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Study of the Gelling Process in the La-Co-Citric Acid System

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The gelling process in the aqueous lanthanum-cobalt-citric acid system was studied using UV-VIS and IR spectroscopic methods, as well as viscosity measurements, to establish the gelling mechanism of transition metal ions (La^{3+} and Co^{2+}) in the presence of chelating agent. Lanthanum and cobalt nitrates and lanthanum and cobalt acetates, respectively, were used as starting reagents, and the citric acid was used as chelating agent. The gelation process was investigated at room temperature and at 80°C. At elevated temperature, the gels were obtained after 30 h, whereas at room temperature, these were obtained in 1 month. Complex gels were formed for the both studied systems. The Co^{2+} ions mainly present an octahedral symmetry during the whole gelation process, whereas the citric acid acts as monodentate or bridging ligand depending on the metal precursors used. The mechanism of formation of the La-Co-CA based gels with the coordinative structures was proposed.

I. Introduction

RECENTLY, the attention has been focus on LnMO_3 perovskite-type oxides (where “Ln” is rare earth element and “M” is a transition metal) due to their specific electrical, magnetic and catalytic properties.

Among this type of materials, LaCoO_3 presented a special interest based on their applications as electrode materials in solid oxide fuel cells or materials for technological chemical sensors.¹

LaCoO_3 has been obtained using a number of methods including conventional ceramic powder technology. This procedure after long calcinations periods, leads to materials with low surface area.^{2,3}

To overcome these limitations, several techniques have been developed for LaCoO_3 synthesis, such as coprecipitation,^{3,4} nitrate decomposition,^{2,5} spray pyrolysis and combustion method,^{6,7} polymerizable complex method^{8,9} or sol-gel processing (alkoxide-based route),¹⁰ and citrate, tartrate or carboxylic sol-gel processing (aqueous route).^{11–13} The citric acid along with ethylene glycol were used for the first time by Pechini¹⁴ to obtain BaNb_2O_6 , SrNb_2O_6 , CaNb_2O_6 , and PbNb_2O_6 for capacitors. Later on, Erer and Anderson¹⁵ reported the preparation of different ceramic oxides such as titanates, ferrites, and cobaltites (LaCoO_3 , YCoO_3 , and PrCoO_3) using the so-called Liquid mix process. This process is in fact a modified Pechini type process.¹⁴ More recently, Popa and Kakihana¹⁶ prepared LaCoO_3 in the presence of citric acid and ethylene

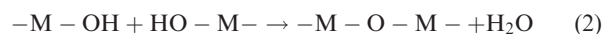
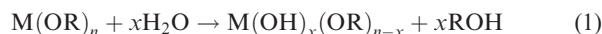
glycol using the same type of process. The Pechini type process employs the individual metal oxides as precursors that are peptized by the citric acid. The transition metal ions are coordinated in the polymeric network formed by polyesterification between citric acid and ethylene glycol.

The hydrolysis of metal cations was first studied by Bjerrum¹⁷ in the early twentieth century. Sillen¹⁸ was the first who suggested a mechanism of hydrolysis in which the hydroxyl groups are linked to cations and lead to the formation of condensed species. Later on, Livage *et al.*^{19,20} and Brinker and Scherer²¹ exhaustively studied the cations hydrolysis and formation of iso- and heteropoly-oxometalate.

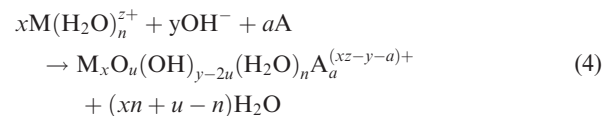
According to Pierre²² for the powders formation via both alkoxide and aqueous sol-gel routes, the precursors undertake the following succession of transformations in the presence of water:



For the case of alkoxide-based route (nonionized precursors), the reactions that occur are the following:



For the case of dissociated precursors (metallic salts in aqueous solutions), the reactions that occur are the followings:



where A = chelating agent

The aqueous sol-gel processes in the presence of citric acid as chelating agent has potential advantages over other methods not only for achieving homogenous mixing of the components at the atomic scale but also for the possibility of forming films or fibers from gel. The sol-gel method using chelating agents (polyethylene glycol, citric acid or polyacrylic acid) presents advantages of a good stoichiometric control of the reaction, fine particles and narrow size distribution, low temperature of processing and short intervals for calcination.²³

The sol-gel method in aqueous solution employs accessible metal salts dissolved in water along with organic ligands. This is a low-cost method, and is an environmental friendly alternative to the classical sol-gel process that uses organic solvents and metal alkoxides.²⁴ In this synthesis pathway, the metal ions are coordinated by organic ligands with a strong

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electron donor character that prevents the precipitation in the solution of the ions as metal hydroxides. By concentration of these soluble metal coordination compounds, an amorphous organic network is formed. In this network, the metal ions are homogeneously dispersed and linked through coordinative bonds. Homogenization takes place at the nanometer scale, and is kept until the LaCoO_3 phase formation.

The grounds of choosing other precursors than alkoxides are, in general, the limited solubility of some alkoxides in alcohols and the difficulty to prepare them in the laboratory. Moreover, the lower cost of some inorganic salts together with the lack of some accessible alkoxides on the market played an important role.

Beside the alkoxides, other typically used precursors are the organic salts such as acetates, acetyl-acetonates, or inorganic salts such as nitrates and chlorides.^{25,26} For the preparation of LaCoO_3 , Taguchi *et al.* used $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ along with poly(acrylic acid)²⁷ or citric acid.¹² Using these methods, they succeeded to decrease the temperature of formation of LaCoO_3 between 500°C and 600°C. The formation of LaCoO_3 occurs usually above 900°C when classical ceramic methods are employed. Using these precursors instead of alkoxides involves a different chemistry and introduces varied problems such as removal of the anions from the system.²¹ In general, the differences in chemical and physical properties such as structure and texture of the end products are expected using precursors other than alkoxides.

Definitely, the salts or the coordinative compounds of the carboxylic acids are appropriate and frequently used precursors in the aqueous sol-gel processes. These compounds are well known and accessible on a large scale for most elements.²⁸ The reaction of hydrolysis of the carboxylate salts can lead to hydroxides and free acids. Moreover, the multiple possibilities of bonding the $-\text{COO}^-$ to the metal ion—involving ionic, bridging or coordinative bonds—can be used to obtain homogeneous gels in the multi-component systems. The rate of hydrolysis can be controlled through the presence of carboxylate ligands. Consequently, using precursors that contain these organic functional groups can be a valid alternative in sol-gel preparation.

The FT-IR spectroscopic investigations are mostly used to characterize the sol-gel process, and the gels resulted from both alkoxide and aqueous routes. However, less information exists on the use of UV-VIS spectroscopy for similar investigation. As a matter of fact, the UV-VIS method is suitable to be used for the systems that present absorption in the visible domain of the spectrum, especially systems containing transition metals.

