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Influence of type of precursors on the sol-gel synthesis of the $LaCoO_3$ nanoparticles

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Abstract: Perovskite-type $LaCoO_3$ was prepared by sol-gel method using nitrates / chlorides as precursors and citric acid as chelating agent. Chemical composition was obtained by means of EDX method. The structures of sintered samples were investigated by scanning electron microscopy (SEM), IR and XRD analysis. The results of X-ray diffraction indicated that the $LaCoO_3$nanopowders obtained using nitrate as precursors had a rhombohedral perovskite-type crystal structure (S. G: R-3c), while that obtained using chloride as precursors had a mixture of $LaCoO_3$, LaOCl and Co_3O_4. The all lanthanum cobaltites exhibit catalytic activity on the decomposition of hydrogen peroxide, ascribed to their higher surface and Co^{3+} concentration.

***Keywords*:** Perovskites, Sol-gel synthesis, X-ray diffraction, Electronic microscopy, Catalytic activity

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Introduction

In the last years, in order to control the morphology of the final product, many investigations of perovskite-type oxides were focused on the development of the nonconventional synthesis.[1,2] These studies are sustained by special applications of lanthanum-based perovskites as materials for solid oxide fuel cells (SOFC), catalysts for hydrocarbon oxidation, giant magnetoresistance or ferroelectric materials[1-6] and gas sensors.[7] The $LaCoO_3$(LCO) is known for its high catalytic activity for oxidation of carbon monoxide, methane, propane, hexane, and toluene[4-6] and it could be used as electrode materials for SOFC.[7,8] At room temperature LCO has a slightly rhombohedral distortion with an angle of 60.48° and CoO_6 octahedron are tilted with the Co-O-Co angle of 163.2°.[9,10] The Co-Co lattice deformation proceeds continuously, Co-O-Co bond angles show a linear correlation with stress factors.[11] These distortions are the basis for the electronic, magnetic and electrochemical properties of cobaltite perovskites.

In order to obtain the best properties and due to their ability to be both electronic and ionic conductors, the synthesis of these compounds was attempted by several methods.[3,4,12-14]

Grice et al.[15] tested the catalytic activity of mixed cobaltite by the decomposition rate of hydrogen peroxide and applied this property for aqueous oxidations of organic molecules using H_2O_2 as oxidant.

The purpose of this paper is to report the investigation of structural properties and testing catalytic activity of nanopowder lanthanum cobaltites synthesized by sol-gel method.

Experimental

Perovskite-type $LaCoO_3$ was prepared by sol-gel method using $La(NO_3)_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and citric acid (Sigma-Aldrich) as precursors. The required quantities of $La(NO_3)_3$ and $CoCl_2$, respectively, $La(NO_3)_3$ and $Co(NO_3)_2$ were dissolved in 50 mL distilled water. The obtained solutions were mixed with appropriate volumes of citric acid aqueous solution. The chelating effect is favored by the pH value. Thus, adequate volumes of 10 % NH_3 solution were added in order to increase the pH value of mixtures to 7. The solutions were heated at 80 ºC under continuously stirring to remove the excess of the solvent. The obtained gels were calcined in air at 250 ºC for 48 h to decompose organic constituents. The resultant powders were ground, pressed into pellets and sintered at different temperatures (650, 700, 800 and 950 ºC) for 4 h in air atmosphere.

In order to determine beginning of the solid-state reaction and the phase composition the sintered samples were monitored by X-ray and FT-IR analysis. XRD analysis was performed with a Huber diffractometer at room temperature, data being handled by FULLPROF 2000.[16] The infrared spectra were recorded using a Fourier transmission infrared spectrometer, Jasco 660 Plus in the range 4000-400 cm^{-1}, in KBr disk. Chemical composition was confirmed by means of EDX method and the particles sizes were investigated by scanning electron microscopy using a JEOL JEM-3010 SEM operating at an accelerating voltage of 300 kV.

The H_2O_2 catalytic decomposition experiments were conducted in a batch reactor that was stirred at a speed to provide a uniform distribution of cobaltite catalyst. The pH was adjusted by using a $HCl\text{-}Na_2HPO_4$ buffer solution. In the reaction vessel 2.5 mL H_2O_2 (30 %), 5 mL buffer solution, 7.5 mL distilled water and 0.05 g catalyst were added. The temperature of reaction chamber was maintained at 25 ^{0}C (±0.1 ^{0}C) by using a Haake F4 pump. Oxygen evolution measurements were carried out with a water barometric system at normal pressure. All experiments were performed under the same conditions.

