



*Dedicated to Professor Bogdan C. Simionescu  
on the occasion of his 70th anniversary*

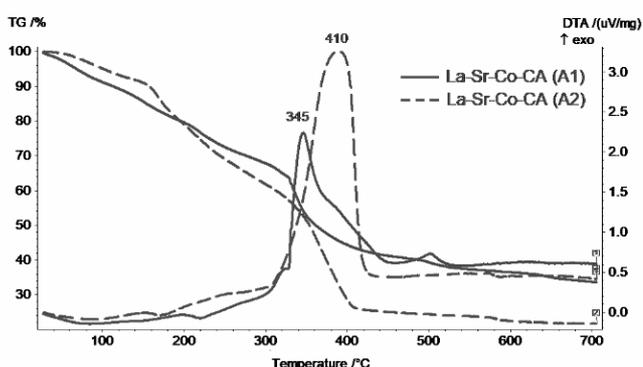
## INFLUENCE OF THE PRECURSORS ON THE $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ FORMATION BY WATER-BASED SOL-GEL METHOD

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Strontium-doped lanthanum-cobalt oxides are studied because they can be used in fuel cells, oxygen penetration membranes, and as electrodes in ferroelectric memory technology due to their relative high electrical and ionic conductivity. In the present paper the influence of the precursors on the formation of the  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (LSCO) obtained by water-based sol-gel method is studied. Metal nitrates or acetates were used as precursors, while citric acid was added as chelating agent. The synthesis was carried out in an aqueous medium at room temperature, leading to amorphous gels formation. The thermal decomposition of the samples was investigated. By thermal treatment of the as-prepared gels, the formation of the  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  perovskite phase was observed already at 600°C. Supplementary thermal treatment at 1000 °C leads to obtaining pure rhombohedral perovskite phase starting with acetates, while using nitrates precursors, beside perovskite small amount of  $\text{Co}_3\text{O}_4$  and SrO could be identified. The relation between the reaction of the precursors in solution, crystallization pathway and the structure and morphology of the resulted  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  is discussed.



### INTRODUCTION

A comprehensive definition of the sol-gel method assumes that the process represents the formation of an inorganic polymeric network by reactions in the solution at low temperatures. In the second step, by adequate thermal treatments, the conversion of the inorganic amorphous polymers takes place either into glasses or crystalline materials.<sup>1</sup>

As it is well established, alkoxides were the first, and are the mostly used reagents in the sol-gel synthesis, but inorganic or organic salts are also frequently used. Based on the type of precursors and on the reaction medium used, two types of sol-gel processes were developed: in alcoholic (organic) or in aqueous medium.

The aqueous sol-gel method has also two pathways: the colloidal route,<sup>2</sup> and the aqueous route using different chelating agents.<sup>3-5</sup>

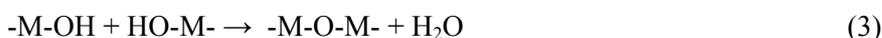
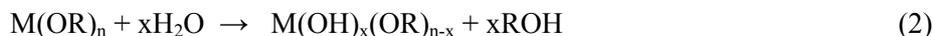
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According to Pierre<sup>5</sup> in both alkoxide and aqueous sol-gel routes, the precursors undertake

the similar succession of transformations in the presence of water:



In the case of alkoxide-based route (non-ionized precursors) the reactions that occur are the following:



while the dissociated precursors (metallic salts in aqueous solutions) react as follows:



where A = chelating agent.

Based on the presented reactions, clearly results that the chelating agent is an important reagent in the aqueous gel formation.

The sol-gel method using chelating agents – polyethylene glycol, citric acid or polyacrylic acid – is considered an important technique since it presents the advantage to control few parameters such as the stoichiometry, particle size distribution, temperature and duration of thermal treatment.

Highly strontium-doped lanthanum-cobalt oxide, such as  $La_{0.5}Sr_{0.5}CoO_3$  (LSCO), is studied due to its relative high electrical and ionic conductivity that makes it applicable in fuel cells, oxygen penetration membranes and as electrodes in ferroelectric memory technology.<sup>6,7</sup> Since LSCO has a cubic perovskite crystal structure it has been used as the electrode with most widely applied perovskite ferroelectrics like  $Pb(Zr,Ti)O_3$ ,  $(Pb,L a)(Zr,Ti)O_3$  and  $(Ba,Sr)TiO_3$ . Compared to the conventional Pt electrode, these devices using LSCO as an electrode material have better structural/chemical compatibility and a cleaner interface (less charged defects) between LSCO and the dielectric materials, which contribute to the superior device performance.<sup>8-10</sup>

Using the aqueous sol-gel method in the presence of chelating agents for preparation of pure  $LaCoO_3$ <sup>11,12</sup> or  $LiCoO_2$ <sup>13,14</sup> was previously mentioned.