Our previous study²⁹ reports the preparation of lanthanum cobaltite using the nitrates as precursors, and explores the thermal stability of the gels along with their decomposition and formation of the LaCoO_3 . We attempted to determine the mechanism of thermal decomposition of these gels. The LaCoO_3 obtained by this method crystallized at 600°C.

In the present work, a systematic study of the gelling process in the aqueous lanthanum-cobalt-citric acid system was approached using mainly UV-VIS and IR spectroscopic methods to establish the gelling mechanism of transition metal ions (La^{3+} and Co^{2+}) in aqueous medium and in the presence of chelating agents.

To our knowledge, this is the first systematic study that investigates the sol-gel chemistry of the La-Co system in aqueous medium using citric acid by means of spectroscopic methods (UV-VIS and FT-IR).

II. Experimental Procedure

The study of the gelling process in the lanthanum-cobalt-citric acid system (La-Co-CA) in 1:1:1 molar ratio was performed using aqueous solutions of 0.25 mol/dm³ of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$, respectively.

Citric acid was added to solutions of lanthanum and cobalt nitrates or acetates, and the mixtures were continuously stirred, until complete dissolution of the precursors. The solutions gelled at room temperature after about 30 days or at 80°C after 36 h.

In addition, the mono metal-ion systems of cobalt-citric acid (Co-CA) and lanthanum-citric acid (La-CA) with 1:1 molar ratio were prepared in aqueous solutions of 0.25 mol/dm³ of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{La}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$, respectively, using the same conditions as for the La-Co systems.

The solutions and the gels obtained using metal nitrates and acetates were labeled (N) and (A), respectively.

The process of gelation of the studied solutions was followed by spectroscopic methods using UV-VIS measurements in the 200–800 nm range recorded with a Perkin Elmer Lambda 35 UV-VIS Spectrometer (Waltham, MA).

The FT-IR spectra of the solutions and gels were obtained using a Thermo Nicolet Spectrometer Nico 6700 FT-IR (Thermo Fisher, Waltham, MA) between 400 and 4000 cm⁻¹.

The spectra of the solutions were recorded using an Attenuate Total Reflection (ATR) attachment, whereas for the gels, the KBr pellet technique was employed.

The viscosities of solutions were measured with a Brookfield (Middleboro, MA) Viscometer DV-II + Pro at room temperature using a volume of 8 mL of reaction mixtures.

The morphology of the gels was determined by SEM using a JEOL JSM-5800 scanning electron microscope (Tokyo, Japan).

The X-Ray patterns were recorded between 10 and 90 with a Bruker AXS D4 Endeavor X-ray diffractometer (Karlsruhe, Germany) using a CuK_α radiation source ($\lambda = 0.15405$ nm).

The thermal behavior of the obtained gels were determined by thermogravimetric/differential thermal analysis (TG/DTA) using a Netzsch STA 409C/CD (Selb, Germany) instrument coupled with a Balzers Thermostar GSD 300D mass spectrometer (MS), in Al_2O_3 crucibles, and in flowing air atmosphere, and the maximum temperature was set at 740°C, and the heating rate was 5°C/min.

The specific surface area (BET method) was measured by nitrogen sorption analysis at -196°C using a Micromeritics ASAP 2020Analyzer (Norcross, GA).

III. Results and Discussion

(1) Characterization of Solutions

The gelling processes of the La-Co-CA solutions starting both with nitrates and acetates precursors were studied and compared with the corresponding mono-metal solutions, labeled as Co-CA and La-CA.

(2) UV-VIS Spectroscopy

The UV-VIS spectra of the La-Co-CA solutions, starting with nitrate (N) and acetate (A) are presented in Figs. 1(a) and (b), and the assignments of the absorbance bands obtained after their deconvolution using a PeakFit software are presented in Table I.

For the nitrate-based solution [Fig. 1(a)], an asymmetric band with a maximum at 510 nm was identified in the UV-VIS spectrum, and was assigned to $^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}$ (P) transition.³⁰ The deconvolution of the spectrum points out that this band covers two split transitions with maxima at 510 and 468 nm. The split structure of this band is due to the admixture of a spin forbidden transition to doublet states or due to spin-orbit coupling, or due to the presence of the some components with a low symmetry.³⁰ The band with the maximum at 468 nm has a lower intensity compared with the band placed at 510 nm, and this is consistent with spin forbidden transitions. The $^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}$ (P) transition identified for this system is characteristic for a Co(II) ion in an

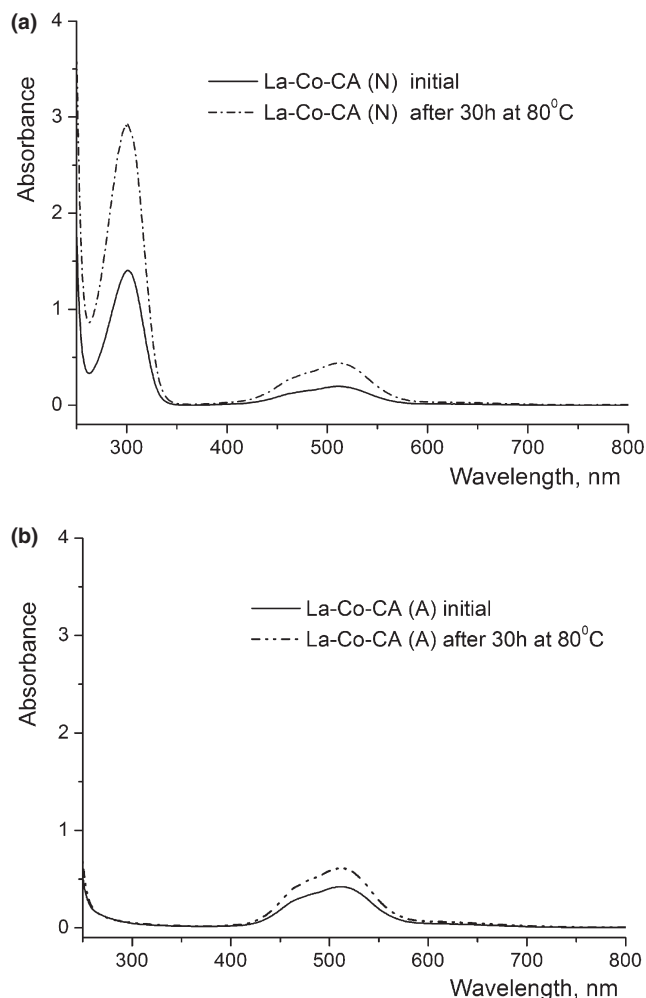


Fig. 1. The UV-VIS spectra of the La-Co-CA solutions, (a) starting with nitrate (N) and (b) starting with acetate (A).