Results and Discussion

The XRD patterns for $LaCoO_3$ obtained using nitrate and chloride precursors are shown in figure 1. X-ray diffraction analysis was performed on samples treated at temperatures of 700, 800, 950 ^{0}C. The results of X-ray diffraction indicated that the $LaCoO_3$ powders, obtained using nitrate as precursors annealed at 700 ^{0}C, is not pure, a small amount of Co_3O_4 was identified, but for the sample annealed at 950 ^{0}C for 4 hours we have obtained the pure phase and it had a rhombohedral perovskite-type crystal structure (spatial group: R-3c) (Figure 2) in agreement with the literature data.[2,4,15]

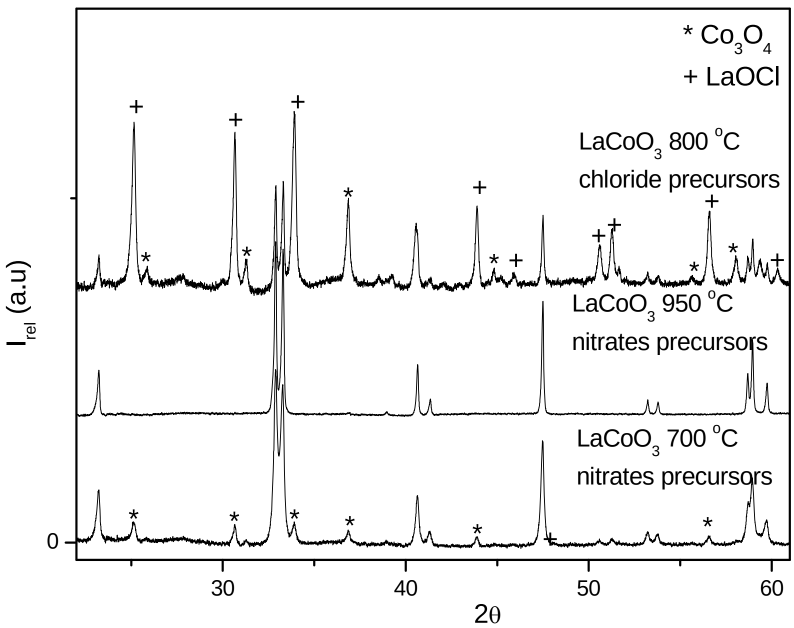


Figure 1. XRD powders obtained using chloride and nitrate precursors sintered at different temperature.

For $LaCoO_3$ sample obtained from chloride precursors, it is noted that in addition $LaCoO_3$ also contains impurities such LaOCl and Co_3O_4 that do not disappear even at a higher treatment temperature (Figure 1).

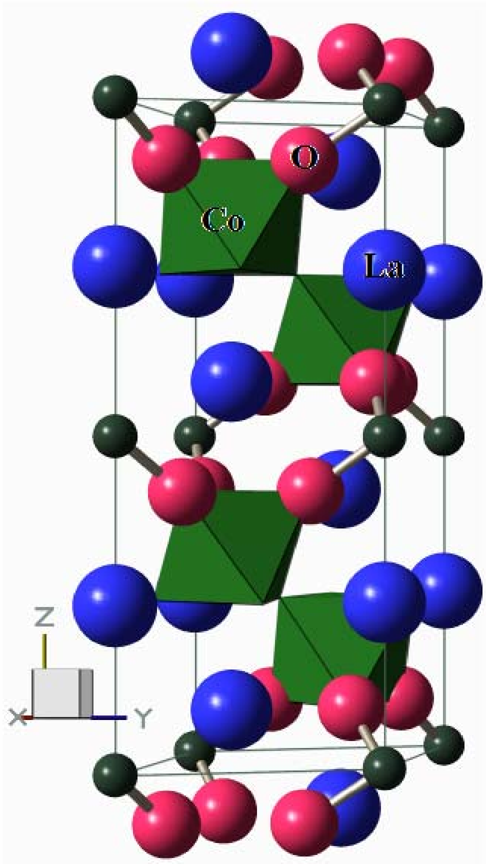
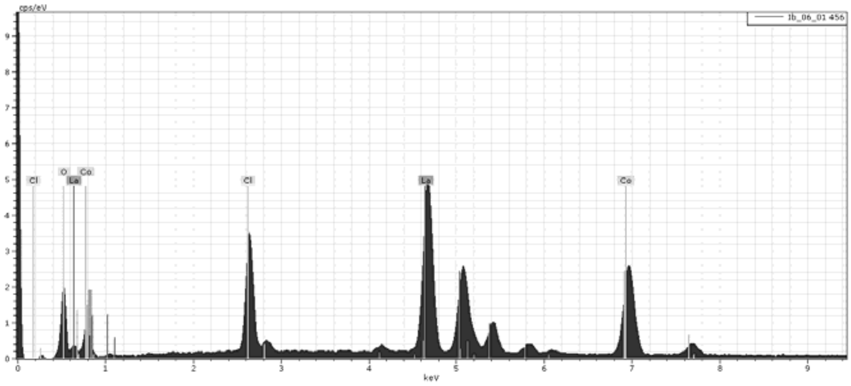