In the present paper the study of the influence of the precursors on the formation of the strontium doped  $LaCoO_3$  obtained by water-based sol-gel method is approached.

## EXPERIMENTAL

### Precursors gel preparation

Lanthanum-strontium-cobalt oxide was prepared from gel precursors obtained by the sol-gel method, inorganic-carboxylic route. The precursors were  $La(NO_3)_3 \cdot 6H_2O$  or  $La(CH_3COO)_3 \cdot 2H_2O$  (Aldrich) as source of  $La_2O_3$ ,  $Sr(NO_3)_2 \cdot 6H_2O$  or  $Sr(CH_3COO)_2 \cdot 4H_2O$  (Aldrich) as source

of  $SrO$ ,  $Co(NO_3)_2 \cdot 6H_2O$  or  $Co(CH_3COO)_2 \cdot 4H_2O$  (Aldrich) as source of  $CoO$  and citric acid (CA) as chelating agent. A lanthanum strontium cobalt citrate precursor with  $La: Sr: Co: CA = 0.5: 0.5: 1: 1$  or  $0.5: 0.5: 1: 2$  molar ratio was realized by the following preparation procedure: 0.25 M aqueous solution of the precursors salt was prepared. To this solution solid citric acid was added and the mixture was intensively stirred, until a clear solution was formed. The as prepared solution was left for gelling at room temperature. The gellation occurred after 30 days.

Based on the results of the thermal investigation presented below, the gels were thermally treated in air at 400°C for 1 h with a heating rate of 1°C/min and at 600°C or 1000°C for 6 h with a heating rate of 5°C/min. The annealed samples were investigated by structural and morphological investigations such as: XRD, SEM and FT-IR.

The samples obtained from nitrates were labeled N, while the samples obtained from acetates were labeled A.

### Investigation methods

The morphology of the samples was investigated by scanning electron microscopy (SEM) using a high-resolution microscope, FEI Quanta 3D FEG model, operating at 15 kV, equipped with an energy dispersive X-ray (EDX) spectrometer Apollo X. The analyses were done in high vacuum mode, with Everhart-Thornley secondary electron detector.

The structural characterization of the gel was carried out by IR spectroscopy using PERKIN ELMER FT-IR Spectrometer 1720X and fluorolube or paraffinum oil.

The thermal behavior of samples was determined by TG/DTA using a NETZSCH STA 409C/CD instrument coupled with a mass spectrometer, Balzers Thermastar GSD 300D, for the analysis of evolved gases (EGA). The maximum temperature was set to 740 °C, the heating rate to 5 °C/min in air atmosphere and  $Al_2O_3$  crucibles were used.

Powder X-ray diffraction experiments were performed by using a BRUKER AXS D4 ENDEAVOR diffractometer using a  $Cu K\alpha$  (wavelength 0.1540 nm) radiation source operating at 40 kV and 30 mA. The diffraction angle ( $2\theta$ ) ranging between 10 and 80 was scanned.

## RESULTS AND DISCUSSION

In the experimental conditions presented above, starting both with nitrates and acetates reagents amorphous red gels were obtained.