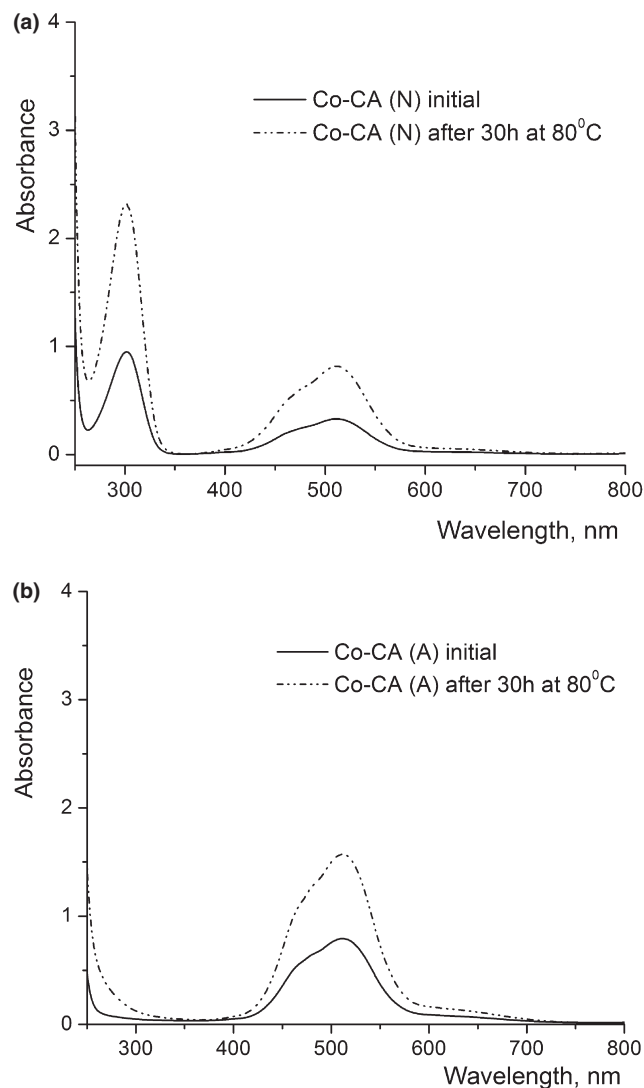


Fig. 2. The UV-VIS spectra of the Co-CA solutions: (a) starting with nitrate (N) b) starting with acetate (A).

Table I. The Maxima of Absorbance Identified in the UV-VIS Spectra Recorded on the Studied Solutions and Their Assignments

Sample	Maxima of absorbance, nm (cm ⁻¹)	Assignments
La-Co-CA (N)	300 (33 231)	CT
	468 (21 368)	Splitting
	510 (19 531)	⁴ T _{1g} → ⁴ T _{1g} (P)
Co-CA (N)	301 (33 222)	CT
	467 (21 413)	Splitting
	511 (19 569)	⁴ T _{1g} → ⁴ T _{1g} (P)
La-Co-CA (A)	467 (20 217)	Splitting
	512 (18 587)	⁴ T _{1g} → ⁴ T _{1g} (P)
	Co-CA (A)	467 (20 217)
512 (18 587)		⁴ T _{1g} → ⁴ T _{1g} (P)

octahedral coordination. A supplementary band at 300 nm was identified that could be assigned to the charge transfer from 3d orbitals of Co(II) to an anti-bonding orbital of nitrate ions [Fig. 1(a)].

For the acetate-based solution [Fig. 1(b)], an asymmetric band at 512 nm was also observed, and it was assigned to ⁴T_{1g} → ⁴T_{1g}(P) transition. This band is split in two bands with maxima at 467 and 512 nm. Those asymmetric bands that appear in the visible domain of the spectrum are characteristic to Co(II) in the octahedral or pseudo-octahedral coordination. The splitting can be attributable to a low symmetry or to a spin forbidden transition.

The UV-VIS spectra of the mono-metal Co-based solutions are displayed in Fig. 2, and the maxima of absorbance are listed in Table I. In the UV-VIS spectra of both mono-metal-ion systems, the maxima of the absorption bands is placed at the same position as in binary system being assigned to cobalt (II) ions in an octahedral geometry. As it is well known, lanthanum (III) ions does not present absorption in the UV-VIS range. Therefore, it can be concluded that in the initial steps of gelling process of the binary La-Co-CA system, the presence of the lanthanum (III) ions does not influence the coordination and geometry of the cobalt (II) ions.

(3) FT-IR Spectroscopy

The FT-IR spectra of the as-prepared La-Co-CA solutions and after 30 h of storage at 80°C are presented in Figs. 3(a) and (b), whereas the corresponding vibration bands are summarized in Tables II and III.

The FT-IR spectrum [Fig. 3(a)] of the nitrate-based solution La-Co-CA(N) initially displays the presence of the vibrations due to the water δHOH (1636 cm⁻¹), nitrate ion ν₃NO₃⁻ (1345 cm⁻¹) ν₂NO₃⁻ and ρCH₃ (1046 cm⁻¹) and carboxyl ν(C-O) (1236 cm⁻¹),³¹ πCH and π(COO) (1079 cm⁻¹).

After the solution was stored for 30 h at 80°C, an additional vibration band at 1718 cm⁻¹ was observed. Moreover, an increasing of the intensity of all the vibration bands in

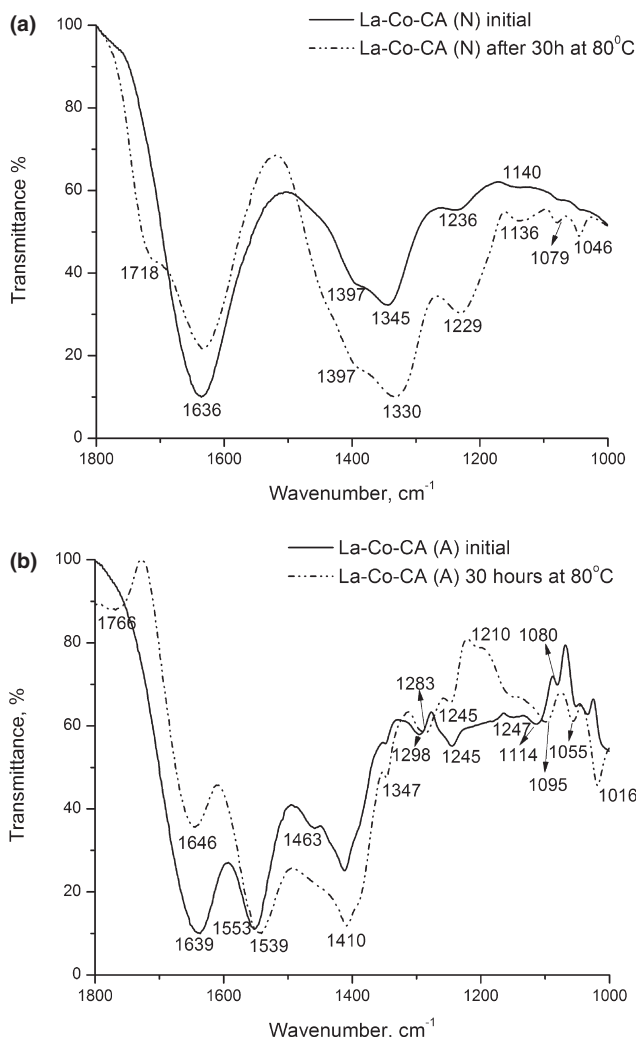


Fig. 3. The FT-IR spectra of the La-Co-CA solutions: (a) starting with nitrate (N) and (b) starting with acetate (A).