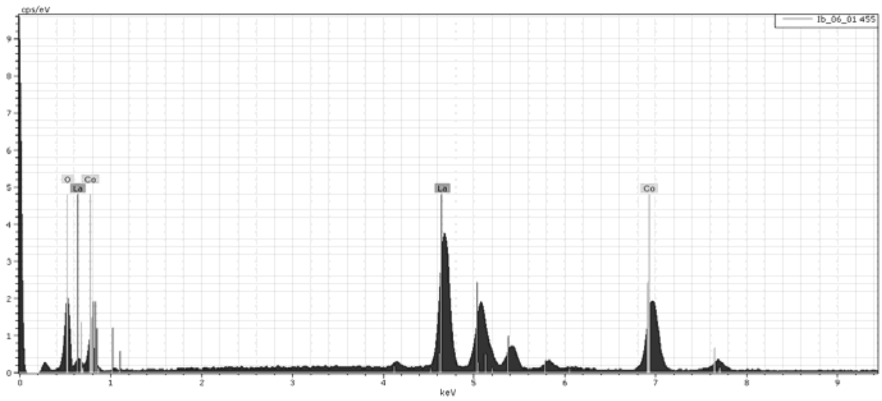
Figure 2. $LaCO_3$ structure ($R\bar{3}c$).

Dziubaniuket al.[16] show in their study that the LaOCl phase has been formed starting with 550 ^{0}C and remain stable at high temperature. The presence of chlorine compounds was confirmed by EDX analysis (Figure 3a). EDX analysis of $LaCoO_3$ sample obtained from nitrate precursors, treated at 950 ^{0}C, confirms only the presence of La: Co: O in 1: 1: 3 molar ratio (Figure 3b).

Elementary cell parameters $LaCoO_3$ samples obtained by nitrate precursors were identified with the program diffract EVA parameters and refinement was performed using the FullProf program.[17] $LaCoO_3$ has a hexagonal structure (H rhombohedral axis) with cell parameters a = b = 5.4436 Å, c = 130924 Å, α = β = 90 º and γ = 120 º, parameters 5.444 Å and 13.093 Å), in accordance with literature data.[4,15]