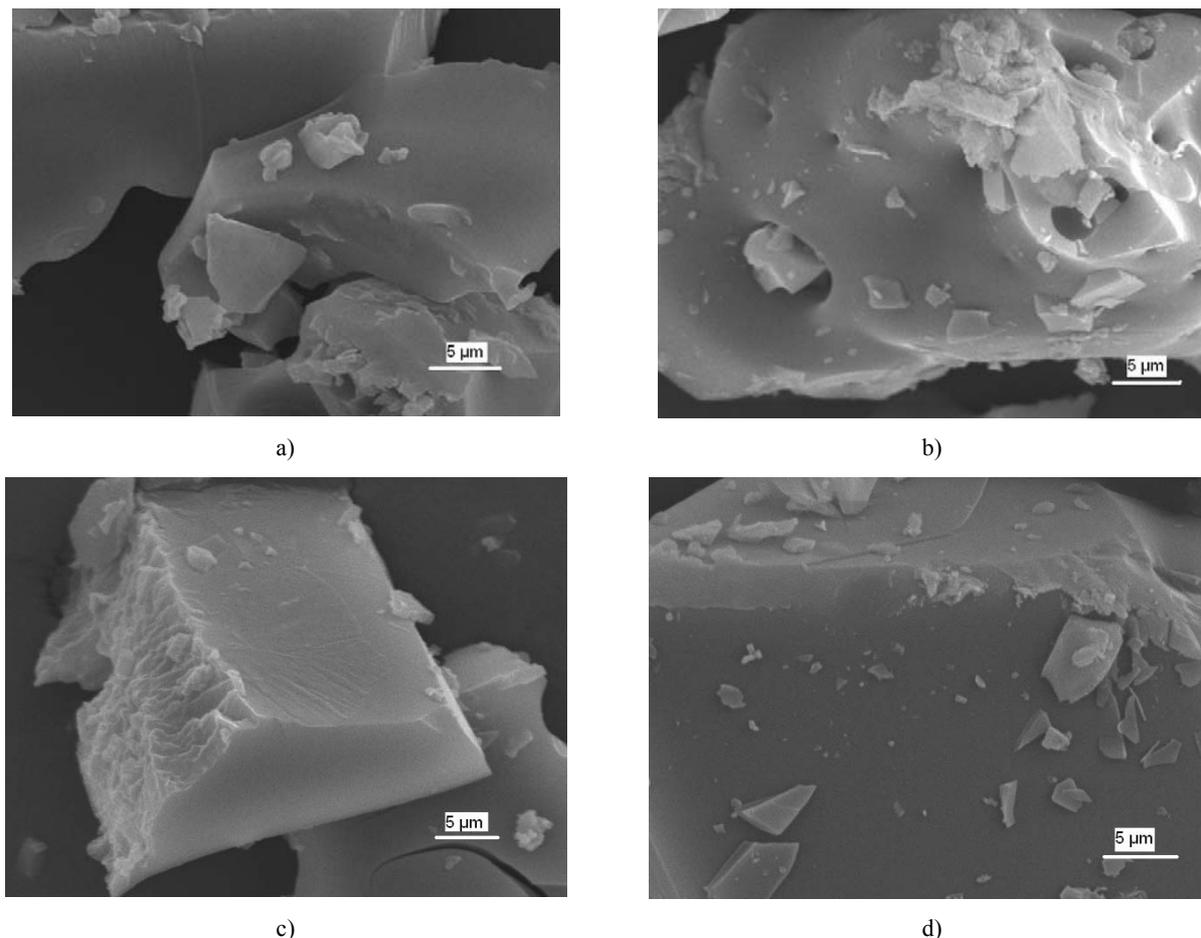


Fig. 1 – SEM images of the samples obtained from La-Sr-Co-CA nitrate or acetate dried gels a) N1, b) N2, c) A1, d) A2.

### As prepared gels

The morphology, structure and thermal behavior of the as prepared gels were established by SEM, FT-IR, XRD and TG/DTA/EGA investigations.

SEM images for the as-prepared gels are presented in Fig. 1.

In the presented SEM micrographs not high differences were noticed in the morphology of as-prepared samples, that corresponds to homogeneous gel aggregates.

The FT-IR spectra of the obtained gels are presented in Fig. 2 a and b.

The broad absorption bands (not shown here) between  $3420\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$  indicate the presence of the hydroxyl groups. The two absorptions can be assigned to the two types of hydroxyl groups in the gel, one belonging to the carboxyl while the other one to the water.

For La-Sr-Co-CA (N) gel the main vibration peaks are situated between  $1800$  and  $1000\text{ cm}^{-1}$ . The carbonyl stretchings are observed between  $1720$  and  $1438\text{ cm}^{-1}$  indicating the ionization of all the carboxyl groups, thus enabling the complex gel formation.<sup>15,16</sup> According to the literature data,<sup>17,18</sup> the frequency

separation between the asymmetric and symmetric stretching vibrations,  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$ ,  $\Delta\nu = 282\text{ cm}^{-1}$ , suggests that the carboxyl groups provided by the citric acid act as monodentate ligand in the nitrate-derived gel.

In the spectrum of the La-Sr-Co-CA (A) gel, the carbonyl stretchings are observed between  $1588$  and  $1400\text{ cm}^{-1}$  with the frequency separation,  $\Delta\nu = 188\text{ cm}^{-1}$ , which indicates that the carboxylic groups act as a bidentate ligand. In the case of the A2 sample with higher amount of chelating agent the supplementary peak observed at  $1717\text{ cm}^{-1}$  could be assigned to the not-coordinated citric acid.

Similar frequency separation was also observed in the case of undoped  $\text{LaCoO}_3$  samples.<sup>11</sup> In the mentioned case  $\Delta\nu$  is  $295\text{ cm}^{-1}$  for nitrate-derived gels and  $193\text{ cm}^{-1}$  for acetate-derived gels.

The band around  $1382\text{ cm}^{-1}$  is assigned to the  $\text{NO}_3^-$  vibration and the band at  $1620\text{ cm}^{-1}$  is assigned to the bending vibration of the molecular water. The bands situated between  $1250$  and  $1000\text{ cm}^{-1}$  are attributed to the vibration modes assigned to the citric acid, namely  $1241$  or  $1235\text{ cm}^{-1}$  to  $\nu\text{-COOH}$ ,  $1150\text{ cm}^{-1}$  to skeleton vibration and  $1078\text{ cm}^{-1}$  to  $\pi\text{CH}$ .