comparison with the spectrum of the initial solution was observed. The band at 1718 cm^{-1} corresponds to $\nu_{\text{as}}(\text{COO}^-)$, and the band at 1229 cm^{-1} was assigned to $\nu(\text{C-O})$.³¹ In agreement with Nakamoto,³² the band at 1397 cm^{-1} is due to $\nu_{\text{sym}}(\text{COO}^-)$, whereas the band at 1330 cm^{-1} is assigned to the $\nu_3\text{NO}_3^-$ ions.

After 30 h of storage at 80°C , equilibrium is reached in the studied system. The vibration bands due to the formation of the coordinative compounds between the Co(II), La(III) and citric acid are more intense.

For the nitrate-derived sample, the frequency separation between the antisymmetric stretching $\nu_{\text{as}}(\text{COO}^-)$ and symmetric

stretching $\nu_{\text{sym}}(\text{COO}^-)$ vibration is $\Delta\nu = 321\text{ cm}^{-1}$. On the other hand, in the ionic compound (sodium citrate), the frequencies separation between the antisymmetric and symmetric stretching of COO^- was measured to be $\Delta\nu_{\text{ionic}} = 193\text{ cm}^{-1}$. On the basis of theory developed by Deacon,^{32,33} comparing the $\Delta\nu_{\text{ionic}}$ with $\Delta\nu$ of the nitrate-derived sample, we can conclude that the carboxylic groups of the citrate act as unidentate ligands.³³

The FT-IR spectrum of the La-Co-CA(A) solution [Fig. 3(b)] after 30 h at 80°C mostly present the same main vibration bands as in the spectrum of the initial solution; only the intensity of the characteristic bands is enhanced. There were identified as water δHOH (1646 cm^{-1}), COO^- groups $\nu_{\text{as}}(\text{COO}^-)$ (1539 cm^{-1}), δCH_3 (1463 cm^{-1}), $\nu_{\text{sym}}(\text{COO}^-)$ (1410 cm^{-1}), $\nu(\text{C-O})$ (1245 cm^{-1}), $\pi\text{CH}/\pi(\text{COO})$ (1095 cm^{-1}), and ρCH_3 (1046 cm^{-1}). The bands at $1300\text{--}1200\text{ cm}^{-1}$ correspond to $\nu_{\text{C-O}}$ from the $-\text{COOH}$ groups of the citric acid. The band from 1646 cm^{-1} corresponds to adsorption of water δHOH .³⁴ The $-\text{COO}^-$ groups showed two characteristic vibrations: the antisymmetric stretching at 1539 cm^{-1} and the symmetric stretching at 1410 cm^{-1} ($\Delta\nu = 119\text{ cm}^{-1}$). According to Deacon,^{32,33} this value shows that the carboxylic groups of the citrate ligands act as bridging ligands.

To obtain more detailed information regarding the contribution of individual Co(II) or La(III) ions in the formation of the coordination complex gels, the FT-IR spectra of the Co-CA and La-CA nitrate-based solutions (N) initially and after 30 h at 80°C are presented in Fig. 4 along with the assignment of the peaks in Table II.

Mainly, the same vibration bands were identified for binary system studied. It should be mentioned that the band at 1490 cm^{-1} occur in the initial solution only in the case of Co-CA, and this is assigned to the un-reacted CA.

The FT-IR of the La-Co-CA(A) solution were compared with spectra of the La-CA and Co-CA acetate-based solutions (A) initially and after 30 h of storage at 80°C and are presented in the Fig. 5 along with their assignments that are listed in the Table III.

In the first moments of the reactions in the spectrum of the Co-CA(A) [Fig. 5(a)], beside water, δHOH 1638 cm^{-1} , the characteristic vibrations for the carboxyl ions $\nu_{\text{as}}(\text{COO}^-)$ (1565 cm^{-1}) and $\nu_{\text{sym}}(\text{COO}^-)$ (1418 cm^{-1}), $\nu_{\text{C-O}}$ (1275 cm^{-1}) were identified. After 30 h of the reaction, the characteristic peaks of the acetate ions and citrate ions present higher intensity. In the spectrum of the initial La-CA acetate-based solution (A) [Fig. 5(b)], characteristic vibrations of $-\text{COO}^-$ at 1576 cm^{-1} and 1414 cm^{-1} beside those of water were also observed. Initially, the relative intensity of the peaks δHOH (1638 cm^{-1})/ $\nu_{\text{as}}(\text{COO}^-)$ (1576 cm^{-1}) is dominated by the δHOH vibration band. After 30 h of reaction at 80°C , the relative intensity of these two peaks is reversed, and is dominated by $\nu_{\text{as}}(\text{COO}^-)$.

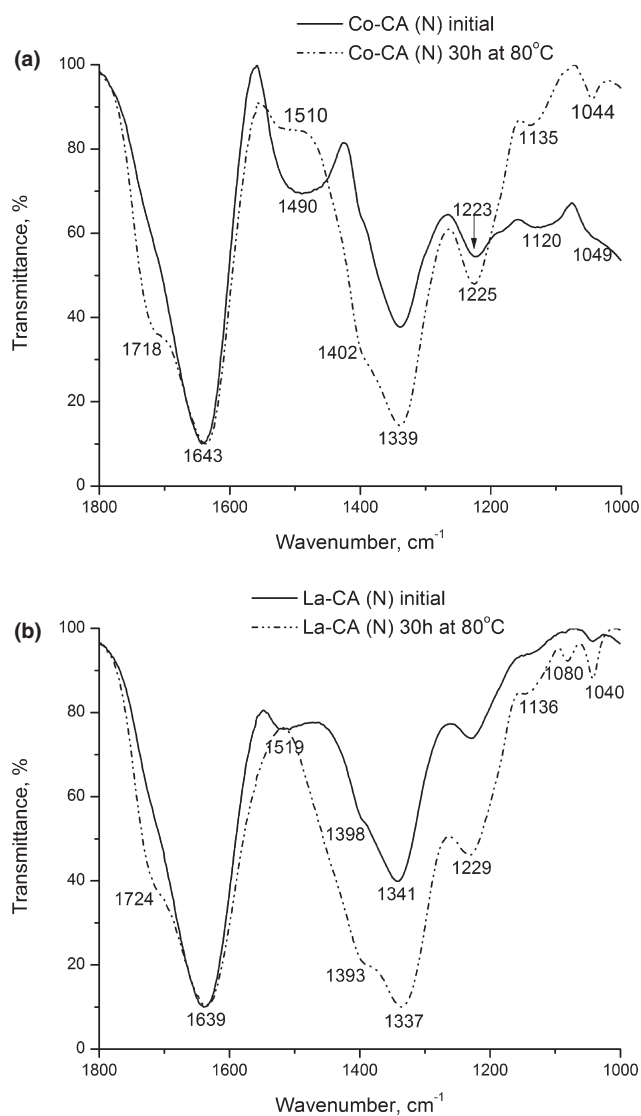
For both the considered systems, after 30 h of storage of the reaction mixtures at 80°C , an amplification of vibrations

