ligands (II). The decomposition of the complex gel occurs in the following steps:

- In the first step, in the range of 150–250°C, the total weight loss was 37.84% and the weakly bound ligands were eliminated.
- In the second step, in the range of 250–400°C, the total weight loss was 28.82% and the coordinated ligands were eliminated; one may assume that at 400°C the gel precursor decomposition is finished.
- In the third step, in the range of 400–700°C, the total weight loss was 7.30% and could be assigned to the evolution of the gases retained on the resulted oxide nanoparticles.

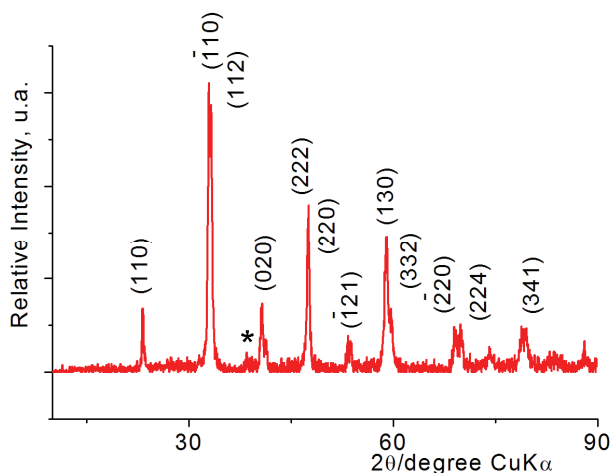


Figure 4. The XRD pattern of LaCoO₃, thermally treated at 600°C (* Al holder)

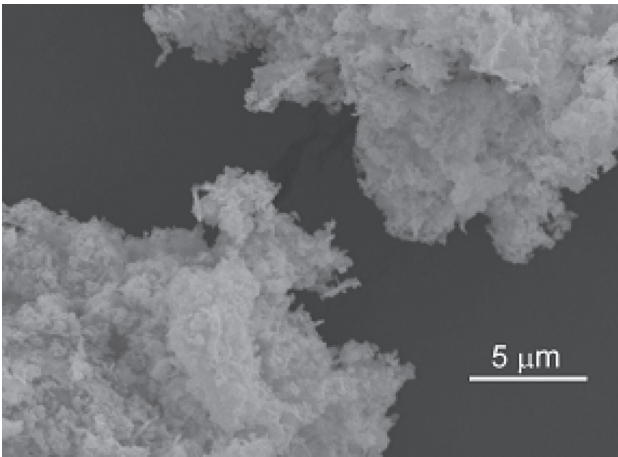


Figure 5. SEM image of the sample thermally treated at 600°C

Based on the thermal behaviour of the complex gel, the thermal treatment for the obtained LaCoO_3 was the following: heating rate of 1°C/min up to 400°C with 1 hour plateau and heating rate of 5°C/min up to 600°C with 6 hours plateau.

In Fig. 4 the XRD patterns of LaCoO_3 thermally treated at 600°C are presented. The X-ray diffraction result evidenced that the pure phase of LaCoO_3 with rhombohedral structure was obtained at 600°C.

The SEM micrograph of the sample, presented in the Fig. 5 show strongly aggregated particles with dimensions in the 10–50 μm range.

Some preliminary investigations on the electrical properties of similar thermally treated powder were previously published [9]. In the present case the protocol of changing the gases was increased to a higher number of cycles in order to achieve a better characterization of the powders (Fig. 6). Three different gases (dry helium, DHe, dry oxygen, DO, and mixture C_3H_6 : air = 1 : 22, CT) and different number of cycles (upto 4) were used. As previously determined, in the present case, at the temperatures between 20 and 400°C the sample also behaves as an n-type semiconductor (Fig. 6).

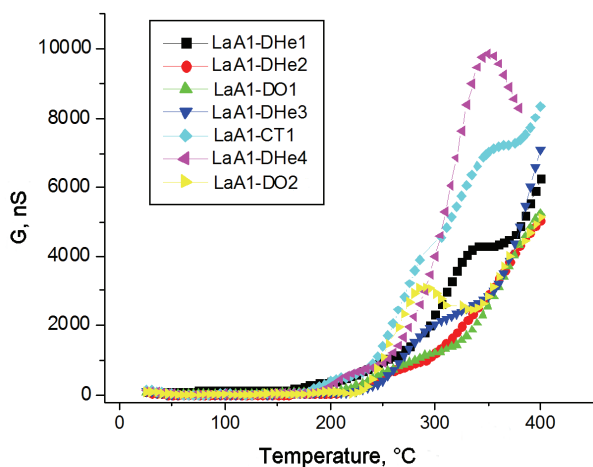


Figure 6. Temperature dependence of LaCoO_3 conductance G during heating in various atmospheres (DHe - dry helium, DO - dry oxygen, CT - C_3H_6 /air mixture)

IV. Conclusions

- LaCoO_3 was prepared from precursors obtained by sol-gel method using citric acid as chelating agent and nitrates as metal precursors.
- The TG/DTA coupled with mass spectrometry showed the complex composition of the obtained gels and their decomposition in several steps.
- By adequate thermal treatment, based on the TG/DTA results pure phase of LaCoO_3 with rhombohedral structure was obtained at 600°C.
- The XRD results confirmed the formation of LaCoO_3 with a perovskite structure.
- SEM showed the agglomeration tendency of the LaCoO_3 particles that forms porous aggregates.
- In the temperature range between 20–400°C the sample behaves as an n-type semiconductor.

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