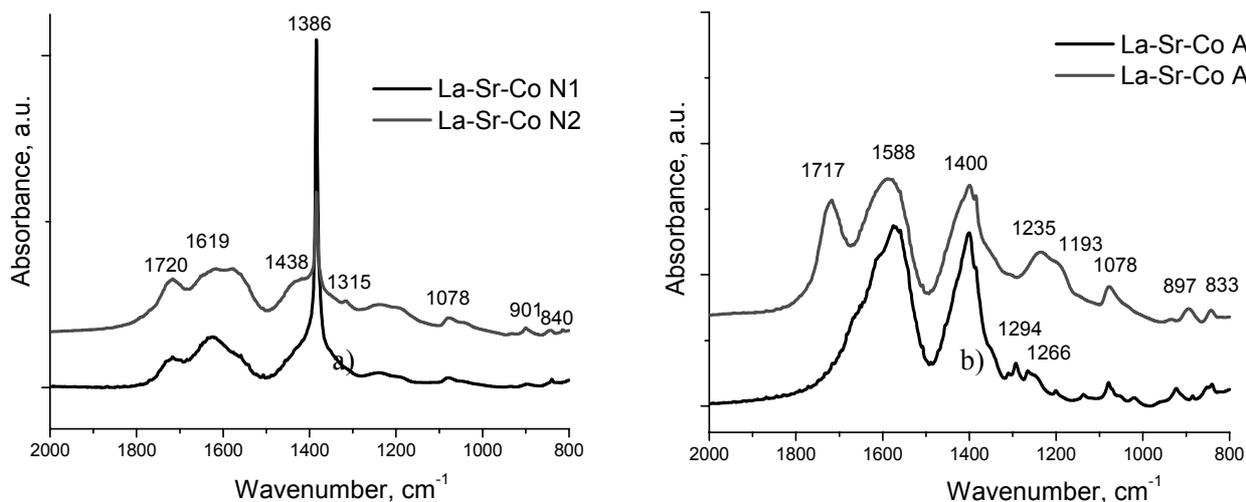


Fig. 2 – The FT-IR spectra of the La-Co-CA gels, starting with nitrate (N) and acetate (A).

The DTA/TG analyses of the obtained gels were presented in Fig. 3 and the TG/EGA in Fig. 4.

The DTA/TG curves of nitrate derived gels are presented in Fig. 3a. The TG curves presented a total mass loss of 69% for both samples. It starts at 80 °C with absorbed water evolution and it occurs stepwise. Over the temperature of 400 °C there is a low change in mass loss slope. On the DTA curve, a strong exothermic effect, with a maximum at 312 °C in case of N1 or 380 °C in case of N2 is observed, indicating that the thermal events can be mainly associated with the gelic compounds decomposition accompanied with the burning out of the organic residues.

In the case of acetate derived gels the DTA/TG curves are presented in Fig. 3b. The total mass loss is different depending on the amount of citric acid (CA). In the case of gel A1 the total mass loss was

56% while in the case of A2 it was 74%. For gels obtained from acetate no weight loss is observed after 400 °C. On the DTA curve, a strong exothermic effect, with a maximum at 345 °C in case of A1, or 410 °C in case of A2 is observed.

In the case of acetate derived gel (A1) the DTA curve shows beside the mentioned main exothermal peak a shoulder at about 364 °C and a small exothermal effect at 502 °C underlying a more complex composition of the resulted gel.

The thermal decomposition of the gel precursors was also 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 curves are presented in Figs. 4 for the N1 and A1 samples, obtained in the presence of the lowest amount of chelating agent.

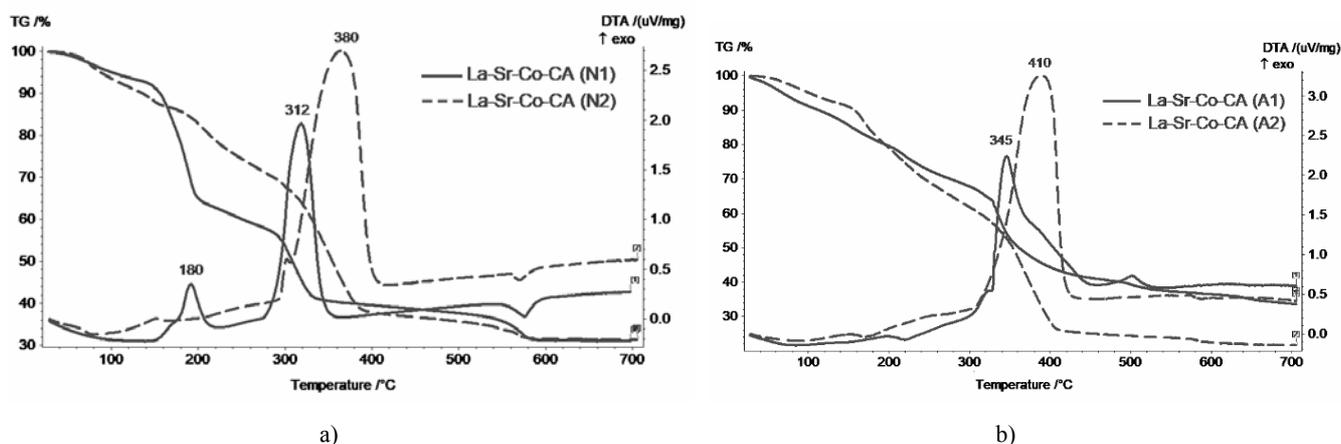


Fig. 3 – DTA/TG curves of the thermal decomposition of the as-prepared gels: a) nitrate (N) and (b) acetate (A).