Table II. The Assignments of the Vibration Bands of the FT-IR Spectra of the Solutions Starting with Nitrate (N)

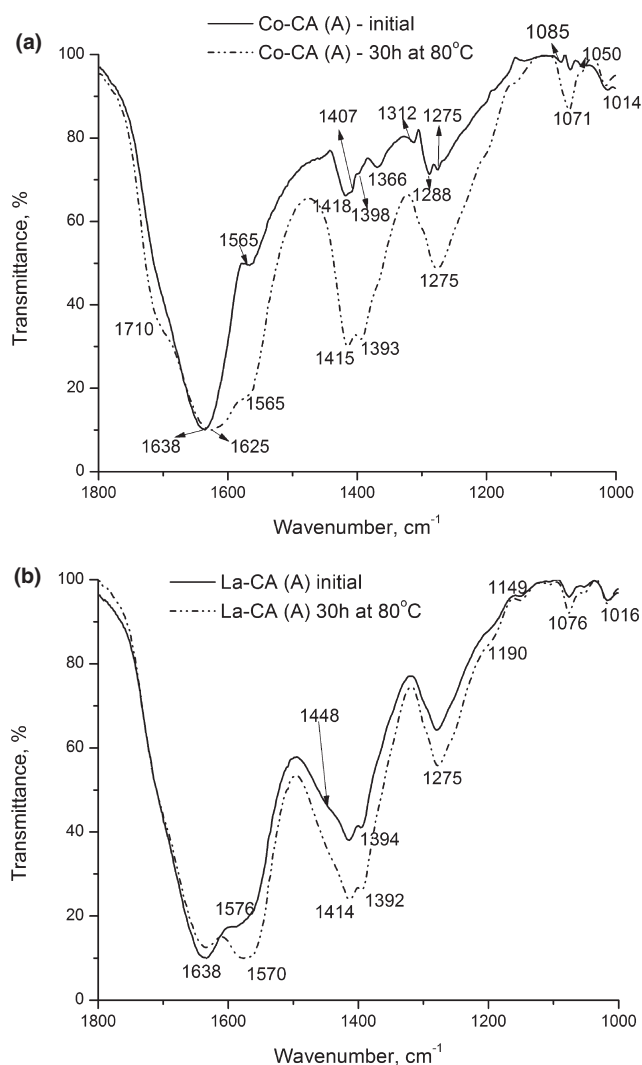
La-Co-CA(N)		Co-CA(N)		La-CA(N)		Vibration mode	Assignments
Initial	30 h, 80°C	Initial	30 h, 80°C	Initial	30 h, 80°C		
3300	3300	3300	3300	3300	3300	νOH	Structural OH group
—	1718	—	1718	—	1724	$\nu_{\text{as}}(\text{COO})$	Carbonyl asymmetric stretching
1636	1636	1643	1643	1639	1639	δ_{HOH}	Adsorption of water
—	—	1490	1510	1519	—	$\nu_{\text{as}}(\text{COO})$	Carbonyl asymmetric stretching
1397	1397	1402	1402	1398	1393	$\nu_{\text{sym}}(\text{COO}^-)$	Carbonyl symmetric stretching
1345	1330	1339	1339	1341	1337	$\nu_3\text{NO}_3^-$	Nitrate ions from precursors
1236	1229	1223	1225	1229	1229	$\nu\text{-COOH}$	Introduced by the citric acid
1140	1136	1120	1135	1136	1136	$\nu\text{C-OH}$	
1079	1079	—	—	1080	1080	$\pi\text{CH}/\pi(\text{COO})$	
1046	1046	1049	1044	1040	1040	$\nu_2\text{NO}_3^-/\rho\text{CH}_3$	

Table III. The Assignments of the Vibration Bands of the FT-IR Spectra of the Solutions Starting with Acetate (A)

La-Co-CA(A)		Co-CA(A)		La-CA(A)		Vibration mode	Assignments
Initial	30 h, 80°C	Initial	30 h, 80°C	Initial	30 h, 80°C		
3300	3300	3300	3300	3300	3300	ν OH	Structural OH group
	1766		1710			$\nu_{as}(\text{COO}^-)$	Carbonyl asymmetric stretching
1639	1646	1638	1625	1638	1638	δ_{HOH}	Adsorption of water
1553	1539	1565	1565	1576	1570	$\nu_{as}(\text{COO})$	Carbonyl asymmetric stretching
1463	1463			1448		δCH_3	
1410	1410	1418	1415	1414	1414	$\nu_{sym}(\text{COO}^-)$	Carbonyl symmetric stretching
		1398	1393	1394	1392		
1347	1347	1366	1366				
		1312					
1298	1283	1288	1275	1275	1275	ν -COOH	Introduced by the citric acid
		1275				ν C-OH	
1245	1245						
	1210			1190	1190		
1147	1147			1149	1149		
1080	1095	1085	1071	1076	1076	$\pi\text{CH}/\pi(\text{COO})$	ρCH_3
	1055	1050					

**Fig. 4.** The FT-IR spectra of nitrate-based solutions (N): (a) Co-CA and (b) La-CA.

due to the carboxyl groups that are involved in the formation of the metal-citric acid coordinative compounds was observed.

**Fig. 5.** The FT-IR spectra of acetate solutions (A): (a) Co-CA and (b) La-CA.

(4) Viscosity Measurements

The viscosities of the La-Co-CA solutions at 80°C between 0 and 30 h are presented in Fig. 6. In both cases, a steady increase of viscosity with time is observed.