a

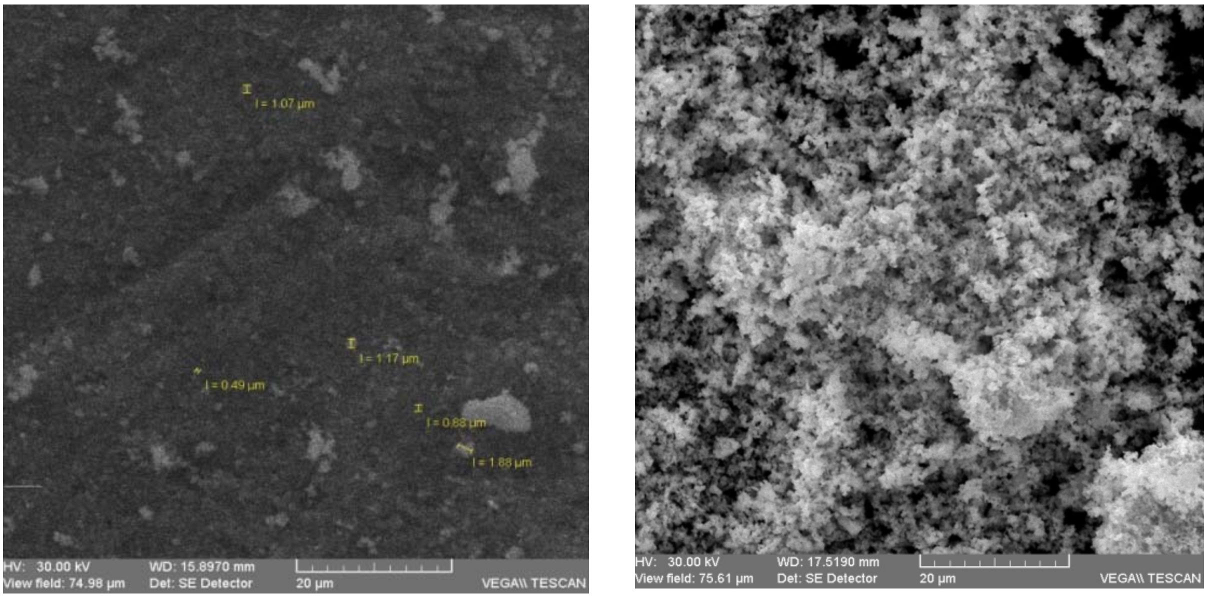


b

Figure 3. EDX spectra for sintered $LaCoO_3$ obtained using: a) chloride precursors and b) nitrates precursors.

The *scanning electron microscopy* for the $LaCoO_3$ obtained using chloride and nitrate precursors, annealed at 800 ^{0}C and 950 ^{0}C, respectively, are shown in figure 4.

From the figure 4, we concluded that the particle sizes of both samples are submicron. The sample obtained using nitrate precursors have a porous texture which means that the compound could be a good catalyst (Figure 4b).



a b

Figure 4. Scanning Electron Microscopy of $LaCoO_3$ samples obtained by: a) chloride precursors annealed at 800 ^{0}C/ 4h and b) nitrate precursors annealed at 950 ^{0}C/4h.

The *vibrational spectra* of $LaCoO_3$ perovskites have been described as the internal vibration of the CoO_6 group containing cobalt cations in II and III oxidation states. The group analysis predicts two infrared active vibration bands:[18] absorption peaks around 400 cm^{-1} corresponding to bending mode of O-Co-O bond angle (δ_{OCoO}) and the peak around 600 cm^{-1} attributed to the Co-O stretching vibrational mode (ν_{CoO}).

Figure 5 shows the FT-IR spectra associated with the $LaCoO_3$ precursors after annealing at 650, 700 and 950 ^{0}C. The spectrum of $LaCoO_3$ treated at 650 ^{0}C reveals two weak broad bands centered at 3410 cm^{-1}($\nu_{O\text{-}H}$) and 1460 cm^{-1} ($\nu_{C=O}$) related to the incomplete oxidation of carboxylate groups. For all samples the major bands at 600 cm^{-1} are associated to cobalt-oxygen stretching frequencies (Figure 5). The width and asymmetry of these bands are a consequence of CoO_6 group asymmetry. This can be related to the existence of cobalt cations into Co^{2+} and Co^{3+} valence states, Jahn-Teller effect of Co^{3+} and supplementary polarization of Co-O bonds induced by local distortion of lattice near grain boundaries or a crystalline structure with lower symmetry.

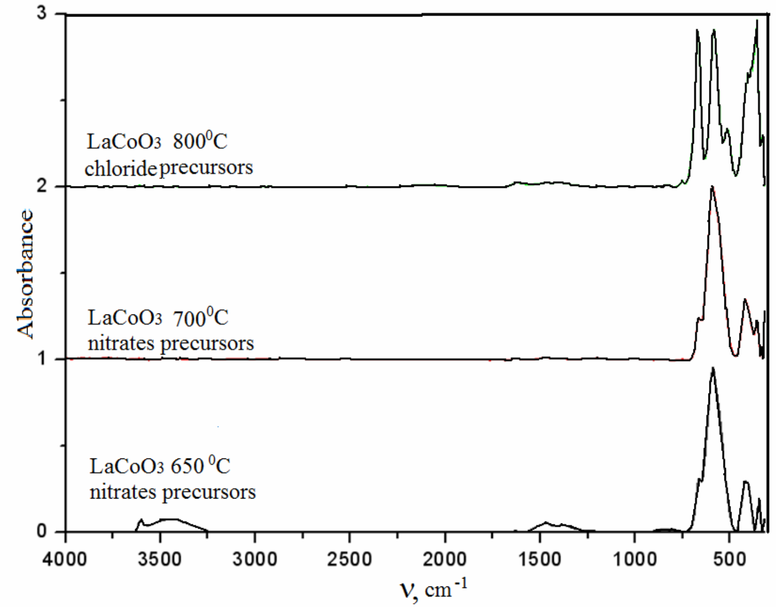


Figure 5. IR spectra of $LaCoO_3$ powders.

All these can be attributed to the formation of $LaCoO_3$ rhombohedral structure. The infrared plot of $LaCoO_3$ chloride precursors shows three main frequency bands. Splitting of ν_{CoO} mode band and intensity of band located at 390 cm^{-1} could be interpreted as a structural triplet allowed by the presence of two or more crystalline phases with different composition.