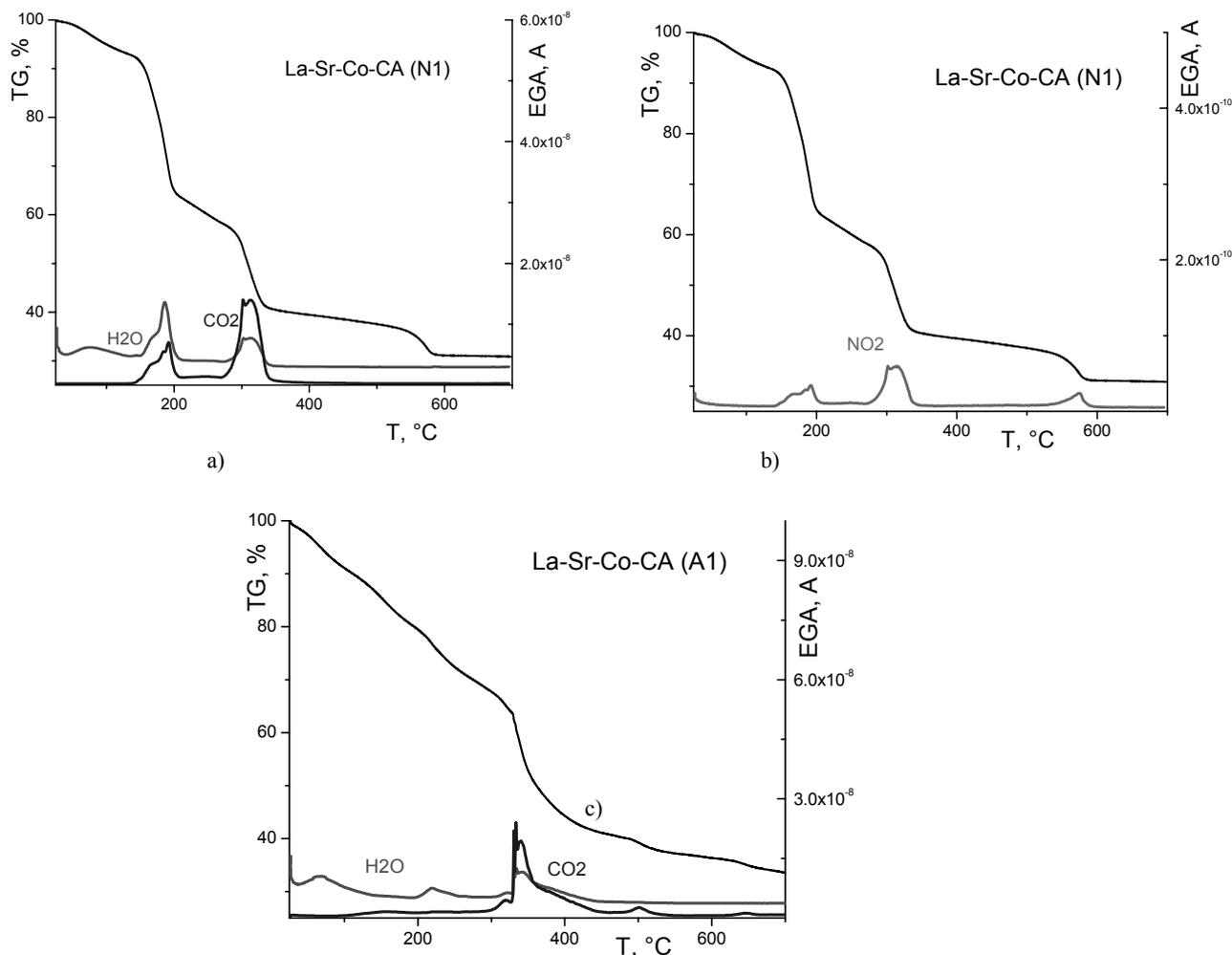


Fig. 4 – TG/EGA curves of the as-prepared gels: (a) and (b) nitrate (N) and (c) acetate (A).

The TG/EGA results show the decomposition of the complex nitrate derived gel (N1) at two different temperatures (190 and 360°C), with the evolution of the same gases (NO<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O) that means that the water, citric acid, and nitric reagents are bound in two positions as weakly bound ligands or coordinated ligands.