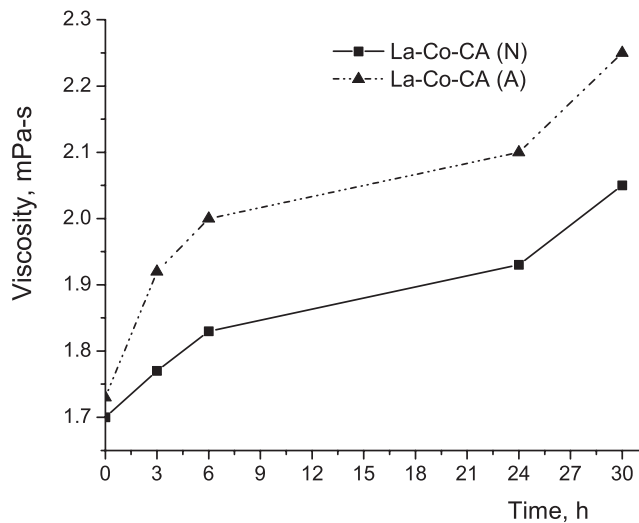


Fig. 6. The viscosities of the La-Co-CA solutions.

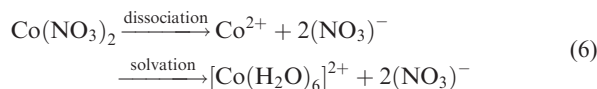
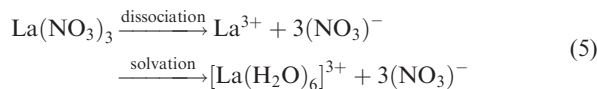
The viscosity of the acetate solutions is higher than that of the nitrate solutions. This fact can be explained by the presence of the acetate ions that can also act as a chelating agent. The increase of the viscosity values takes place between 1.7 and 2.05 mPa·s for the nitrate-derived solution, and 1.75 and 2.25 mPa·s for the acetate-derived solution. The increase of viscosity with time is due to dissociation of the acetate ions (refer to the following chemical equations) and formation of new coordinative bonds. After dissociation, the acetate ions present in the solution can act as individual chelating agents. They can generate acetate bidentate bridges between the La³⁺ and Co²⁺ ions. The presence of these bidentate bridges has resulted in the increase in the viscosity of the La-Co-CA(A) solution.

(5) Mechanism of Gel Formation

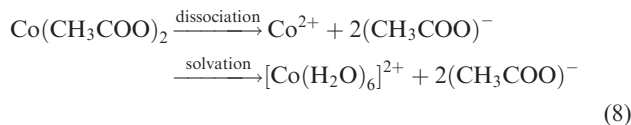
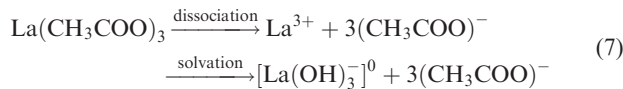
Based on the literature data,¹⁹ the following gelation mechanism is considered:

1. Dissolution of metal salts in water

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

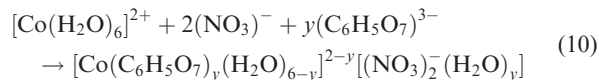
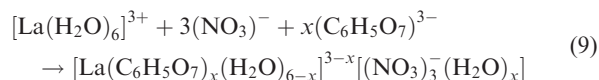


In the acetate-salt solution with pH = 8, Co aquo-cations and La neutral hydroxyl species are formed:

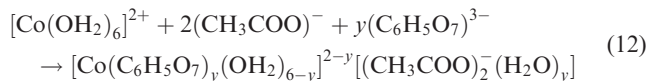
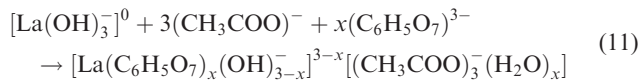


2. Complexation and chemically controlled condensation in the presence of the citric acid

For the nitrate solution:

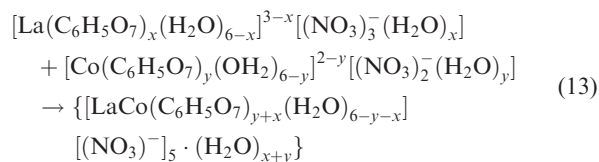


For the acetate solution:

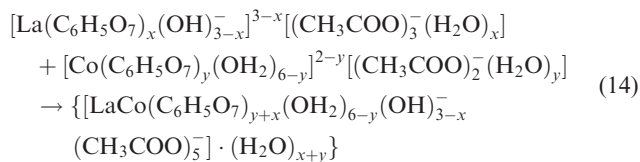


3. Formation of metals-citric acid chelate

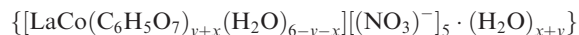
For the nitrate solution:



For the acetate solution:



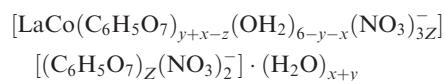
As mentioned above, for the gels obtained starting with nitrates, the initially proposed formula, based on literature data, is the following:



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

However, previous TG/AEG results²⁹ have shown the decomposition of the complex gel at two different temperatures (200°C and 350°C), with the evolution of the same gases (NO₂, CO₂, and H₂O), which means that the water, citric acid, and nitric reagents are bound in two different ways in the heteropolynuclear amorphous complex.

Based on the mentioned 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. The presence of nitrate as coordinated ligand in the presented heteropolynuclear amorphous complex could also be correlated with the UV-VIS band at 300 nm, which could be assigned to the charge transfer from 3d orbitals of the Co(II) to an anti-bonding orbital of the nitrate ions.

(6) Characterization of the Gels

Under the above mentioned experimental conditions, amorphous red gels were obtained. The amorphous state of both gels is supported by the X-ray diffraction patterns (not shown here).

(7) UV-VIS Spectroscopy

The UV-VIS spectra of the gels and the assignments of the transition are presented in Fig. 7 and Table IV, respectively.

In the spectrum of the nitrate-derived gel (Fig. 7), three transitions were identified. Beside the charge transfer band at 356 nm, three additional bands were identified at 406 nm (${}^4T_{1g} \rightarrow {}^4A_{2g}$), at 532 nm (${}^4T_{1g} \rightarrow {}^4E_g$), and at 671 nm (${}^4T_{1g} \rightarrow {}^4B_{1g}$). The $d-d$ transitions correspond to the Co(II) ion in the tetragonal distorted geometry,^{30,35} which is an octahedral distorted geometry along the z -axis of the octahedron. For this geometry, the ${}^4T_{1g}(P)$ splits in ${}^4A_{2g}$ and 4E_g ; the ${}^4A_{2g}$ is shifted to higher energy and becomes ${}^4B_{1g}$. In the acetate-derived gel (Fig. 7), beside the charge transfer band at 372 nm, two $d-d$ transitions were identified (Table III). The ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions indicate the formation of complex gels in which Co(II) ion has an octahedral symmetry.

(8) FT-IR Spectroscopy

The FT-IR spectra of the gels are presented in Fig. 8.