In order to establish the role of precursors on the catalytic activity of lanthanum cobaltite, we examined the evolution of O_2 resulted from *decomposition of hydrogen peroxide* in the presence of $LaCoO_3$ powder (Figure 6). The fit of H_2O_2 concentration data to a straight line indicates that the decomposition of H_2O_2 follows a second kinetic order rate law: $1/[H_2O_2]-1/[H_2O_2]_0 = k_{obs}t$ at square correlation coefficient (R^2) >0.995. $[H_2O_2]_0$ and $[H_2O_2]$ are the concentrations of H_2O_2 in solution at time zero and any time t, k_{obs} is observed rate law.

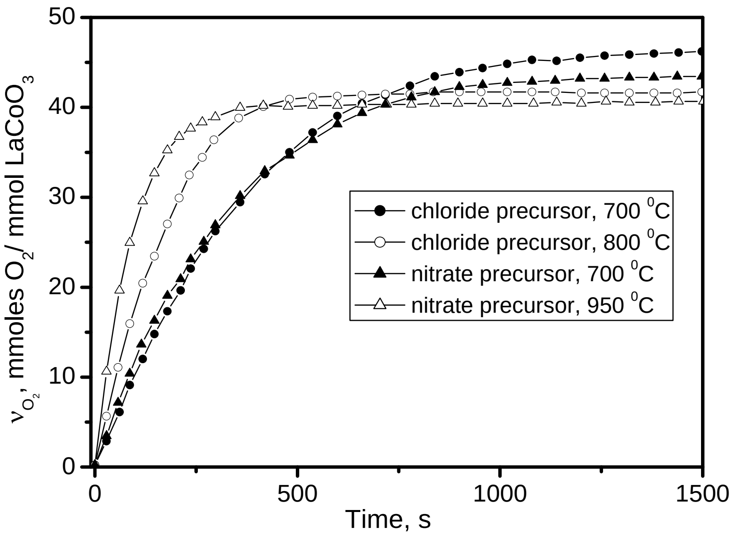


Figure 6. Variation of O_2 quantity with time in presence of lanthanum cobaltite as catalyst.

In accordance with equation, the second order k_{obs} have been found: 0.2205 $M^{-1}\cdot s^{-1}$ (chloride precursor, 700 ^0C), 0.4522 $M^{-1}\cdot s^{-1}$ (chloride precursor, 800 ^0C), 0.2963 $M^{-1}\cdot s^{-1}$ (nitrate precursor, 700 ^0C) and 0.9959 $M^{-1}\cdot s^{-1}$ (nitrate precursor, 950^0C). It can be expected that any heterogeneous mechanisms for the decomposition of hydrogen peroxide to be influenced by the surface area (bulk) and crystalline phases composition. Catalytic studies indicate that the ability of the surface to chemisorption of H_2O_2 changes with cobalt oxidation state.[15] In the lanthanum cobaltite molar ratio of $Co^{3+}/Co^{2+} > 1$, Co^{3+} (d^6) exists either a high spin or in intermediary spin state with partial occupancy of e_g level. At surface of catalyst the symmetry of CoO_6 octahedra is broken and this decrease the coordination number of Co cation (CoO_5) and raises the catalyst capacity to link oxygen atom of hydrogen peroxide. In consequence the lanthanum cobaltite with higher Co^{3+} content (obtained by chloride-800 ^0C and nitrate - 950 ^0C precursors) show a higher rate constant as expected. This result implies that rate constant of H_2O_2 catalytic decomposition is directly proportional to surface area, Co^{3+}/Co^{2+} molar ratio and crystalline structure of perovskites.[19]

Conclusions

Lanthanum cobaltites were synthesized by sol-gel method using chloride and nitrate precursors. The obtained powders have a similar structure but different morphologies. The XRD patterns of the prepared samples confirm formation of single phase with rhombohedral crystal structure for $LaCoO_3$ obtained to nitrate precursor at 800 ^{0}C whereas samples obtained from chloride precursors have tendency to separate into two crystalline phases. FTIR spectra confirm the presence of Co-O stretching vibration bands characteristic of CoO_6 group. The $LaCoO_3$ perovskites exhibit a good catalytic activity for the hydrogen peroxide decomposition. In the lanthanum cobaltite series, pure rhombohedral $LaCoO_3$ have the highest value of the second-order rate constant, k_{obs}= 0.9959 $M^{-1}{\bullet}s^{-1}$.

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