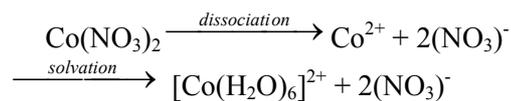
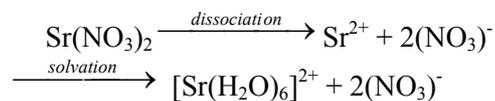
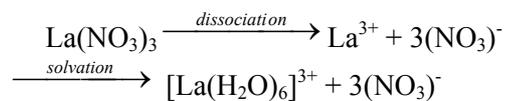
A supplementary small weight loss occurs at about 570°C with release of NO<sub>2</sub>. This effect could be assigned to the decomposition of a La<sub>3</sub>O<sub>4</sub>NO<sub>3</sub> type compound, that could be formed as a secondary phase during the complex gel decomposition.<sup>19</sup>

The complex acetate derived gel (A1) presents in the TG/EGA curves water elimination at 80 and 210°C. At higher temperature, namely 340°C, both water and CO<sub>2</sub> are eliminated. A very small CO<sub>2</sub> elimination is noticed at 500°C.

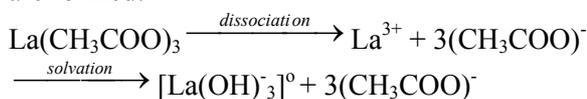
Based on the literature data<sup>3, 11</sup> the following gelation mechanism could be considered:

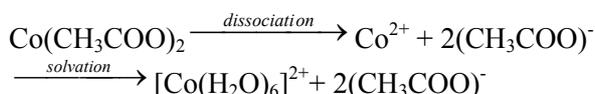
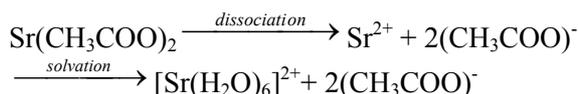
#### (1) Dissolution of metal salts in water

In the nitrate-salt solution with pH = 3, aquo-cations are formed:



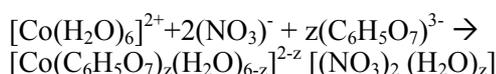
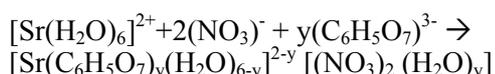
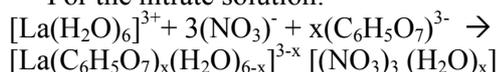
In the acetate-salt solution with pH = 8, Co and Sr aquo-cations and La neutral hydroxyl species are formed:



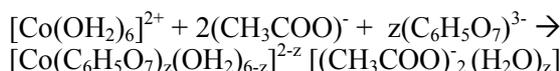
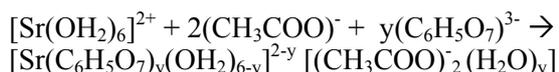
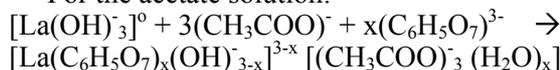


(2) *Complexation and chemically controlled condensation* in the presence of citric acid

For the nitrate solution:

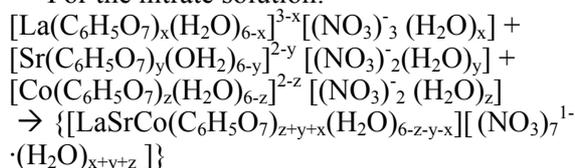


For the acetate solution:

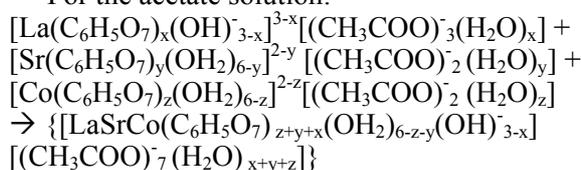


(3) *Formation of metals-citric acid chelates*

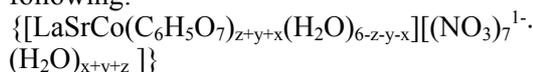
For the nitrate solution:



For the acetate solution:

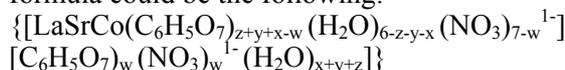


In the case of *nitrate* solution the initially proposed formula based on literature data was the following:



In this formula citric acid is bound in the position of a coordinated ligand.

However, based on the TG/AEG results the real formula could be the following:



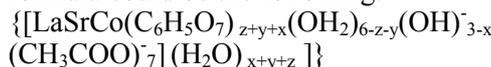
In this formula citric acid and the nitrate are bound in two positions as weakly bound ligands and as coordinated ligands.

In the case of *acetate* solution the initially proposed formula based on literature data was the following:



In this formula citric acid is bound in the position of a coordinated ligand, replacing acetate ions.

However, based on the TG/EGA results the real formula could be the following:



In this formula both citric and the acetate ions are bound in positions of coordinated ligands and only water remains weakly coordinated.