The main vibration peaks in the spectrum of the nitrate-derived gel are situated at 1717 cm^{-1} due to $\nu_{\text{as}}(\text{COO}^-)$, 1422 cm^{-1} assigned to $\nu_{\text{sym}}(\text{COO}^-)$, 1611 cm^{-1} attributed to δHOH , 1384 cm^{-1} attributed to $\nu_3\text{NO}_3^{3-}$, and 1078 cm^{-1} assigned to $\pi\text{CH}/\pi(\text{COO})$.

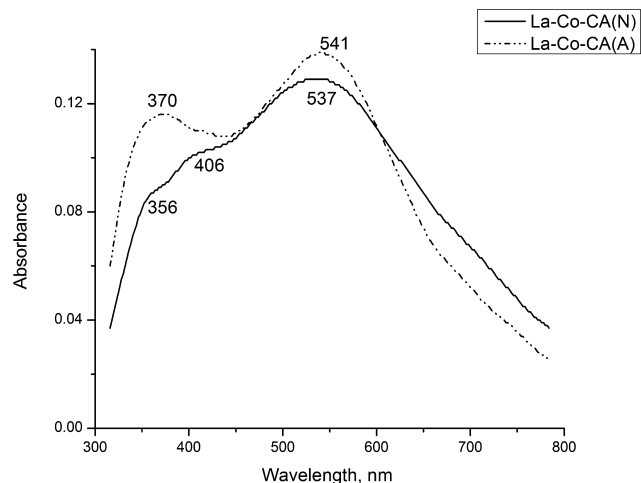


Fig. 7. The UV-VIS spectra of the La-Co-CA gels, starting with nitrate (N) and acetate (A).

Table IV. The Maxima of Absorbance Identified in the UV-VIS Spectra Recorded on the Studied Gels and Their Assignments

Sample	Maxima of absorbance, nm (cm^{-1})	Assignments
La-Co-CA(N)	356 (28 089)	CT
	406 (24 639)	${}^4T_{1g} \rightarrow {}^4A_{2g}$
	532 (18 797)	${}^4T_{1g} \rightarrow {}^4E_g$
	671 (14 903)	${}^4T_{1g} \rightarrow {}^4B_{1g}$
La-Co-CA(A)	372 (26 881)	CT
	540 (18 518)	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$
	685 (14 598)	${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$

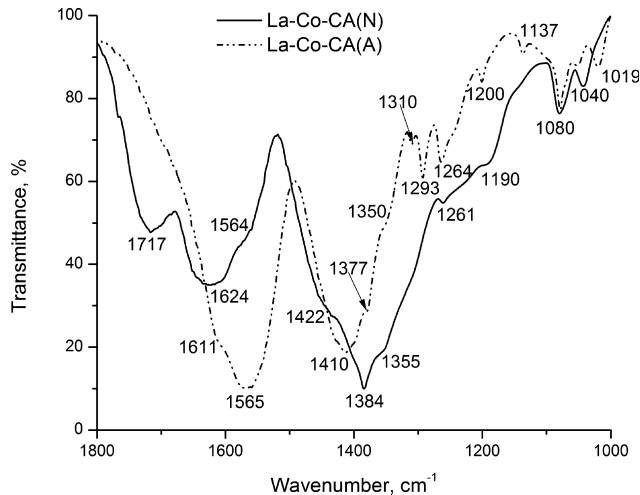


Fig. 8. The FT-IR spectra of the La-Co-CA gels, starting with nitrate (N) and acetate (A).

In the spectrum of the acetate-derived gel, the main vibration bands were identified at 1565 cm^{-1} due to $\nu_{\text{as}}(\text{COO}^-)$, 1410 cm^{-1} assigned to $\nu_{\text{sym}}(\text{COO}^-)$, 1624 cm^{-1} attributed to δHOH , and 1080 cm^{-1} assigned to the πCH or $\pi(\text{COO})$.³¹

The frequency difference between carbonyl stretching of the antisymmetric and symmetric vibration of carboxylic groups of the citric acid in the nitrate-derived gel is $\Delta\nu = 295 \text{ cm}^{-1}$, whereas, in the case of the acetate-derived gel, it is $\Delta\nu = 155 \text{ cm}^{-1}$. By comparing those data with the values obtained for the ionic compound $\Delta\nu_{\text{ionic}} = 193 \text{ cm}^{-1}$, we can conclude that in the first case, the carboxylic groups of the citric acid act as monodentate ligands, whereas in the second case, they act as bridging ligands.^{32,33}

In agreement with the literature data, the bands in the range of 1300–1200 cm^{-1} correspond to $\nu_{\text{C-O}}$ from $-\text{COOH}$ group of the citric acid.

(9) Thermal Analysis

In a previous study, the thermal behavior of the La-Co-CA nitrate-based gel was investigated.²⁹ The thermal decomposition of both La-Co-CA nitrate and acetate-based gels, determined in the present work when compared with those of the gels obtained in the mono metal-ion systems is presented in Fig. 9.

The main decomposition effect of the binary La-Co-CA nitrate and acetate-based gels lies between the main decomposition effects of the mono-metal complexes. This observation allows concluding that the binary metal-ion systems are not physical mixtures of phases, but complex coordinative gels, confirming the results obtained by spectroscopic measurements.

(10) Characterization of the LaCoO_3 Powders Obtained at 600°C

Based on the results of the DTA/TGA measurements and our previous results,²⁹ the obtained gels were thermally treated at 600°C, for 6 h.

The BET surface area of LaCoO_3 obtained by calcinations at 600°C of La-Co-CA(A) gel was 13.30 m^2/g , whereas the surface area of the lanthanum cobaltite prepared using La-Co-CA (N) gel was 8.82 m^2/g . The higher surface area of LaCoO_3 prepared using La-Co-CA(A) can be explained by the higher organic content in the precursor gel due to the presence of the acetate anions. The thermal decomposition of the acetate-based gel shows [Fig. 9(b)] that this gel is stable up to $\sim 550^\circ\text{C}$, whereas the nitrate-based gel decomposes at $\sim 420^\circ\text{C}$ [Fig. 9(a)]. The organic content being stable up to higher temperatures in the acetate-based gel determines a