### Powders resulted by thermal treatment

By thermal treatment of the gels at 600°C or 1000°C, in the experimental conditions presented above, black nanosized powders were obtained.

The SEM micrographs of the samples thermally treated at 600°C are presented in Fig. 5a for nitrate and in 5b for acetate derived powders, while for the samples thermally treated at 1000°C the results are presented in Fig. 5c for nitrate and in 5d for acetate. It could be noticed that strongly aggregated fine particles are obtained and the choice of the precursors does not influence the morphology of the powders, but their size. The size of the powders obtained starting with acetates is lower than in the case of the powders obtained starting with nitrates. The lower size in the later case could be explained by the higher amount of organics in the acetates gels composition. Due to this fact during the thermal treatment of the gels a competition between the organic residues elimination and crystals size growth of the resulted powders could occur.

X-ray diffraction patterns of the samples annealed at 600°C for 6h are presented in Fig. 6.

In both cases samples with low degree of crystallisation were obtained. Rhombohedral phase (S.G. R3c) of lanthanum strontium cobalt oxide was obtained in the case of the samples obtained from acetate; while in the case of the samples obtained from nitrates besides lanthanum strontium cobalt oxide, traces of Co<sub>3</sub>O<sub>4</sub> and SrO are present.

X-ray diffraction patterns of the samples annealed at 1000°C for 6h (not shown here) indicate in both cases, samples with increased degree of crystallisation, as compared with the powders thermally treated at 600 °C. The traces of Co<sub>3</sub>O<sub>4</sub> and SrO are still identified in the samples starting from nitrates.

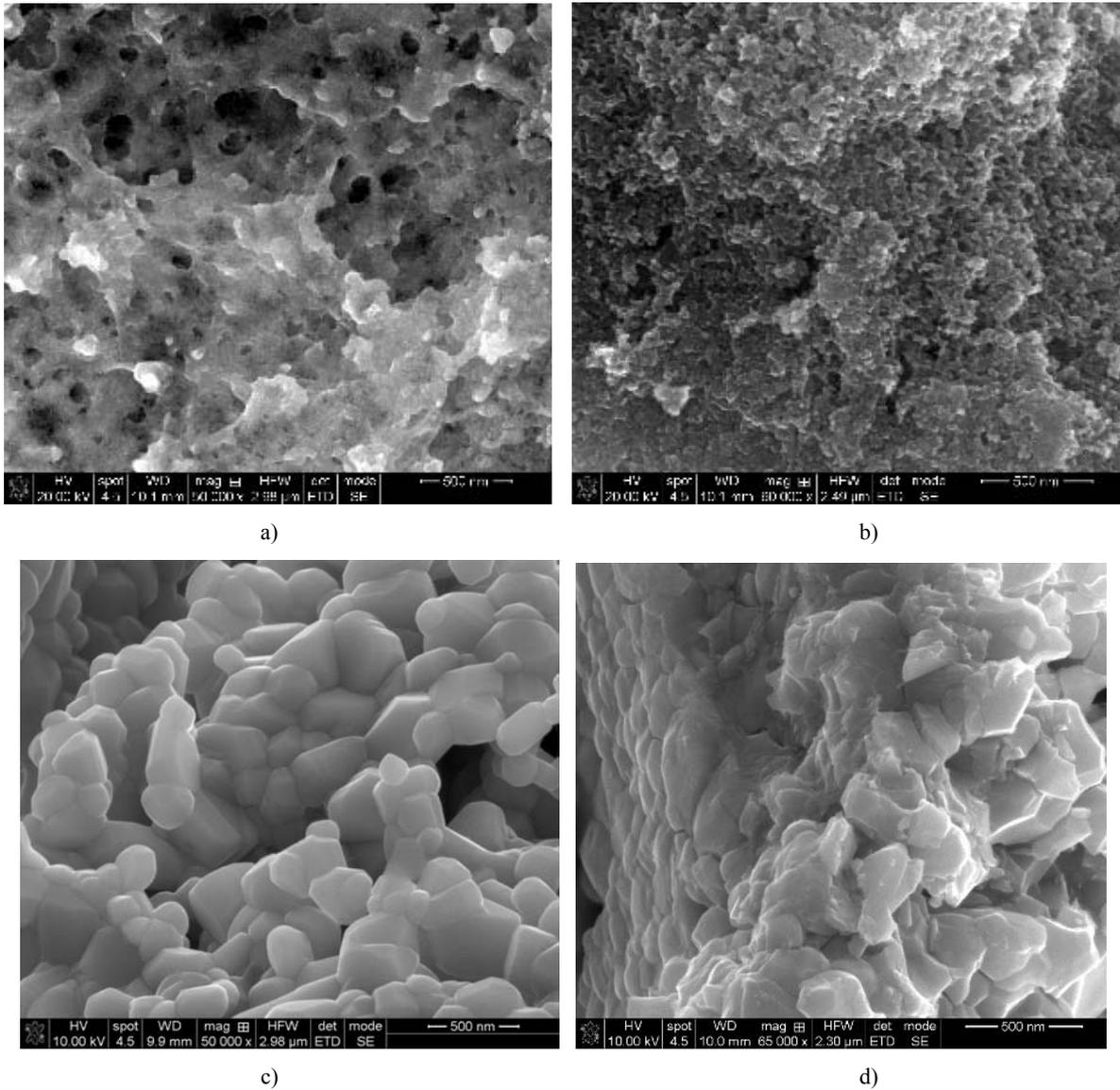


Fig. 5 – SEM images of the samples obtained from La-Sr-Co-CA nitrate or acetate thermally treated at 600 °C a) N1 and b) A1 or at 1000 °C c) N1 and d) A1.

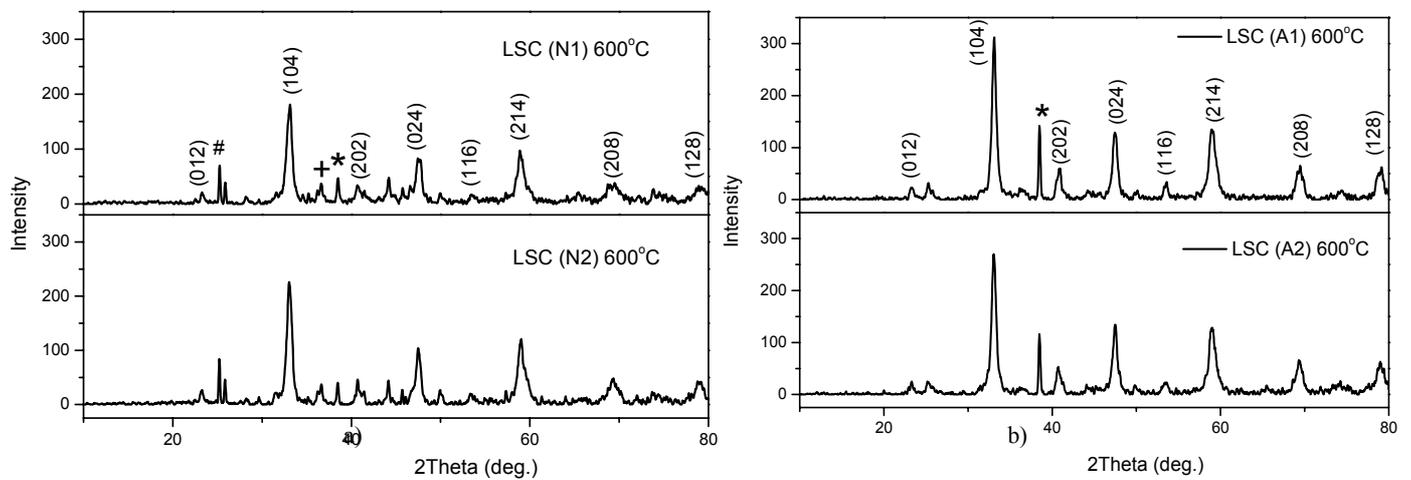


Fig. 6 – X-ray diffraction patterns of the samples annealed at 600 °C for 6h, (a) sample N and (b) sample A (# SrO, + Co<sub>3</sub>O<sub>4</sub> and \* holder).

The absence of the traces of  $\text{Co}_3\text{O}_4$  and  $\text{SrO}$ , in the case of samples prepared starting with acetates, could be explained by the fact that in this case the A type samples the acetic groups resulted during the sol-gel process could act also as chelating agent beside the citric acid.

In previous studies regarding formation of LSCO using solution preparation methods, the pure phase formation was always attended by using a high amount of chelating agents.<sup>20</sup>

## CONCLUSIONS

The sol-gel process in aqueous medium was studied for synthesis of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ , starting with La, Sr and Co-nitrates or acetates reagents, respectively, and citric acid as chelating agent.

As result of the sol-gel process, lanthanum strontium cobalt citrate gels with a coordinative structure were obtained.

The frequency separation between the stretching anti-symmetric  $\nu_{\text{asym}}(\text{COO}^-)$  and symmetric  $\nu_{\text{sym}}(\text{COO}^-)$  vibration suggests that citrate groups act as monodentate in the case of nitrate derived gels and bidentate ligands in the case of acetate derived gels.

By TG/DTA/EGA investigations the gelation mechanism and the complex compositions of the obtained gels were proposed.

By XRD-analysis rhombohedral phase (S.G. R3c) of lanthanum strontium cobalt oxide was obtained in both cases. In the case of nitrate derived samples besides rhombohedral phase (S.G. R3c) of lanthanum strontium cobalt oxide, supplementary traces of  $\text{Co}_3\text{O}_4$  and  $\text{SrO}$  are noticed.

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