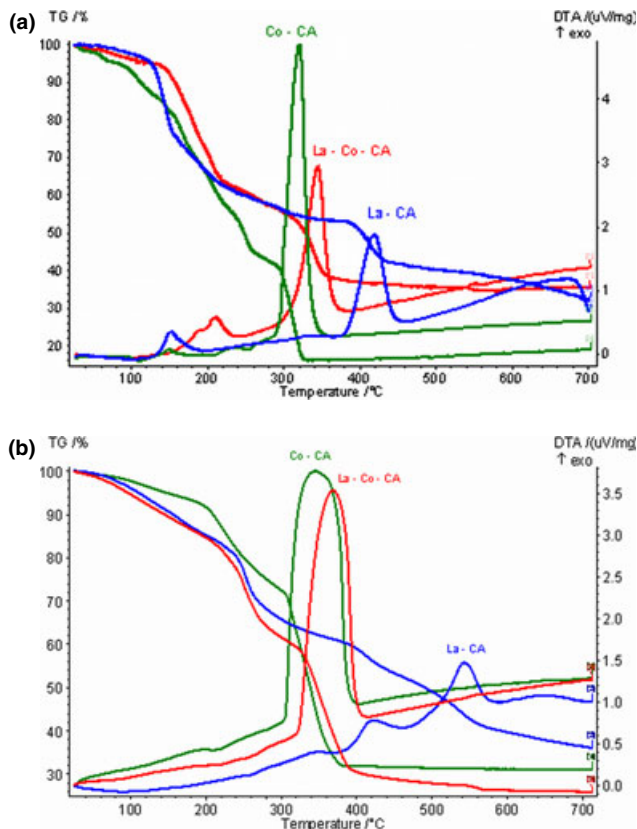


Fig. 9. Thermal decomposition of mono and binary gels, (a) starting with nitrates (N), (b) starting with acetates (A).

later formation of the pores that do not have time to shrink, compared with the nitrate-based gel that decomposes at lower temperatures, and therefore, the pores formed are shrinking up to the temperature of the thermal treatment. The higher organic content and the higher thermal stability of the La-Co-CA(A) explain the higher BET surface area of the LaCoO_3 obtained in the acetate-based system.

(11) X-Ray and SEM Measurements

The X-ray patterns of the LaCoO_3 powders obtained by thermal treatment of the La-Co-CA acetate and nitrate-based gels are presented in Fig. 10. After the thermal treatment at 600°C for 6 h, in both systems, a single phase of rhombohedral perovskite of lanthanum cobaltite (LaCoO_3) was identified (JCPDS 84-0848).

Figure 11 displays the SEM images of the LaCoO_3 powders obtained after the thermal treatment at 600°C of both studied gels. The SEM analysis was shown for both systems aggregates of particles with an average size between 43 and 72 nm. The SEM picture of the LaCoO_3 obtained from La-Co-CA (A) gel [Fig. 10(b)] shows a higher agglomeration of the particles than the particles of the lanthanum cobaltite prepared from La-Co-CA (N) gel [Fig. 10(a)].

IV. Conclusions

A spectroscopic study of the gelation processes in the lanthanum-cobalt-citric acid systems starting from metal nitrates or acetates in aqueous medium was carried out. The Lanthanum-cobalt citrate gels consist of coordination polynuclear species where the covalent coordinate bonds play an important role in the symmetry of the Co(II) and La(III) ions.

The mono and binary metal-ion precursor solutions were characterized by spectroscopic measurements. The UV-VIS spectra of the solutions revealed that Co(II) ions are present in octahedral geometry for all studied samples.

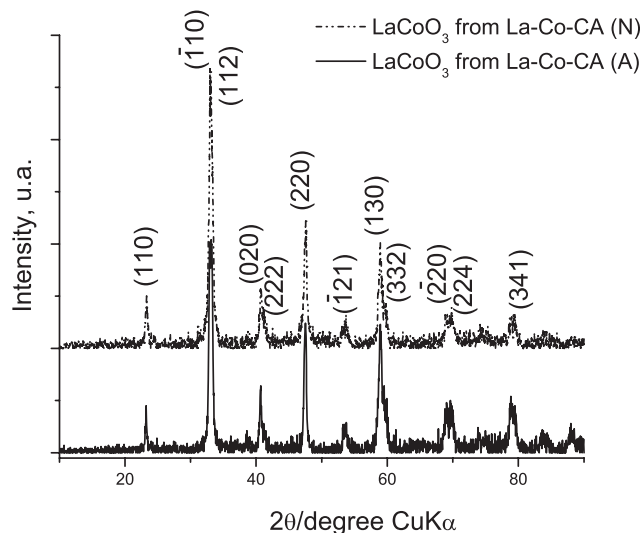


Fig. 10. The X-Ray diffraction patterns of the LaCoO_3 of the samples obtained in the both studied systems.

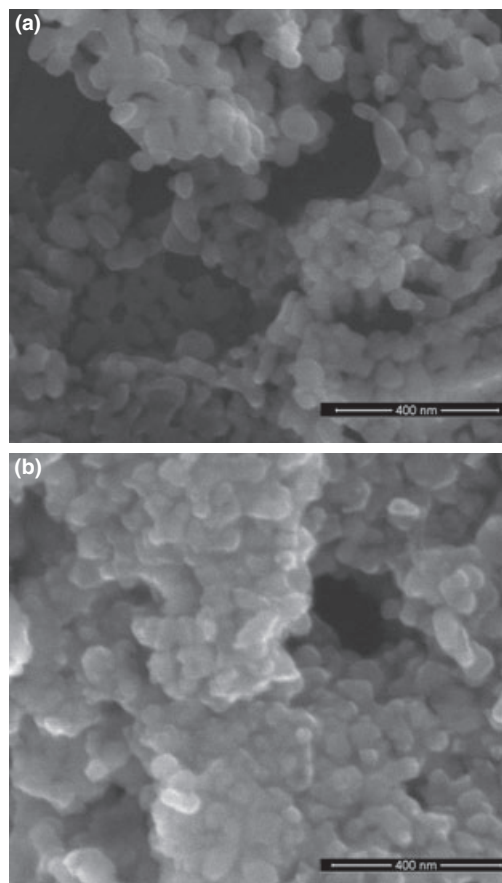


Fig. 11. The SEM micrographs of the LaCoO_3 obtained by calcinations at 600°C of La-Co-CA gels (a) in the nitrate (N) system, (b) in the acetate (A) system.

The frequency separation between the antisymmetric stretching $\nu_{\text{as}}(\text{COO}^-)$ and symmetric stretching $\nu_{\text{sym}}(\text{COO}^-)$ vibrations obtained from the FT-IR data was used to establish the coordination of the citrate ions as ligands. The spectroscopy data showed carboxylic groups of the citrate acted as monodentate and bridging ligands.

For the obtained gels, based on the UV-VIS data, Co(II) ions were identified to be in octahedral (O_h) and tetragonal

(D_{4h}) symmetry; from the FTIR data, the frequency separation between the antisymmetric stretching $\nu_{\text{asym}}(\text{COO}^-)$ and symmetric stretching $\nu_{\text{sym}}(\text{COO}^-)$ pointed out that the carboxylic groups of the citrate ions acted as monodentate and bridging ligands.

The thermal decomposition of the La-Co-CA gels has confirmed that the binary metal-ion systems are not physical mixtures of phases, but complex coordinative gels.

By thermal treatment of the gels at 600°C, for both systems, single phase lanthanum cobaltite (LaCoO₃) with a perovskite structure and particles in nanometric range (43 and 72 nm) were identified.

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